Chemically Induced Dynamic Nuclear Polarization during Thermal Decomposition of Peroxides and Azo Compounds

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During rapid radical reactions in liquids, the nuclear magnetic resonance spectra of the reacting solutions often show emission and/or enhanced absorption lines which become absorption lines of normal intensities at the end of the reaction. We have observed such effects during thermal decompositions of organic peroxides and azo compounds;[2-5] similar observations have been made independently by Ward and Lawler[6-9] in respect to reactions of alkyl halides with lithium alkyls. The effects during the latter reactions have also been studied by Lepley, et al.[10,11]

In all cases the nuclei which show abnormal intensities in their nmr transitions belong to the products of the reactions, and in most cases they had belonged to the reactants initially. The nuclei Y were thus originally with the parent compounds R–Y, then with the intermediate free radicals ·R–Y, and finally with the product molecules R'Y.

$$RY \rightarrow \cdot R\text{--}Y \rightarrow R'Y \qquad (1)$$
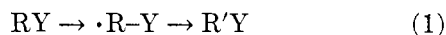
A qualitative explanation which describes why the nuclear spin state populations of the products R'Y may deviate strongly from the thermal equilibrium populations so that emission or enhanced absorption occurs has been put forward.[3,8] This explanation is based on the theory of the long-known physical effect of dynamic nuclear polarization (DNP)[12,13] as specified for nuclei of free radicals in solution.[13] According to this theory the nuclear spin states of free radicals may in fact become populated by relaxations due to magnetic electron–nuclear interactions in such a way that the corresponding nmr transitions show emission or enhanced

absorption if the electron spin states of the radicals are equally populated. Further, the explanation[3,8] requires that during radical formation in chemical reactions two radicals with antiparallel electron spins are always generated simultaneously and that nuclei conserve their nuclear spin states during product formation from radicals. With these assumptions the electron spin states of the radicals are initially equally populated, the populations of the nuclear spin states are then changed by DNP, and the result of this change is subsequently observed in the nmr spectra of the product molecules.

Since, according to this qualitative picture the effect of nmr emission and/or enhanced absorption during radical reactions is closely related to the physical effect of DNP, it has been named chemically induced dynamic nuclear polarization (CIDNP).[3,8] The similar and related effect of optically induced dynamic nuclear polarization of molecules in the solid state[14,15] and in solution[16] arising from DNP in their triplet states has also recently been discovered. In this Account we summarize the main experimental results on CIDNP during thermal decomposition of peroxides and azo compounds. The present stage of the theory is presented, and some potentialities and limits are discussed. Similarities of our results to the results of Ward and others are pointed out, but an account of their work will be published by Ward elsewhere.

Results

Solutions of peroxides or azo compounds were prepared at room temperature and transferred to the preheated probe of the nmr spectrometer. The spectra were then recorded repeatedly. Sometimes the transient CIDNP effects were observed only when the reaction temperatures were so high that the reactions were complete in times shorter than the time required for spectra recording. Then a special recording technique,[2] which consisted of combining the nmr spectrometer with a tape recorder, was applied. During the reactions the spectra were stored rapidly on the tape, and they were displayed afterward.

As an example of emission, Figure 1 shows nmr

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(2) J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch.*, **22a**, 1551 (1967).
(3) J. Bargon and H. Fischer, *ibid.*, **22a**, 1556 (1967).
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(6) H. R. Ward, *J. Am. Chem. Soc.*, **89**, 5517 (1967).
(7) H. R. Ward and R. G. Lawler, *ibid.*, **89**, 5518 (1967).
(8) R. G. Lawler, *ibid.*, **89**, 5519 (1967).
(9) *Chem. Eng. News*, **46**, 40 (Jan 15, 1968).
(10) A. R. Lepley, *J. Am. Chem. Soc.*, **90**, 2710 (1968).
(11) A. R. Lepley, and R. L. Landau, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract ORGN-130.
(12) A. Abragam, "Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961.
(13) K. H. Hausser and D. Stehlik, *Advan. Mag. Resonance*, **3**, 79 (1968).

(14) G. Maier, U. Haeberlen, H. C. Wolf, and K. H. Hausser, *Phys. Letters*, **25A**, 284 (1967).
(15) G. Maier and H. C. Wolf, *Z. Naturforsch.*, **23a**, 1068 (1968).
(16) M. Cocivera, *J. Am. Chem. Soc.*, **90**, 3261 (1968).

