Time-Resolved CIDNP: Applications to Radical and Biradical Chemistry

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Nuclear magnetic resonance has long been one of the most useful tools for investigating reaction kinetics. The direct method follows resonance intensities as a function of time and correlates them with reactant or product concentrations. This approach can be applied only to slow reactions, although flow and stopped-flow techniques can reduce the time scale to approximately 10^{-2} s.[1] With use of line-shape analysis, kinetic measurements can be carried out under dynamic equilibrium conditions.[2] With modern high-field spectrometers rates up to 10^4 s^{-1} can be measured in diamagnetic molecules. The fundamental limit for the time resolution is imposed by the weakness of the interactions of the nuclear spins with the molecular environment or the lattice. In systems containing unpaired electrons the strong hyperfine (hf) interactions allow measurements of diamagnetic–paramagnetic exchange rates up to 10^{10} s^{-1}.[3] In this Account we want to review a new NMR method for measuring rates of irreversible reactions with a time resolution approaching 10^{-8} s. This extends the previous limit for irreversible reactions by 5–6 orders of magnitude! The method is an extension of chemically induced dynamic nuclear polarization (CIDNP) originating from radical pair chemistry via the hyperfine interaction.[4]

Although it may be assumed that the mechanism giving rise to CIDNP is common knowledge by now, it will be useful to summarize its salient features. Scheme I sketches the reactions underlying the radical pair mechanism of CIDNP. A precursor molecule, $^\mu M$, with a given electron spin multiplicity, μ (singlet or triplet), undergoes a thermally or photochemically initiated dissociation to form a radical pair, $\overline{R_1 \cdots R_2}$, where the bar denotes its geminate origin. The original caged radical pair can give geminate combination and disproportionation products or the components can diffuse apart. The probability that the components of a separated geminate pair, $\overline{R_1 \cdot |S| \cdot R_2}$, encounter each other again is

Scheme I
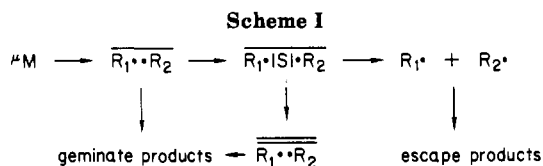
finite but falls off with time and in typical organic solvents becomes negligible after $\sim 10^{-7}$ s.

Now, CIDNP can be seen to develop in the following way. The initial spin state of the caged radical pair is the same as that of $^\mu M$. While caged there is little mixing of the spin states because the exchange energy $2J$, that is the singlet–triplet splitting is large. However, J decreases exponentially with distance so that once the radicals separate the spin functions evolve under the influence of the hf interaction and possible differences of the electron g factors of the two components. The total spin multiplicity of the pair changes from triplet to singlet and vice versa depending on the initial state. Pairs with different nuclear spin states undergo this change with different rates. When the components reencounter (double bar in Scheme I), they have different degrees of singlet and triplet character depending on their nuclear spin states. With the assumption that the reaction probability in a reencounter is proportional to the singlet character, the geminate products will be enriched in certain nuclear spin states and depleted in others. For example, starting with a triplet state, the more time it takes to acquire singlet character the smaller the chance of a geminate reaction and the more likely it becomes that the components will react in nongeminate ways. If the initial state is singlet, those nuclear spin states causing the faster evolution to the triplet will be enriched in the escape products, while those that are slow to cross to the triplet will be found predominately in the geminate products. This sorting process will lead to large nuclear polarizations in the geminate products and an equally large polarization of *opposite sign* in the radicals that give rise to the escape products.

Now, let us examine the time scales involved. With a nitrogen, Excimer, or YAG laser it is possible to create radical pairs within 10^{-8} s. The spin-sorting process in typical organic radicals with hf constants of 5–20 G

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(1) Fyfe, C. A.; Cocivera, M.; Damji, S. W. H. *Acc. Chem. Res.* **1978,** *11,* 277.

(2) Jackman, L. M.; Cotton, F. A., Eds. "Dynamic Nuclear Resonance Spectroscopy"; Academic Press: New York, 1975.

(3) Kreilick, R. W. *Adv. Magn. Reson.* **1973,** *6,* 141.

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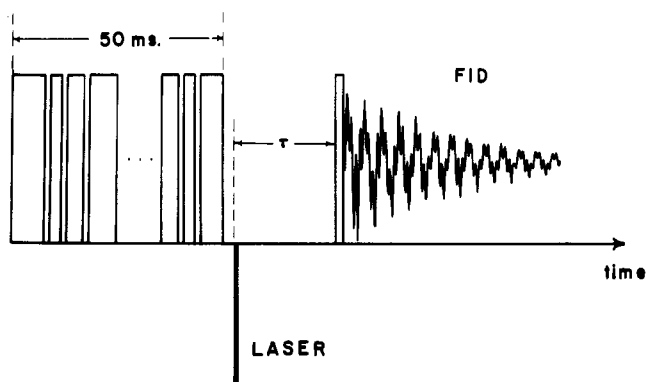
Figure 1. Typical pulse sequence used for time-resolved CIDNP.

takes no more than 10^{-8} s, and geminate product formation stops after 10^{-7} s. But depending on concentrations and scavenger reactivity, the escaping radicals may live as long as 10^{-5}–10^{-4} s. Electron spin relaxation times are of the order of 10^{-6} s, and nuclear spin relaxation in free radicals takes approximately 10^{-4} s. Finally, the polarization in the products will last for seconds. Therefore if we could measure the NMR spectrum at 10^{-7} s after the laser flash, we would get the spectrum of the geminate products only. At 10^{-4} s we would get the polarized spectrum of the geminate *and* the escape products, and at 10^2 s we would get the Boltzmann spectrum of all the products. With FT NMR these experiments are possible and represent time-resolved CIDNP.

