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EPR AND NMR DETECTION OF TRANSIENT RADICALS AND REACTION PRODUCTS

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ABSTRACT

Magnetic resonance methods in radiation chemistry are illustrated. The most recent developments in pulsed EPR and NMR studies in pulse radiolysis are outlined with emphasis on the study of transient radicals and their reaction products.

INTRODUCTION

Magnetic resonance techniques in radiation chemistry are relative newcomers. To be sure, people have for many years irradiated solids or frozen solutions and studied the resulting paramagnetic species by EPR. But, that sort of application of magnetic resonance, while obviously useful, can be used to observe only radicals that live for an extended time and will not be of prime concern to our discussion here. We focus here on the methods that allow us to study transient radicals.

In particular, we will focus on the most recent developments that allow us to observe and study transient radicals in the microsecond and nanosecond time domains (1,2). Thus, an area of application of EPR which involves study of transient radicals by continuous irradiation ("steady state") will not be covered here. Everything we have to say about the magnetic resonance methods would, of course, include those topics as well. But, my intention here is to tell you how to go to the present limits of technique. If you can do that, you will also have the capability to do all the other types of "non-time resolved variety".

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Implicit in all this discussion is that somehow the magnetic resonance method can provide some unique information, that in spite of its limitations, it has some superior attributes compared to the more conventional optical spectroscopy. Well, that obviously is determined by your point of view. Magnetic resonance can never equal the time resolution and only sometimes can approach the sensitivity of optical spectroscopy. But, where magnetic resonance excells is in the information content of the spectra; one can usually make a definitive assignment of the identity and structure of the transient radical on the basis of EPR and NMR; this is not so straightforward in optical spectra.

Before we plunge into the details of various magnetic resonance methods in radiation chemistry, let me, for the sake of those not so familiar with it, remind you of some very basic principles of magnetic resonance (3).

Magnetic Resonance

Any study of magnetic resonance involves the study of the spin energy levels and the populations of these levels in magnetic fields.

We concern ourselves either with electron spin in the study of EPR or with the nuclear spin in NMR. Here, we concern ourselves only with spin 1/2 systems, as this includes most of the cases of interest.

In a magnetic field H, the spin has two possibilities:

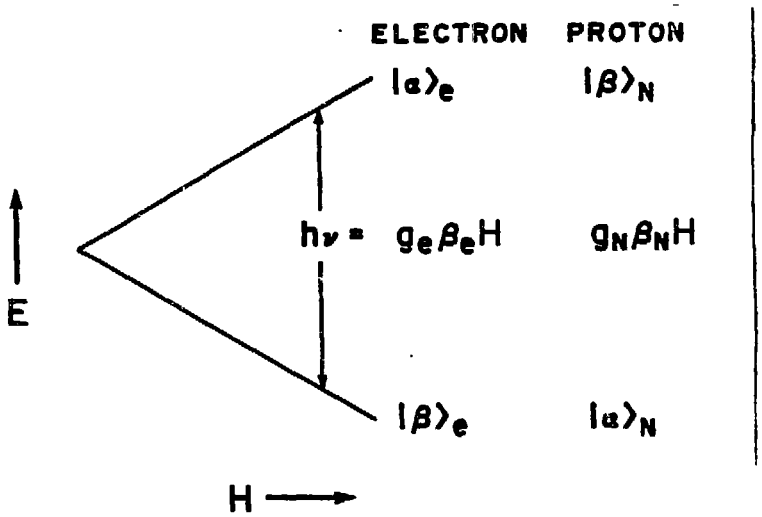


Figure 1. Energy levels of a spin 1/2 species in a magnetic field.

The steady state magnetic field, H, interacts with the magnetic moment of the spin μ. This is usually represented by a Hamiltonian

$$\mathcal{H}_N = -\mu_N \cdot H = -\gamma_N h H \cdot I = -g_N \beta_N H \cdot I \qquad (1a)$$

$$\mathcal{H}_E = -\mu_E \cdot H = +\gamma h H \cdot S = +g_E \beta_E H \cdot S \qquad (1b)$$

Since I and S have ± 1/2 values, the energy gap $h\nu = g\beta H$. The difference in the magnetogyric ratios of the electron and nucleus are $\sim 10^3$ so we observe NMR in the 10^6 Hz range and EPR in the 10^9 Hz range. Also, note that since at thermal equilibrium $N_\alpha / N_\beta = \exp^{-(g N \beta N H)/(kT)}$ according to the Boltzman law, there will be considerably larger population differences in EPR than in NMR by a factor of 10^3.