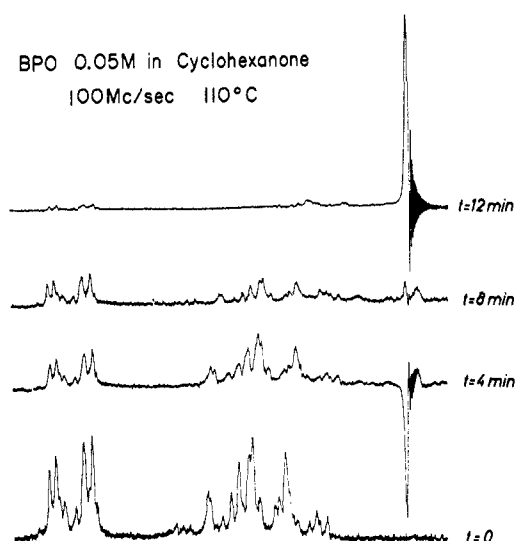BPO 0.05M in Cyclohexanone
100Mc/sec 110°C

Figure 1. Nmr spectra during thermal decomposition of dibenzoyl peroxide.

spectra during the decomposition of dibenzoyl peroxide (BPO) at 100° in cyclohexanone. At $t = 0$, immediately after transfer of the sample to the probe, in the phenyl proton region only the normal absorption lines of the BPO protons are observed. During the reaction these lines vanish and an emission line appears. Its amplitude reaches a maximum after ~4 min, then decreases, and after ~7 min the line reappears in absorption, reaching a constant maximum amplitude at the end of the reaction. From the line position and from product analysis the line is assigned to the protons of benzene molecules formed through hydrogen abstraction from the solvent S by transient phenyl radicals.
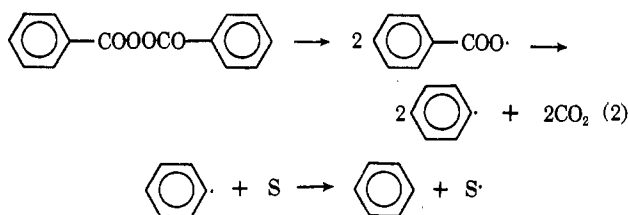
Thus the product benzene is formed with nonequilibrium nuclear spin state populations. Other minor lines in the spectrum of products in Figure 1 are due to reaction products of solvent-derived radicals.

The emission behavior of the benzene line can be stated in more quantitative terms from the results of the following experiment. The BPO decomposition was carried out in solutions containing paramagnetic ions.[3] As anticipated from the CIDNP explanation, the emission decreased with increasing ion concentrations because the ions cause relaxations of the free-radical electron spins and thus cause DNP to be avoided. For a concentration of 0.01 M, the benzene line appeared only in absorption, slowly increasing to the final absorption amplitude. Since in this case the formation of benzene is followed directly without the complications of emission, one can derive from the

experiments with and without paramagnetic ions an experimental enhancement factor for the CIDNP

$$V_{\text{exptl}} = \frac{A^* - A^0}{A^0} \qquad (3)$$

where A^0 is the absorption amplitude of the nonemitting benzene at the time where otherwise the emission reaches its maximum, and A^* is the (negative) maximum emission amplitude.[17]
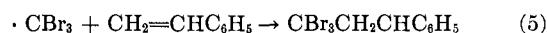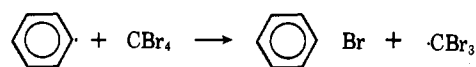
At the various operating frequencies of the nmr spectrometers available, V_{exptl} was found to be -2.9 at 100 MHz, -8.5 at 56.4 MHz, and -20 at 40 MHz for the benzene emission line. Recently similar low values of V_{exptl} were observed during photolytic decompositions of BPO at room temperature at 56.4 MHz.[18] With other systems single transient emission lines were also found for the chlorobenzene formed during p-chlorodibenzoyl peroxide decomposition and for the benzene formed during diazoaminobenzene decomposition.[4,5] In both cases V_{exptl} was of the same order of magnitude as given above, and the products were formed in reactions similar to (2).

During thermal decompositions of dialkyl peroxides,[4,5] which have also been studied by Kaptein,[19] a single emission line was observed for diacetyl peroxide in dimethyl phthalate at 100°. For higher alkyl peroxides the transient spectra showed many lines, some of emissive, some of enhanced absorptive character. Some of the lines were due to olefins arising from disproportionation reactions of the initial alkyl radicals (eq 4),

$$2\text{RCH}_2\dot{\text{C}}\text{H}_2 \rightarrow \text{RCH}{=}\text{CH}_2 + \text{RCH}_2\text{CH}_3 \qquad (4)$$
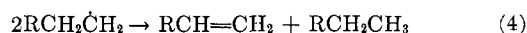
and these show a particularly interesting feature. In the multiplets of nmr transitions of a given set of protons both emission and enhanced absorption occur, and thus the populations of the spin states of these protons depend on the spin states of the other protons. This effect was previously observed by Ward and Lawler and also by Lepley during olefin formation in their special reactions.[6-11]

Another case of the same effect is the transient nmr spectrum of $\text{CBr}_3\text{CH}_2\text{CHBrC}_6\text{H}_5$ during reactions 5 in solutions containing BPO, CBr_4, and styrene.[4] At

$$\cdot\,\text{CBr}_3 + \text{CH}_2{=}\text{CHC}_6\text{H}_5 \rightarrow \text{CBr}_3\text{CH}_2\dot{\text{C}}\text{HC}_6\text{H}_5 \qquad (5)$$
$$\text{CBr}_3\text{CH}_2\dot{\text{C}}\text{HC}_6\text{H}_5 + \text{CBr}_4 \rightarrow \text{CBr}_3\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{Br} + \cdot\text{CBr}_3$$