The Experiment

The equipment necessary for time-resolved CIDNP is not particularly elaborate and requires an excitation source which may be a flash lamp[5] or a suitable pulsed laser and a FT NMR spectrometer modified to admit light in to the probe. Of course, it is necessary to synchronize the excitation and radio-frequency (rf) pulses. Additional modifications to improve the time resolution will be discussed below.[6]

The simple two pulse sequence with appropriate delays is shown in Figure 1. Belore applying the laser pulse it is advantageous[7] but not necessary to remove any equilibrium polarization or residual CIDNP from the preceding sequence by a train of homonuclear saturation pulses conveniently provided by the instrument's decoupler. This takes only a few milliseconds and has the advantage that only pure CIDNP signals appear in the final spectrum. Then the laser pulse is fired to prepare the radical pairs, and during an appropriate and variable delay, τ, the chemistry evolves as described above. Next the magnetization of the diamagnetic polarized products formed during τ is probed by application of an rf pulse, usually of duration much less than $\pi/2$. After this the FID is acquired in the normal way and the experiment is repeated as many times as necessary for signal averaging. A kinetic profile for the appearance of the products is obtained by varying τ.

It is instructive to point out some of the differences between this method and conventional optical flash photolysis. First, our experiment monitors only the

rates of formation of the final products. Intermediates cannot be seen. A "snapshot" picture of the reaction is taken at the time τ, giving us the concentrations of the products at that particular time. Any products formed later are not seen because their magnetization remains parallel to the main applied field and does not induce any EMF in the probe coil. The nuclei in the free radicals are not excited by the rf pulse because they are shifted out of range by the hf interaction. To complete the comparison, our method produces a complete spectrum with conventional high resolution, but only one kinetic point per flash, while optical methods usually give a complete kinetic profile but only for one wavelength.

The time resolution of the experiment depends on both the excitation and probing pulse widths. While there is no problem with shortening the laser pulse, at present the limit is determined by the rf pulse. The task is to build up a B_1 field in the probe coil of sufficient magnitude to rotate the sample magnetization in as short a time as possible by an amount sufficient to give adequate signal-to-noise ratios. Obviously, the more rf power the better, but high-power amplifiers are expensive. But even given lots of rf power a second problem arises from the high Q of conventional NMR probes. A high Q means a high-quality resonant circuit with narrow bandwidth and associated slow rise and fall times. A low Q single coil spectrometer means poor sensitivity in signal detection. We have approached this problem by electronically switching the Q: low Q for transmitting and high Q for receiving. A simple PIN diode switch activated by the computer accomplishes this. Together with a home-built 1-Kw pulsed amplifier we have generated useful rf pulses of $\sim$120-ns (fwhm) duration on our 60-MHz spectrometer and hope to do considerably better at higher frequencies.[6,8] The time resolution of the experiment can be improved by using deconvolution methods. At small tip angles the time response of the instrument is a function of the envelop of the rf pulse, $F(t,\tau)$, and the concentration $c(t)$ of the polarized product. If we approximate $F(t,\tau)$ by a Gaussian function, we obtain for the signal intensity

$$\ln t(\tau) \propto \int_0^\infty dc(t) \int_t^\infty e^{-a(t-\tau)^2} \, dt, \, dt$$

where a defines the width of the pulse and τ is defined as the interval between the laser pulse and the center of the rf pulse. Of course it is possible to determine $F(t,\tau)$ experimentally and use its numerically integrated form. By substituting the differential rate expression for $dc(t)$ followed by numerical integration, the resulting curves can be fitted to the data. With this procedure the time resolution of our present experiment is approximately 25 ns, that is we can clearly distinguish between product formations with 25- and 50-ns rise times.
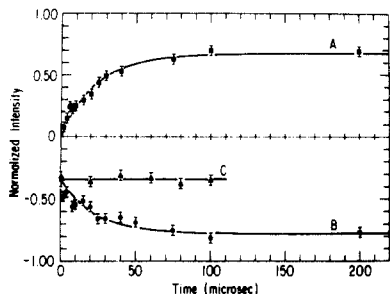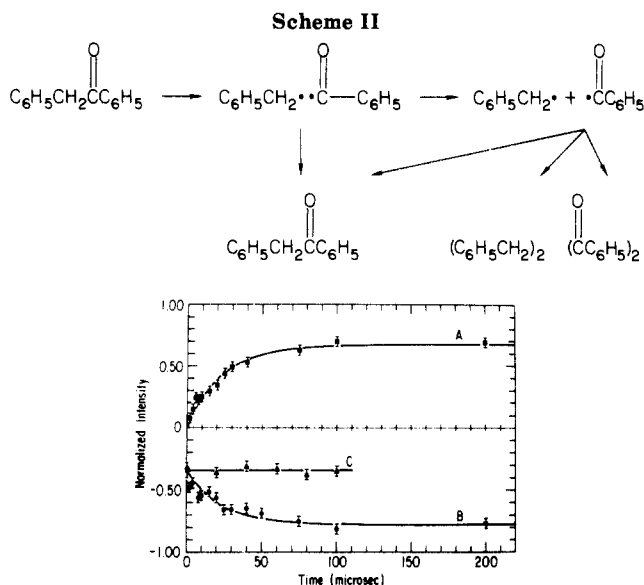
Applications