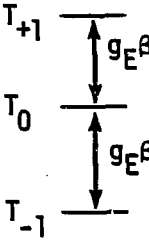
When we have a radical with electron spins coupled to nuclear spins, we get a more complicated set of energy levels. I will show such energy level schemes later. However, the basic picture is the same.

What will concern us quite a bit when we use time resolved magnetic resonance is that usually we will observe the NMR or EPR transitions before they have attained equilibrium, that is Boltzman population ratios. This non-equilibrium population (chemically induced magnetic polarization, CIDNP, and CIDEP) arises because transient radicals in solutions encounter and react or separate without reaction depending on their spin levels. For example, the reactive encounter (the bond making) requires spin phasing to be ↑↓- (this is singlet). Thus spin, while its energy gap is tiny in size when compared to the chemical energy, does play a very important role in controlling the outcome of the chemical reaction. The use of magnetic fields allows us to both study and, to some extent, influence the outcome of the chemical reaction. The effects are small, but if we can make the chemistry repeat itself in a sort of cyclical fashion, we can accomplish, for example, isotope separation between isotopes with different magnetic properties (4).

In order to gain some understanding of how spin enters into chemical reaction, we must consider pairs of reacting radicals in a magnetic field:

$$\begin{array}{ccccc} R - R & \longrightarrow & R \cdot\cdot R & \overset{\text{diff}}{\rightleftharpoons} & R\cdot + R\cdot \\ & & \downarrow & & \text{EPR} \\ & & R - R & & \\ & & \text{NMR} & & \end{array} \qquad (2)$$

In the magnetic field, the electron spin levels are singlet or triplet:



$$S = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle): \quad T_1 = |\alpha\alpha\rangle$$

$$T_0 = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle): \quad T_{-1} = |\beta\beta\rangle \qquad (3)$$

If we are doing chemistry in a magnetic field, which is of some magnitude H, which in the case of NMR will be ∿18 kg or EPR ∿3 kg, only the S and T_0 will be close in energy to each other.

After the pair of radicals is created in some spin phasing, e.g., $S \equiv R\uparrow\downarrow R$, say after breaking the bond, in time the interaction of the electron spin ↓ with the magnetic environment at R may dephase it to become to some extent $R\uparrow\uparrow R \equiv T_0$. This time evolution is summarized by the following time dependent Schrödinger equation:

$$[-J(2S_1 \cdot S_2 + 1/2) + \mathcal{H}]\psi(t) = i\frac{\partial\psi}{\partial t} \qquad (4)$$

$\mathcal{H}$ is the magnetic Hamiltonian:

$$\mathcal{H} = \beta(g_1 S_1 + g_2 S_2)\cdot H_0 + \Sigma A_{1n} I_{1n} \cdot S_1 + \Sigma A_{2n} I_{2n} \cdot S_2 \qquad (5)$$

where β is the Bohr magnetron, H_0 is the external magnetic field, g_1 and g_2 are the electron g factors of the two radicals, A's are the hyperfine coupling constants and J is the electron exchange integral.

Chemically Induced Dynamic Nuclear Polarization (CIDNP) arises from the spin selective reactions of the radical pair. The word "polarization" is used to describe non-equilibrium spin population of nuclei (CIDNP) or electrons (CIDEP). The recombination probability can be assumed to be proportional to the S character and will thus depend on the S-T_0 mixing.

Electron Spin Polarization (CIDEP) originates at interradical separation where the exchange J is nonzero, as the interplay of S-T_0 mixing and J.

Without going into a much more detailed picture of CIDEP and CIDNP, one can see that the nature of the radicals, i.e., their g-factors and their hyperfine couplings will play a role in the patterns of polarization created by the interactions of such transient radicals.

By studying CIDEP and CIDNP, we can gain information on the past history of the radical or the radical reaction product. This is what we are after when we study reaction mechanisms.

TIME RESOLVED EPR

When very short-lived radicals are studied, nonstandard EPR techniques have to be employed. The conventional EPR spectrometer that one can buy from the manufacturer, uses 100 kHz field modulation and typically time constants are ∿1 sec. This improves the sensitivity. The modified commercial equipment can be used to study radicals that live longer than 20-100 μsec. To study shorter lived radicals, ∿1 μsec, one can utilize higher field modulation. Historically this was done first (5,6). At Argonne, B. Smaller constructed the 2 MHz field modulated EPR spectrometer (5). Smaller and co-workers were the first to observe the EPR of e_{aq}^- (7). However, modulation introduces problems in kinetic analysis, so the better choice is to not use it at all. That is the most popular course now and one can easily study radicals with time resolution of 0.2-0.3 μsec (8,9).

The main changes from the commercial instrument are a broad-band amplifier, a boxcar integrator and/or a fast transient recorder. The use of a broad-band amplifier reduces sensitivity. We are talking about $\sim 10^3$ less sensitive instrument. This is to some extent made up by the use of boxcar averaging and the fact that nonequilibrium electron spin populations are almost always observed, giving considerable signal enhancement.

The most recent development is pulsed EPR, where two or three microwave pulses are utilized (2). With this approach, time resolution up to the frequency definition limit, which is several nanoseconds, is possible.

Pulsed EPR

The X band microwave bridge which can be utilized for direct detection is modified for use in the pulsed EPR experiment by incorporating three microwave switches, traveling wave tube amplifier (10 watt - TWT) and Ga-As FET amplifier (2). The instrument schematic is illustrated in Figure 2. The microwaves from the Gunn diode are switched by a fast microwave switch #1. This switch provides up to three microwave pulses of appropriate length

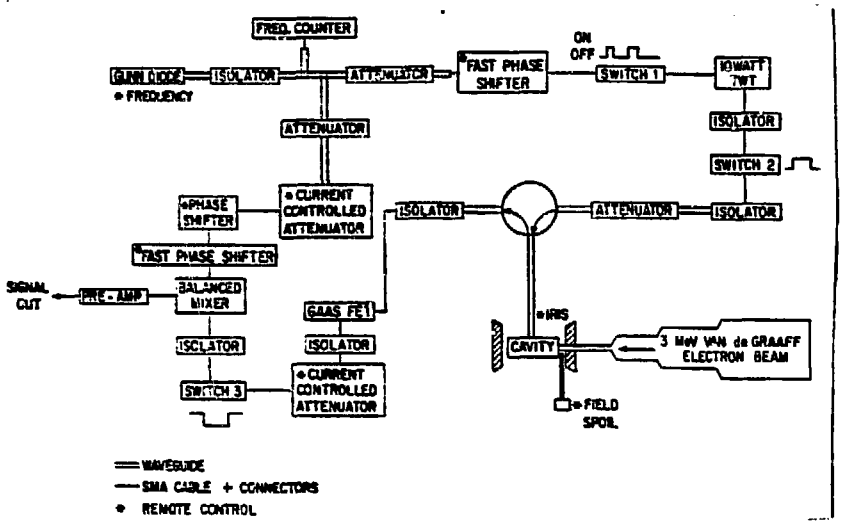


Figure 2. Schematic of microwave network used in pulsed EPR experiments with the Van de Graff accelerator. The switching functions of the microwave switches are also indicated.

(∿10 nsec-1 μsec) and spacing (for example, 90-τ-180; 180-τ-90-τ-180; 90-τ-90-τ-90° sequences). A 90° pulse is typically 30-100 nsec. That means that the microwave field H_1 available at the sample is ∿1 gauss ($H_1 = \pi/\gamma\, t_p$).

Switches #2 and #3 are not as fast as switch #1, and are used to protect the detection network from noise and overloads during the time that the 10 watt TWT is amplifying. When switch #1 is providing pulses, switch #2 is open to allow them to get to the cavity and sample, but switch #3 is closed. At the time when the echo is detected, only switch #3 is open.

The microwave switching is controlled by a pulse sequencer, and timing can be automatically swept by the time-delay programmer. The whole system of pulse timing is controlled by 100 MHz clocks, where the smallest time increment is 10 nsec (one can get 1 nsec increments) and the time jitter is ∿2 nsec in our experiment.

In pulse radiolysis, the EPR magnet control, and the microwave bridge tuning must be performed remotely. Remote functions include Gunn diode frequency, phase, phase arm bias, microwave signal attenuation, TWT gain, iris tuning, and magnetic field setting and sweeping.

Additional and somewhat unusual features are the field spoil and the fast phase shifter. They are used to reduce free induction decay interference as will be illustrated.

Time Resolved Spectra (Field Sweep). After a transient radical is generated by a short electron beam pulse, we can examine this magnetization by applying a two pulse microwave sequence (90°-τ-180°) at a fixed time t after the electron beam pulse and sweeping the magnetic field. Thus, the EPR spectrum at that instant of time is obtained. This timing of pulses is illustrated in Figure 3. The action of the microwave pulse on the spin system can be best understood if we use a rotating frame picture (Figures 4 and 5).