The first time-resolved CIDNP experiment was carried out with a conventional flash lamp working on the millisecond time scale and was not intended to study fast chemical reactions.[5] It will be briefly discussed in the section on coherence phenomena. It is convenient to separate the discussion of the chemical applications

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(6) Miller, R. J.; Closs, G. L. *Rev. Sci. Instrum.* **1981**, *52*, 1876.
(7) Schäublin, S.; Wokaun, A.; Ernst, R. R. *J. Magn. Reson.* **1977**, *27*, 273.

(8) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 3586.

Scheme II

$$C_6H_5CH_2\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5 \longrightarrow C_6H_5CH_2{\cdot}{\cdot}\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \longrightarrow C_6H_5CH_2{\cdot} + {\cdot}\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5$$

$$C_6H_5CH_2\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5 \qquad (C_6H_5CH_2)_2 \quad (\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5)_2$$

Figure 2. Intensity of CH_2 resonance as function of τ in (A) dibenzyl, (B) deoxybenzoin, and (C) deoxybenzoin in presence of thiol scavenger.

into reactions studied in the microsecond and nanosecond time domains. This division follows the natural line between free radical reactions on the one hand and geminate pair and biradical processes on the other.

Microsecond Time-Resolved CIDNP. The first microsecond experiments were designed to separate geminate from free radical processes and provide a general test for the method.[9] For this the photolysis of deoxybenzoin (1) was studied in the absence and presence of radical scavengers. This simple system gave the expected results for the chemistry indicated in Scheme II. The only possible geminate reaction is reformation of 1, and accordingly at the earliest time measured (~ 1 μs) the CH_2 group of 1 shows substantial emission. The escaping radicals are carrying opposite polarization which is clearly shown in the enhanced absorption of the bibenzyl appearing at later times. As shown in Figure 2, its intensity extrapolates back to zero as is expected for free radical dimerization. Also on the same time scale the ketone CH_2 emission becomes stronger. The quantitative analysis of the bibenzyl formation does not follow second-order kinetics because competing with dimerization is the loss of polarization in the free radicals by spin–lattice relaxation. The mixed-order analysis gave values for the dimerization rate constant of 4×10^9 M^{-1} s^{-1} and for $1/T_1 \approx 10^4$ s^{-1}.[10] It is interesting to note that free radical combination via uncorrelated pairs yielding the ketone 1 enhance geminate polarization. This is in accord with theory only if there has been substantial nuclear relaxation during the lifetime of the free radicals. Finally, an experiment with dodecylhydrogen sulfide which scavenges the benzoyl radicals on a time scale slower than geminate combination shows a flat time response for the ketone emission.

In summary, this experiment confirmed the practicality of the method and accomplished the temporal resolution of geminate and free radical processes. Be-

Scheme III

$$D^* + A \longrightarrow \overline{D^{+}{\cdot}\ A^{-}{\cdot}} \longrightarrow D^{+}{\cdot} + A^{-}{\cdot}$$

$$D + A$$

sides free radical kinetics nuclear T_1 values can be measured. These are difficult to obtain by other means and only a handful are known.

With the same method, Fischer and co-workers have studied the photolysis of two ketones.[11] The first, di-*tert*-butyl ketone yields the geminate products ketone, pivalylaldehyde, and isobutene and gives *tert*-butyl as the only escaping radical because decarbonylation is very fast. Rate constants for disproportionation and dimerization of *tert*-butyl as well as proton T_1 were obtained. By adding tributylin hydride, the escaping radicals were converted to isobutane before relaxation and the sum of the integrals of the geminate and escape products was found to be zero as required by theory (vide supra). Photolysis of methyl *tert*-butyl ketone generates a two radical system as the acetyl radical does not decarbonylate. Besides obtaining kinetic data for the various radical reactions, some subtle points of the radical pair theory were confirmed. Turro and colaborators have used time-resolved CIDNP to measure radical kinetics associated with micellar dynamics.[12] Benzyl radicals created inside a micelle by photolysis of dibenzyl ketone were scavenged in the aqueous phase by Fremy's salt, and the appearance rate of the polarized product was equated with the exit rate of benzyl radical from the micelle.