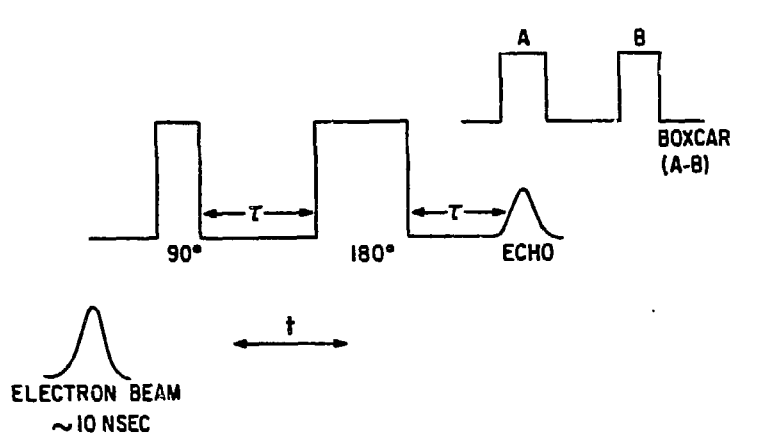


Figure 3. Timing sequence of the electron beam pulse, microwave pulses and the observation (boxcar) gates.

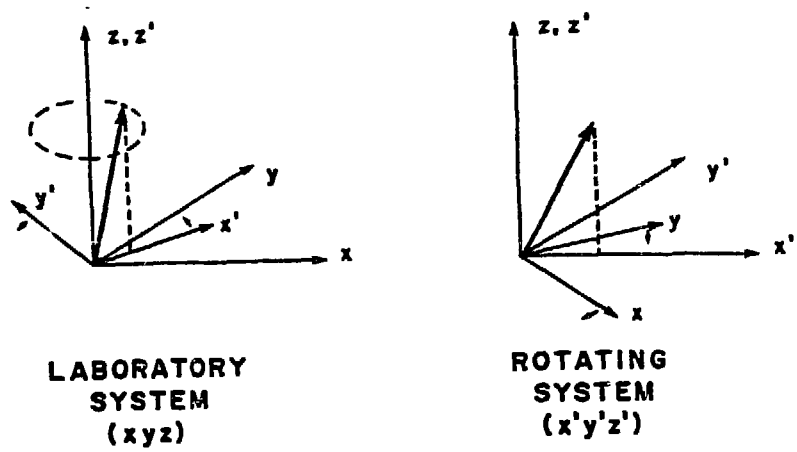


Figure 4. Precessing vector in laboratory and rotating coordinate systems.

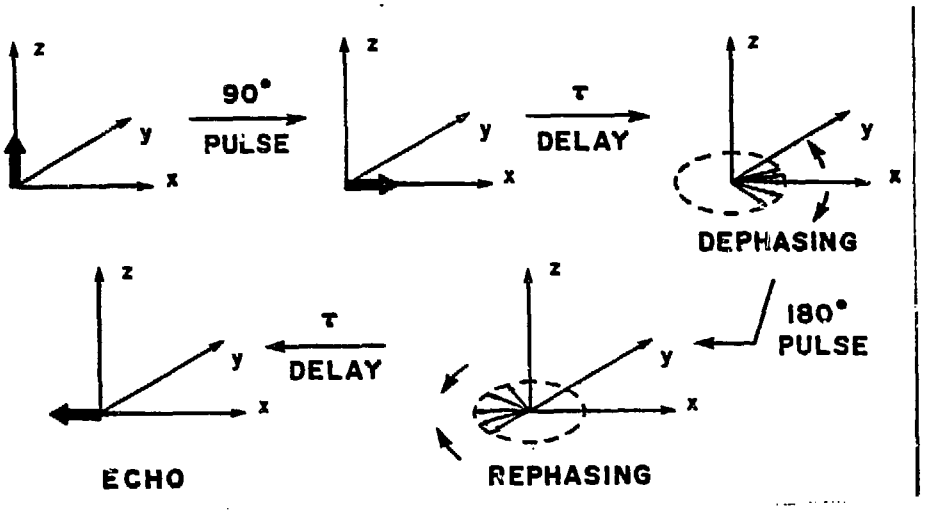


Figure 5. Pulse sequence to observe a spin echo.

The main thing is to realize that only the magnetization sampled during the time of the 90° pulse is refocused to give an echo. The EPR spectrum is obtained on the radical species present during the 90° pulse application. This can be transient or steady state magnetization present at that time.

For example, if we look at the aqueous radicals of sodium acetate, we can see the radical $\cdot CH_2COO^-$ in neutral or slightly basic solution, as shown in Figure 6A. The big signal in the middle is from the suprasil walls of the EPR flat cell. We can reduce it somewhat by using phase shifted microwave pulse sequences. This essentially provides light-dark subtraction. However, we lose $\sqrt{2}$ signal-to-noise. This is shown in Figures 6A and 7.

So, by applying the 90° pulse at any time, we obtain time-resolved spectra of a transient at that window of time. We can also obtain kinetic information (formation decay curves) by sweeping time.

Time Sweep (Kinetics). The magnetic field is positioned on the desired EPR line and the sweep of time t is initiated. Time t is the time between the electron beam pulse and the time when the 90° pulse is applied. The two pulse microwave sequence and the observing boxcar gates are swept relative to the electron beam pulse. In practice, the 90° pulse is set to sweep ~200 nsec before the electron pulse in order to obtain the baseline. A baseline can also be obtained when the signal decays to noise but requires longer time sweep.

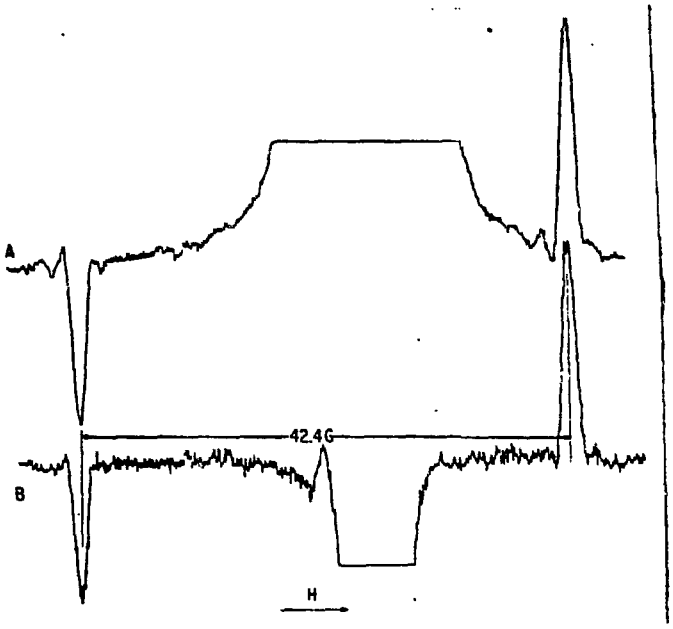


Figure 6. Field swept EPR spectrum (at 1 μsec) obtained during radiolysis of aqueous 0.5 M potassium acetate at pH ∿ 11 (N_2O sat); the middle line of the $\cdot CH_2CO_2^-$ radical can be seen (B) when the quartz signal is reduced by beam-no beam subtraction.

The kinetic sweep of the two acetate radical lines are illustrated in Figure 8.

Free Induction Decay. The free induction decay (FID) following the 90° and 180° microwave pulses interferes with the echo. For radicals in non-viscous liquids $T_2 \sim T_1$, thus in a homogeneous magnetic field the FID may last for several microseconds. T_1 and T_2 are the spin lattice and spin-spin relaxation times. Modern NMR is based on the utilization of FID to obtain spectra. However, the EPR FID does not last seconds as in NMR and too much of the EPR FID is lost at early times, so it is hard to apply the Fourier transformation. Nevertheless, one can obtain "FID" spectra using a single microwave pulse as shown in Figure 9.

In the spin echo experiment, FID interference has to be minimized. We accomplish this by making the magnetic field artificially more inhomogeneous by the use of a field spoil and by phase alternation of the 180° pulses.

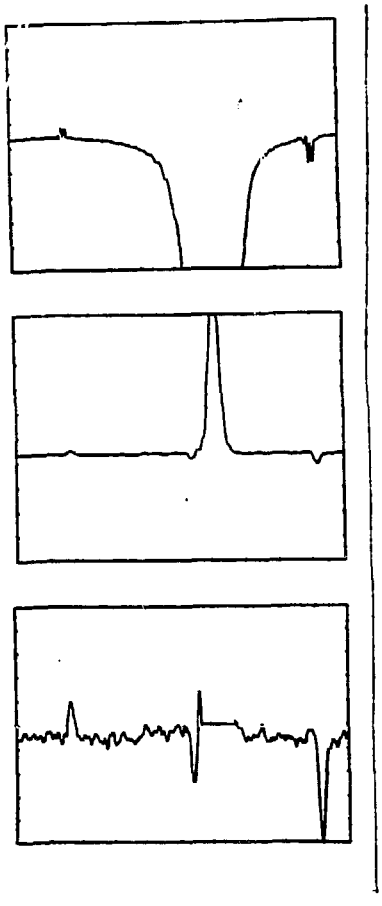


Figure 7. EPR spectra of $\cdot CH_2CO_2^-$ radical at 1 μsec. Top-without and middle-with the phase shifted pulse sequences, bottom-the y-enlarged version of the middle spectrum.