A most interesting situation arises in CIDNP spectroscopy when a radical reaction is cyclic and produces no net chemical change. In that case the reactant, geminate, and free radical products are all the same. This situation is most often found in electron transfer reactions in which the radical ions are stable, and the only way for the system to relax is back transfer regenerating the reactant. Scheme III summarizes this situation. In this case the spin-sorting mechanism described above predicts zero polarization because of mutual cancellation of contributions by geminate and free radical products. What saves the CIDNP spectroscopist is the relatively long lifetime of the free radicals allowing them to undergo at least partial spin–lattice relaxation, thus making the cancellation less than complete.[13] As pointed out in the Introduction, for this to be effective the lifetime of the radicals has to be on the order of 10^{-4} s or longer. There exist situations when this is difficult to achieve because what counts is the lifetime of the individual ions or radicals and not the macroscopic lifetime of the ensemble. For example self-exchange of the type

$$D^+ + D \rightleftharpoons D + D^+$$
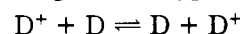
has no macroscopic effect but shortens the life of the individual ions. Even with less than millimolar ground-state concentrations self-exchange is often sufficiently fast to reduce the ion lifetime to a few microseconds, much shorter than the nuclear T_1. One
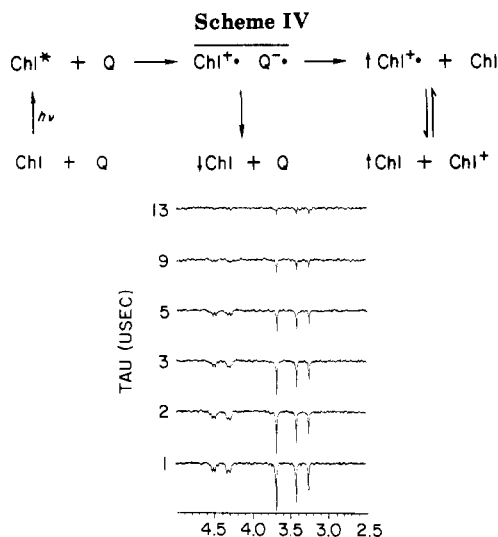
(9) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 1639.
(10) To simplify the kinetics and reduce the system to one radical *n*-dodecylhydrogen sulfide was added to scavenge the benzoyl radical: Closs, G. L.; Miller, R. J., unpublished results.
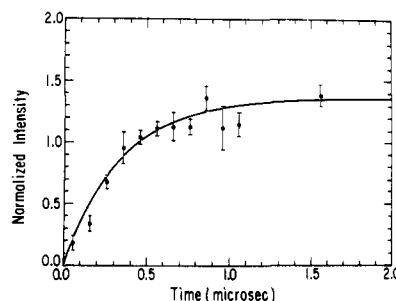
(11) Vollenweider, J. K.; Fischer, H.; Henning, J.; Leuschner, R., submitted for publication in *Chem. Phys.* See also: Läufer, M.; Dreeskamp, H, *J. Magn. Reson.* **1984**, *60*, 357.
(12) Turro, N. J.; Zimmt, M. B.; Gould, I. R. *J. Am. Chem. Soc.* **1983**, *105*, 6347.
(13) Closs, G. L. *Chem. Phys. Lett.* **1975**, *32*, 277.

Scheme IV

$$Chl^* + Q \longrightarrow \overline{Chl^{+\cdot}\ Q^{-\cdot}} \longrightarrow \uparrow Chl^{+\cdot} + Chl$$

$$\downarrow h\nu \qquad\qquad \downarrow \qquad\qquad \Updownarrow$$

$$Chl + Q \qquad \downarrow Chl + Q \qquad \uparrow Chl + Chl^+$$

Figure 3. Proton spectra at 200 MHz of pyromethylpheophorbide *a* as function of delay τ.

of the first electron-transfer reactions studied by CID-NP was the photooxidation of chlorophyll (Chl) and its derivatives by quinones (Q). Both radical ions are stable and revert to reactants. Strong quinone polarization was observed in steady state, but no trace of the more interesting chlorophyll polarization could be found.[14] Presumably, no relaxation takes place in the Chl^+ possibly because of fast self-exchange.[15] This situation is summarized in Scheme IV where opposite arrows indicated opposite polarization, and the quinone has been omitted from the right side for clarity. Time-resolved CIDNP has not only confirmed this scheme but has also yielded self-exchange rate constants.[16] This is because the geminate process is over in much less than a microsecond, and the products can be probed before the oppositely polarized free ions convert to the same product. The result is shown in Figure 3 in which the signal decays with the self-exchange rate. We believe this to be the only way to measure fast self-exchange rates by an actual signal decay rather than line-shape analysis. Optical methods of course are of no use here.

Signals can also be destroyed in cyclic reactions by unusually fast recombination or disproportionation of free radicals or ions. The latter pathway was found to be important in electron transfer between *N*-acetyltryptophane and flavins as studied with time-resolved CIDNP by Kaptein and collaborators.[17]

Nanosecond Time-Resolved CIDNP of Radical Pairs and Biradicals. By modifying a commercial spectrometer as briefly outlined above, it is possible to improve the time resolution significantly by shortening the rf pulse.[6] The first experiment in the nanosecond time domain once again was carried out on deoxybenzoin.[8] In the time regime of less than 1 μs only signals from ketone 1 was observable. The rise of the geminate product signals (Figure 4) is much too slow to correspond to the geminate combination rate. Of

(14) Tomkiewcz, M.; Klein, M. P. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 143. Lamola, A. A.; Manion, M. L.; Roth, H. D. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 3265.
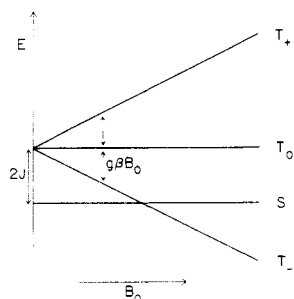(15) Kaptein, R.; Dijkstra, K.; Muller, F.; van Schagen, C. G.; Visser, A. J. W. *J. Magn. Reson.* **1978**, *31*, 171.
(16) Closs, G. L.; Sitzmann, E. V. *J. Am. Chem. Soc.* **1981**, *103*, 3217.
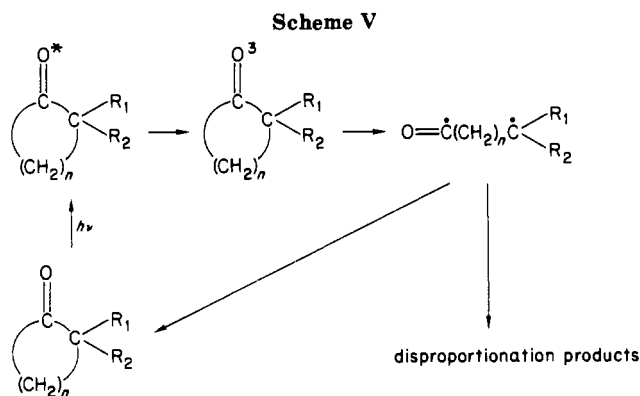(17) Hore, P. J.; Zuiderweg, E. R. P.; Kaptein, R.; Dijkstra, K. *Chem. Phys. Lett.* **1981**, *83*, 376.

Figure 4. Intensity of emission of the CH_2 signal in deoxybenzoin on the submicrosecond time scale.
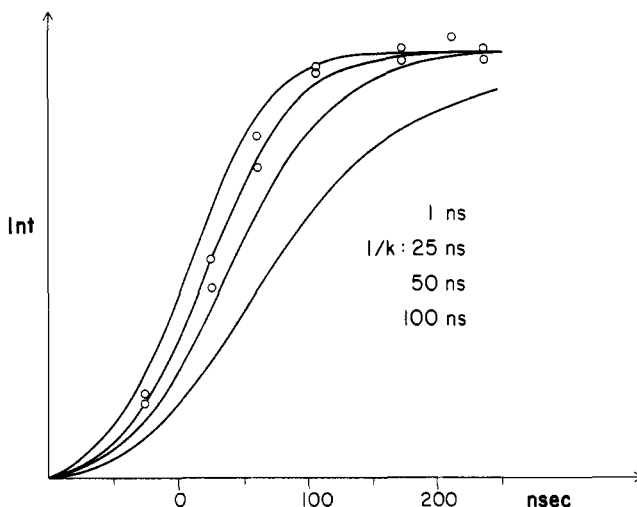
Figure 5. Calculated response for exponential rise with time constants as indicated. Calculations assume a rf pulse of Gaussian shape with 120-ns fwhm. Experimental points were obtained for the CH_2 group in dibenzyl ketone photolysis.

course the product formation is a two-step process, the first being the formation of the radical pair. We attribute the measured rate to this step, or in other words we are measuring the triplet lifetime of 1. Comparison with optically obtained data supports this conclusion. The advantage of nanosecond measurements is the absence of relaxation and free radical processes. Only geminate products are observed, and the spectral assignments are usually unambiguous.

A ketone whose triplet lifetime is known to be less than a nanosecond is dibenzyl ketone (2). When its time-resolved CIDNP spectrum was run, it was found to give a very fast rise of the geminate product 2. The best fit with a single exponential using the deconvolution equation gives us a time constant of 25 ns (Figure 5).[18] Probably this represents the limit of our spectrometer, and it is likely that the geminate combination is 3–5 times faster than that.

However, this time resolution is sufficient to examine the chemistry of some triplet generated biradicals. Biradical CIDNP differs in several important ways from that in radical pairs.[19] First, there is no unlimited separation of the radical centers in the absence of bimolecular reactions. The only pathway for collapse corresponds to the geminate route. This seems to prevent CIDNP altogether because the spin-sorting process requires escape products. What makes biradical CIDNP possible is that singlet and triplet states are

(18) Closs, G. L.; Redwine, O. D., unpublished results.
(19) Closs, G. L. *Adv. Magn. Reson.* **1977**, *7*, 157.

Figure 6. Schematic energy level diagram of a static biradical with singlet triplet separation of $2J < 0$ as function of applied field, B_0.