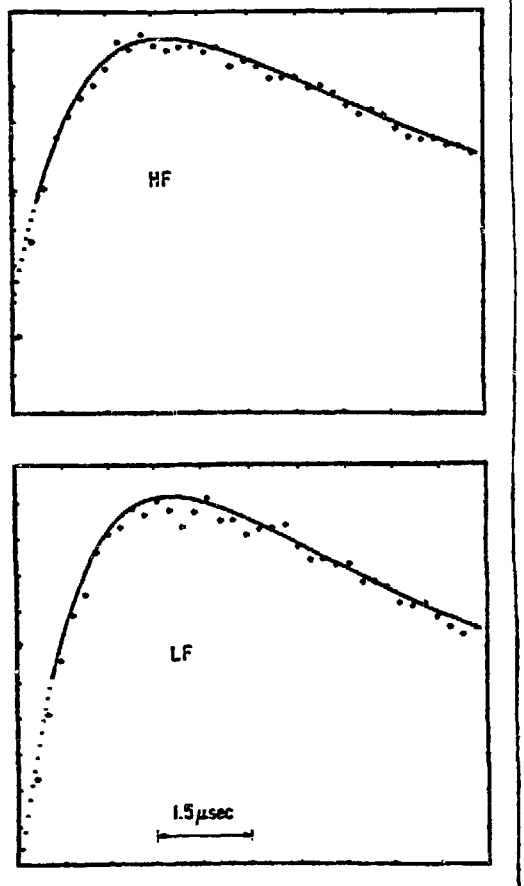


Figure 8. Least squares fitting (solid line) of data (crosses) of kinetic traces of the two lines of the acetate radical. Dots indicate the calculated line through data points that were not used in the least squares fitting. The plots show absolute, normalized intensities of the two lines.

Data analysis and other varieties of pulsed EPR will be discussed later. We will also try to point out the advantages and problems encountered in certain applications of pulsed EPR to radiolytic systems.

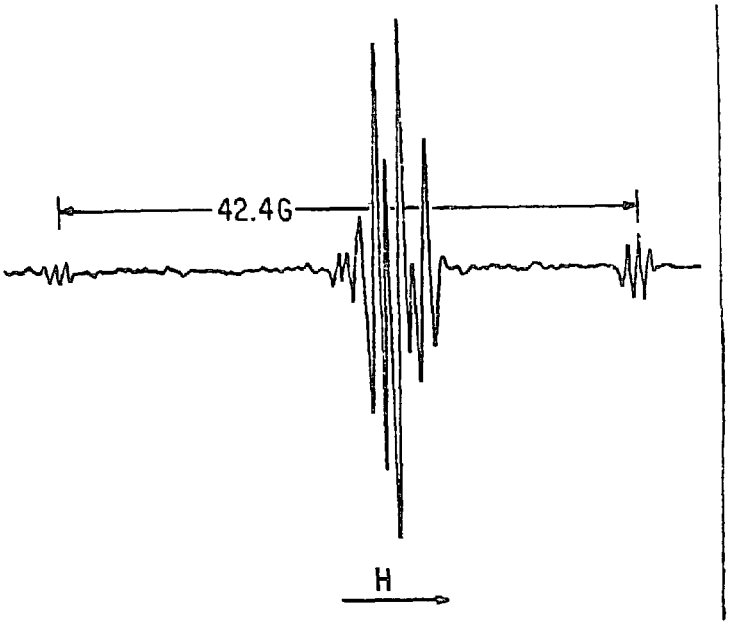


Figure 9. "FID" spectrum of the acetate radical (at 1 μsec) obtained by using only a 90° pulse.

NMR IN RADIATION CHEMISTRY

Over the last two decades, NMR has revolutionized several areas of chemistry. Organic chemists, especially, have found NMR an indispensable tool for analysis of reaction products, etc. Then, over the last ten years, pulsed NMR-Fourier Transfer NMR has made another quantum improvement in NMR, opening a whole new set of possibilities.

It is perhaps surprising that NMR has not become a tool in radiation chemistry. It appears that radiation chemists are a very conservative lot, even the EPR - especially time resolved EPR - is not very widespread. So far, we at Argonne are the only ones to use NMR in radiolysis (10-12).

Our approach aims at using NMR to study products of radical reactions in radiolysis and, as you will see, we have recently developed some new NMR based detection methods that allow us to obtain time resolved information on the reacting radicals.

The NMR magnet has to be very homogeneous since we are studying energy differences between the nuclear spin levels, and as you remember, they are 10^{-3} smaller than the electron spin energy difference observed by EPR. We cannot make axial holes in the NMR magnet and still do high resolution NMR. So, we use two magnets.