Scheme V

disproportionation products

never completely degenerate except for very long biradicals. If one plots the energies of the four states of a biradical as a function of magnetic field (Figure 6), one sees that for a small singlet–triplet separation, $2J$, there is a level crossing at a field corresponding to $2J = g\beta B_0$, where g is the electron g factor and β is the Bohr magneton. For most cases J is negative leading to S–T_ crossing. At the crossing the two levels are mixed by the hf interaction resulting in an avoided crossing. All of CIDNP is based on the principle of conservation of angular momentum. In the absence of strong orbital components this leads to the selection rule for mixing of $(\Delta m_z)_S + (\Delta m_z)_I = 0$ where the terms denote the change in the z component of the spins of the electron and nucleus, respectively. For T_0–S mixing in radical pairs, $(\Delta m_z)_S = 0$, and therefore the nuclear term has to be zero too. No nuclear spin flip is involved and polarization occurs by spin sorting. In biradicals with T_–S mixing, $(\Delta m_z)_S = 1$, and therefore the nuclear spins have to flip by −1 in crossing from triplet to singlet. This gives rise to an all emissive spectrum for T_–S processes or an all enhanced absorption for T_+–S without the need for an escape route. In conformationally flexible biradicals the situation becomes complicated by the fact that J is conformation dependent changing the crossing point along the B_0 axis. Nevertheless, we may think of an average J and predict that the longer the biradical the lower the field where crossing occurs. This has been experimentally confirmed for a series of 1,6–1,11 biradicals by field-dependent CIDNP.[19,20]

Recently, we have measured the time-resolved CIDNP of a similar series of biradicals generated from the corresponding cyclic ketones by the Norrish type 1

(20) Closs, G. L.; Doubleday, C., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 9248; **1973**, *95*, 2735. De Kanter, F. J. J.; Den Hollander, J. A.; Huizer, A. H.; Kaptein, R. *Mol. Phys.* **1977**, *34*, 857. Doubleday, C., Jr. *Chem. Phys. Lett.* **1981**, *77*, 131; **1982**, *85*, 65.

Table I

biradical	length	fwhm, ns	disprop/ cycliz	10^2- $(EF/EF_{max})^a$
$\dot{C}H_2(CH_2)_6\dot{C}O$	1,8	100	0.48	0.62
$(CH_3)_2\dot{C}(CH_2)_6\dot{C}O$	1,8	83	2.4	2.28
$\dot{C}H_2)_5\dot{C}O$	1,7	100 (140)	0.51	0.94
$CH_3\dot{C}H(CH_2)_5\dot{C}O$	1,7	110	0.61	1.47
$(CH_3)_2\dot{C}(CH_2)_5\dot{C}O$	1,7	130	2.0	3.72
$\cdot\langle\!\rangle\!-\!(CH_2)_2\dot{C}O$	1,6	77	7.0	1.25
$(CH_3)_2\dot{C}(CH_2)_4$ $\dot{C}O$	1,8	150 (200)	3.0	

^{a} EF/EF_{max} is the fraction of the maximum theoretical enhancement factor.
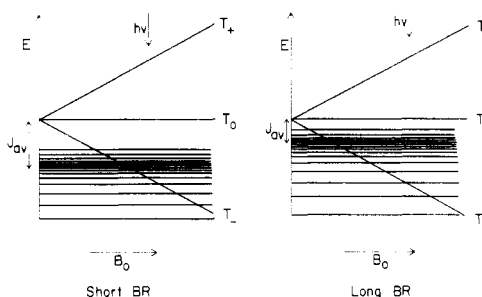
Figure 7. Schematic energy level diagrams of flexible biradicals resulting in variable J. The individual conformations are represented by the energy changes in the singlet levels with their probability represented by the density of lines. For clarity the triplet energy is held constant.

photocleavage. The chemistry is shown in Scheme V and the compounds are listed in Table I.[21] The appearance rates of the cyclic coupling and acyclic disproportionation products give a direct measure of the biradical lifetimes provided the formation rate is fast compared to the biradical annihilation. This is the case for all compounds listed in the table except two where the fit was made with a double exponential representing both formation and annihilation rates. It can be seen that the rates are all of the order of 10^7 s^{-1}.

As shown above, triplet–singlet crossing in radical pairs however is complete in 10^{-8} s or less. Thus one has the curious situation that triplet biradicals stay in the triplet state longer than radical pairs. As it turns out this is quite understandable if one considers that the components of a radical pair can separate to distances where J has become negligible making S and T_0 perfectly degenerate. At that point singlet–triplet mixing is at its maximum and intersystem crossing is complete in a few nanoseconds. Of course only a small fraction of the geminate pair components find each other again limiting the yield of geminate product severely (<5%). On the other hand in biradicals yield is no problem because the centers cannot get away from each other. Here triplet singlet crossing is the rate-determining step. In Figure 7 we have pictured schematic energy diagrams of conformationally flexible biradicals covering a range of J corresponding to the various conformations. If the applied field is indicated by the arrow, it can be seen that T_–S degeneracy is restricted to a small fraction of all the conformations. Most of the time there is an energy gap between the two

(21) Closs, G. L.; Redwine, O. D., submitted for publication in *J. Am. Chem. Soc.*
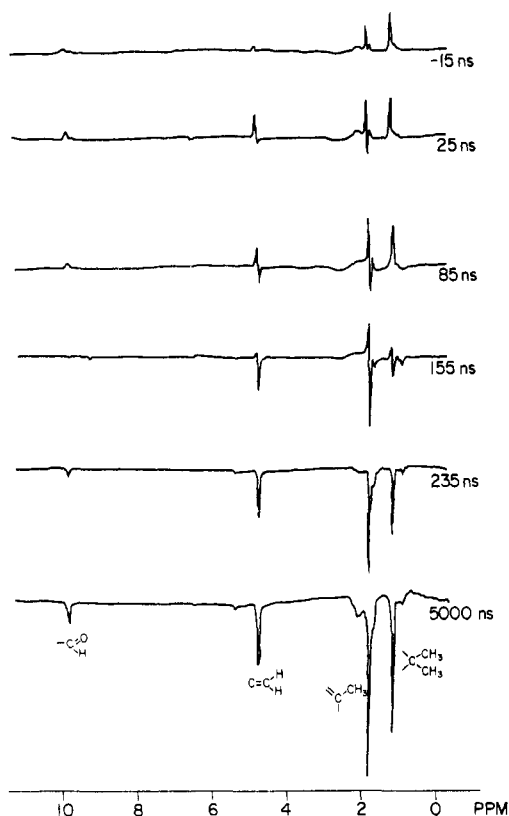
Figure 8. 60-MHz spectra obtained from laser photolysis of 2,2-dimethylcyclooctanone as function of delay τ. Negative τ corresponds to center of rf pulse preceding the laser flash.

levels. Since the mixing falls off with $1/(\Delta E)^2$, it can become very small indeed. The CIDNP results support this conclusion quite convincingly. By measuring the enhancement factor, it is found that only a small fraction of the biradicals undergo intersystem crossing via the hyperfine mechanism, while most of them make use of spin–orbit coupling and uncorrelated electron spin–lattice relaxation.[22]

Time-resolved CIDNP has led to another very interesting phenomenon. We consider Figure 7 once again. For a biradical of a given chain length there is a minimum J, presumably associated with the fully extended conformation.[23] The longer the biradical the smaller the minimum. There is no maximum on the energy scale we consider here because the two ends can always come closer to each other. With this, Figure 7a corresponds to a shorter biradical than shown in Figure 7b. In Figure 7a the maximum probability for J puts S closest to T_- while in Figure 7b the probability maximum is closer to T_0 at the measuring field. This means that in the longer biradicals there is more mixing with T_0 than T_- at practical NMR fields. In both cases the mixing is less than the T_0–S mixing in radical pairs. With nanosecond time resolution this has been confirmed in a striking way.[18] As Figure 8 shows, at a very early time (less than 100 ns), the spectra obtained from

cyclooctanones at 60 MHz show a clear T_0–S mixing pattern that is replaced at later time by a pure T_-–S spectrum. Cycloheptanone, however, is a pure T_-–S spectrum at all times. This corresponds to parts a and b of Figure 7, respectively.

What we have here is electron and nuclear state selective chemistry observable because the finite J has slowed down the intersystem crossing enough to allow us to measure the rates of the individual nuclear spin states! At later times even the slower T_0 nuclear states have crossed, wiping out the T_0–S pattern and leaving a T_-–S spectrum. This means that with fast enough time resolution spin sorting can be dispensed with even in T_0–S processes!

Coherence Phenomena

In an ordinary CW CIDNP experiment the density matrix describing the evolving radical pair has only diagonal elements at all times because the continuous generation of pairs assures randomization of all phases. With pulsed excitation, however, all radical pairs start their life at the same time in the same electronic state. The electron spin functions evolve coherently and the off-diagonal elements containing hf and Δg terms give rise to oscillations damped by the radical pair distribution function. This suggests a hypothetical experiment. Our two-pulse, time-resolved experiment has all the necessary ingredients for two-dimensional FT spectroscopy if coherence is maintained during the evolution time τ. Collection of a data set with varied τ, transformation of the FID's, and a second transformation along the τ axis should give a two-dimensional spectrum with chemical shifts as one axis and the hf couplings and Δg for each proton on the other. Although a highly useful experiment, it has not yet been realized and possibly never will be.[24] Besides technical problems such as a probing pulse of less than 5 ns, there is the problem of maintaining coherence in the radical pair long enough to achieve useful resolution along the hyperfine axis. The heavy damping caused by radical pair combination may make this impossible.

However, coherence effects have been observed on a time scale approximately a million times slower than our hypothetical experiment. They arise from the coherent evolution of the nuclear spin functions in the product molecules. When two radicals, geminate or not, combine, the nuclear spin functions of the product can be formed in a nonstationary state and oscillations may occur. This is the case if protons in the product are coupled by nuclear–nuclear coupling (J coupling) which gets "turned on" suddenly by product formation. This leads to observable oscillations among the components of the J coupling multiplets with frequencies determined by the magnitude of J and the chemical shift differences. Experiments of this type have been described by Ernst and collaborators in the flash lamp photolysis of 4-chlorobenzoyl peroxide.[5] In our laboratory we have seen equivalent effects in spin multiplets such as occur in methylcyloheptanone.[18] The oscillations occur on the millisecond time scale and have to be taken into account in time-resolved CIDNP with long delays.