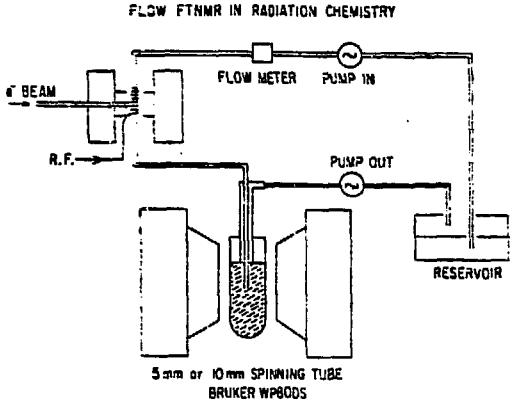


Figure 10. The schematic of the flow NMR experiment for pulse radiolysis.

The electron beam enters axially a small electromagnet (0-8 kg) in which the sample irradiation is carried out (Figure 10). A fast flow system is used to transfer the irradiated solution to the probe of the NMR spectrometer. All the radical reactions are over in ~100 μsec and only the diamagnetic products are transferred to the NMR probe for examination. However, in the nuclear spin population levels of these diamagnetic products is contained the memory of the radical encounters of precursors of this product. The nonequilibrium nuclear spin population - CIDNP - will be observable as long as the examination of the diamagnetic product is carried out before nuclear spin relaxation (T_1) obliterates it.

In protons, $T_1 \sim$ 1-3 seconds and in ^{13}C T_1's are even longer; so as long as the flow system is capable of transferring the irradiated solution to the NMR probe within 1-2 seconds, the experiment is feasible.

As it turns out, and I will illustrate this further, it is very convenient that we can do chemistry (irradiation) in a variable magnetic field, because there is much information to be gained from the field dependence of CIDNP.

To illustrate how we do the NMR experiments and what sort of information is obtainable, I will use a simple system of aqueous methanol radiolysis. The principal radical intermediate is the hydroxymethyl radical. The principal products seen by NMR-CIDNP are methanol and ethylene glycol. Formaldehyde, another known product, is not seen. Apparently, either a nonradical mechanism

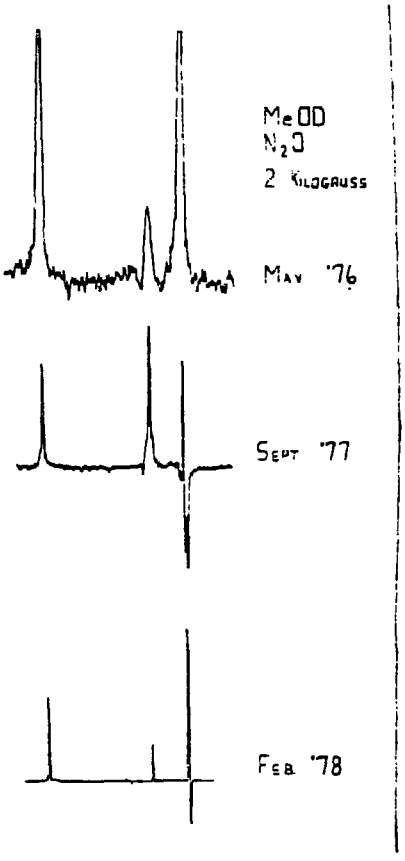


Figure 11. NMR spectra showing CIDNP of products observed in methanol radiolysis. Evolution of experimental technique is illustrated. Top and middle spectra were obtained using CW-NMR. Bottom spectrum was obtained using FTNMR.

is responsible for formaldehyde formation, or there is no efficient polarization pathway.

The observed polarization (Figure 11) is explained by the following scheme (* indicates polarization):

$$e^-_{aq} + \cdot CH_2OD \begin{cases} \xrightarrow{D^+} CH_2OD^* \longrightarrow DCH_2OD \text{ (E)} \\ \xrightarrow{\cdot CH_2OD} \cdot CH_2OD^* \longrightarrow (CH_2OD_2) \text{ (A)} \end{cases} \qquad (6)$$