(22) The contributions to triplet–singlet mixing by nuclear spin independent processes has been suggested by: Closs, G. L. In "Chemically Induced Magnetic Polarization"; Muus, L. T., Atkins P. W., McLauchlan, K. A., Pedersen, J. B., Eds.; D. Reidel Publishing Co.: Dordrecht, 1977; Chapter 20. Also by: Doubleday, C., Jr. in ref 20. Quantitative modeling has been attempted by: De Kanter, F. J. J.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759.

(23) Because of through-bond interactions there may be conformations in which *J* cancels to zero or even becomes positive, but they are not considered important components in the average.

(24) Optically detected oscillations due to spin coherence in radical pairs have recently been detected by: Anisimov, O. A.; Bizyaev, V. L.; Lukzen, N. N.; Grigorrylants, V. M.; Molin, Yu. N. *Chem. Phys. Lett.* **1983**, *101*, 131.

Outlook

The future developement of time-resolved CIDNP may go in the direction all optical spectroscopy has gone by improving the time resolution. Improvement is possible by using higher field spectrometers and more powerful amplifiers. But the ultimate limit is given by the period of the rf frequency which is 2 ns for the highest field commercial spectrometer to date. By coming close to this limit we will be able to measure the kinetics of the geminate processes including the rates of individual nuclear spin states. Another possible direction has been pointed out by Blümlich,[25] who suggested combining the advantages of stochastic resonance, low rf and laser power, with time-resolved CIDNP. No attempts have as yet been made to realize that experiment. All time-resolved CIDNP reported so far has been on protons. Other nuclei may be investigated in the future. The achievable time resolution is proportional to the gyromagnetic ratio and will accordingly be less for nuclei other than protons.

It is clear that the temporal resolution of CIDNP will never come close to the frontier of optical spectroscopy. However the information obtained by the two methods is highly complementary. The superior information content of high-resolution NMR spectra make it easy to assign kinetics to specific products even if there is a complicated mixture of them. Self-exchange reactions cannot be studied at all with optical methods. Most importantly the detailed spin dynamics being revealed by CIDNP remains obscured in optical measurements.

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Molecular Aspects of Rubberlike Elasticity

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The elasticity associated with rubberlike materials is very different from that exhibited by atomic or low molecular weight substances such as metals, crystals, and glasses.[1-3] In particular, the extensibility of "elastomers" is much higher, frequently amounting to well over 1000%. Most strikingly, such high deformations are generally completely recoverable. The way this recoverability is achieved, however, is the main source of the problems encountered in characterizing rubberlike materials and in developing useful structure-property relationships.[3,4]

Specifically, elastomers consist of polymer chains and the extraordinarily large numbers of spatial arrangements such molecules can exhibit is the origin of their very high extensibility.[1-3] Achieving recoverability requires preventing the chains from irreversibility sliding by one another, and this is accomplished by joining different chains with "cross-links", as is illustrated in Figure 1.[3] Relatively few are required, with a typical degree of cross-linking involving only one skeletal atom out of approximately 200. The techniques generally used to introduce cross-links are peroxide thermolysis, high-energy irradiation, and sulfur addition to skeletal or side-chain unsaturation.[1] All are statistical processes, and the number of cross-links thus introduced and their placements along the chains are uncontrolled and essentially unknown. Furthermore, their introduction into the material makes it intractable in that it is no longer soluble in any solvent. The numerous standard characterization techniques based on measurements on isolated chains in solution[1] are therefore categorically inapplicable. Thus, the very process of forming the required network structure thwarts its characterization. It is the lack of reliable structural information that is the problem in obtaining structure-property relationships in the area of rubberlike elasticity.

Now, however, it is possible to prepare "model" elastomeric networks,[4-15] which are materials prepared in a way that provides independent information on their structures. An important example is reaction 1 in which

$$4HO\text{---}OH + Si(OEt)_4 \longrightarrow \quad + 4EtOH \quad (1)$$
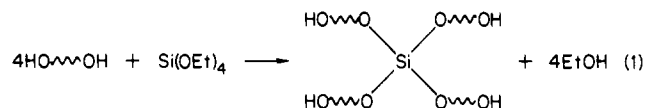
OH---OH represents a hydroxyl-terminated chain of poly(dimethylsiloxane) (PDMS) $[-Si(CH_3)_2O-]$.[11] In this approach, some solution characterization technique such as gel permeation chromatography is first used to obtain the number-average molecular weight M_n of the uncross-linked chains and the distribution about this average. Then carrying out the above reaction so as to

A biographical sketch of the author was published earlier, in *Acc. Chem. Res.* 1974, *7*, 218, and 1979, *12*, 49. He is spending the 1985-1986 academic year at the IBM Research Laboratory in San Jose, CA.

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