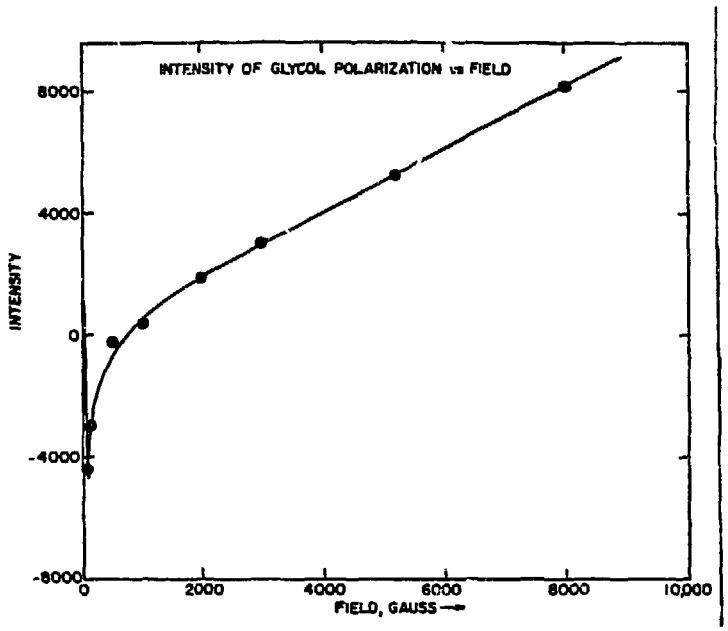


Figure 12. Field dependence of glycol polarization in pulse radiolysis of aqueous methanol (D_2O solution).

The e^-_{aq} is the important partner in producing polarization as substantiated by observing the field dependence of the ethylene glycol polarization. Figure 12, which clearly indicates that polarization is very much field dependent, i.e., g-factor difference between the radicals in the radical pair is substantial. Also, N_2O addition substantially reduces the polarization.

Radiolysis of several simple compounds was studied in some detail. Acetone, acetaldehyde, acetate, dimethylsulfoxide, and reactions involving H radicals were studied. In many radiolytic systems NMR is ideally suited to provide considerable information on the mechanism of radical reactions. Also, compared to EPR, the experiment is rather straightforward. Only the interpretation of the more complex NMR spectra can be difficult and time consuming. Also, one can do ^{13}C experiments using natural abundance or enriched samples, and we have done so (13).

So, in combination with just detecting and sorting out all the various products found in radiolysis of a given chemical system, flow NMR can provide details of the reaction mechanism, i.e., the history of a product or product fragment in terms of the reactions and encounters of its precursor radical.

Actually, the NMR experiment, as illustrated, is not a time resolved one. A rather simple modification provides us with a whole new approach to the study of transient radicals (14). In

that experiment, we observe nuclear resonance of transient radicals by NMR by applying a pulse of rf at the radical NMR frequency during the radical lifetime. One gets a sort of ENDOR spectrum of the transient radicals, and thus, one obtains hyperfine coupling constants with great precision. One can do kinetics and get all sorts of other information, as will be illustrated later.

CONCLUSION

State-of-the-art of magnetic resonance in radiation chemistry has been illustrated. The experimental aspects of the technique were outlined.

Magnetic resonance, while lacking the sensitivity and the time resolution of conventional optical methods, can provide much more definitive information about the reactive radical intermediates in solution.

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REFERENCES

(1) Trifunac, A.D. and Thurnauer, M.C.: 1979, *Time Domain Electron Spin Resonance*, ed. L. Kevan and R. N. Schwartz, John Wiley & Sons, Inc., New York.
(2) Trifunac, A.D., Norris, J.R., and Lawler, R.G.: 1979, J. Chem. Phys. 71, p. 4380.
(3) Carrington, A. and McLachlan, A.D.: 1967, *Introduction to Magnetic Resonance*, Harper and Row, New York.
(4) *Chemically Induced Magnetic Polarization*,: 1977, L. T. Muus *et al.*, eds. (NATO ASI), D. Reidel, Publishers, Dordrecht.
(5) Smaller, B., Remko, J.R., and Avery E.C.: 1968, J. Chem. Phys. 78, p. 5174.
(6) Atkins, P.W., McLauchlan, K.A., and Simpson, A.F.: 1970, J. Phys. (E) 3, p. 547.
(7) Avery, E.C., Remko, J.R., and Smaller, B.: 1968, J. Chem. Phys. 79, p. 951.
(8) Trifunac, A.D., Johnson, K.W., Clifft, B.E., and Lowers, R.H.: 1975, Chem. Phys. Lett. 35, p. 566.
(9) Verma, N.C. and Fessenden, R.W.: 1976, J. Chem. Phys. 65, p. 2139.
(10) Trifunac, A.D., Johnson, K.W., and Lowers, R.H.: 1976, J. Am. Chem. Soc. 98, p. 6067.

(11) Trifunac, A.D. and Nelson, D.J.: 1977, J. Am. Chem. Soc. 99, p. 1745.
(12) Nelson, D.J., Trifunac, A.D., Thurnauer, M.C., and Norris, J.R.: 1979, Revs: Chem. Intermediates 3, p. 131.
(13) Lawler, R.G., Nelson, D.J., and Trifunac, A.D.: 1979, J. Phys. Chem. 83, p. 3444.
(14) Trifunac, A.D. and Evanochko, W.T.: 1980, J. Am. Chem. Soc. 102, p. 4598.