56.4 MHz the nmr transitions of the methylene and methine protons are a doublet and a triplet, respectively. In the doublet the low-field component emits and the high-field component absorbs, and in the triplet the low-field component emits, the high-field compo-

(17) More correctly, intensities should be inserted in eq 3. Amplitudes can be used if the line width is the same in both experiments; this was the case for benzene.
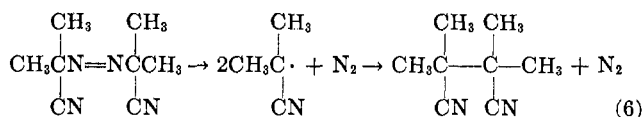(18) M. Lehnig, unpublished results.
(19) R. Kaptein, *Chem. Phys. Letters*, **2**, 261 (1968).

nent absorbs, and the intermediate component does not show appreciable CIDNP.

The multiplet effect thus occurs for molecules with nonequivalent protons formed by disproportionation reactions (eq 4) as well as for molecules formed in abstraction reactions. Relative intensities of the components have been rationalized by Lepley;[11] they may, however, depend on reaction conditions.

The features of CIDNP described so far also hold for the nmr spectra of products of azo compound decompositions.[4,5] Some results obtained during decomposition of azobis(isobutyronitrile)[5] seem to be of special importance and are therefore given here in some detail. If azobis(isobutyronitrile) (AIBN) decomposes at 100° in tetrachloroethane the main product, tetramethylsuccinodinitrile, shows a single nmr line of the methyl protons which increases regularly without transient emission or enhanced absorption. If, on the

$$
\begin{array}{ccccc}
CH_3 & CH_3 & & CH_3 & CH_3\ CH_3 \\
| & | & & | & | \quad | \\
CH_3CN{=}NCCH_3 \rightarrow & 2CH_3C\cdot + N_2 \rightarrow & CH_3C{-}C{-}CH_3 + N_2 \\
| & | & & | \quad | \\
CN & CN & & CN & CN\ CN
\end{array} \quad (6)
$$

other hand, the solution contains CBr_4, one of the main products is α-bromobutyronitrile, and the methyl proton line of this compound does show CIDNP emission. Thus the combination product of the

$$
\begin{array}{ccc}
CH_3 & & CH_3 \\
| & & | \\
CH_3C\cdot + CBr_4 \rightarrow & CH_3CBr \\
| & & | \\
CN & & CN
\end{array} \quad (7)
$$
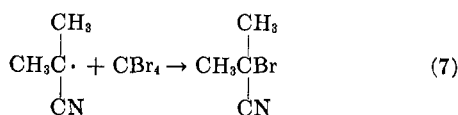
cyanoisopropyl radicals (eq 6) is not formed with nonequilibrium nuclear spin state populations whereas the abstraction reaction product (eq 7) is. In this context it should be mentioned that some disproportionation products of cyanoisopropyl radicals which appear as side products also exhibit CIDNP.[5]

Whether this and the other results given in this section may be generalized cannot yet be safely concluded since the amount of experimental information available up to now is quite limited. They may serve, however, as starting points for the theoretical discussion given below.

Theory and Discussion

For a formal treatment of CIDNP we have to calculate the populations, n_k, of the product molecule's nuclear spin states, $|k\rangle$, and the populations, N_{ik}, of the electron–nuclear spin states, $|i,k\rangle$, of the free radicals, where k refers to nuclear and i to electron spins, taking into account the time dependences of n_k and N_{ik} due to magnetic relaxations and the connections between n_k and N_{ik} by chemical reactions. Differences of the n_k are then proportional to the product nmr intensities, and thus theoretical enhancement factors of CIDNP can be derived. In particular, radical formation populates $|i,k\rangle$ with rates r_{ik}, and product formation depopulates $|i,k\rangle$ with rates r'_{ik}. Further the populations of $|i,k\rangle$ change with time, the rates being governed by

relaxation probabilities $w_{ik,i'k'}$ connecting states $|i,k\rangle$ and $|i',k'\rangle$ during the lifetime of the radicals. Following the usual treatment of spin lattice relaxation,[12] and denoting by N^0_{ik} thermal equilibrium populations, we thus have as total change of N_{ik} per time unit.

$$
\frac{dN_{ik}}{dt} = - \sum_{i',k'} w_{ik,i'k'} \{ (N_{ik} - N_{i'k'}) - \\
(N^0_{ik} - N^0_{i'k'}) \} + r_{ik} - r'_{ik} \quad (8)
$$

For the molecular states $|k\rangle$, on the other hand, the time dependence of n_k contains rates, r_k, of the production of molecules in states $|k\rangle$ and relaxation terms connecting $|k\rangle$ and $|k'\rangle$; thus

$$
\frac{dn_k}{dt} = - \sum_{k'} w_{kk'} \{ (n_k - n_{k'}) - (n^0_k - n^0_{k'}) \} + r_k \quad (9)
$$

In high-field approximation $|i,k\rangle = |i\rangle|k\rangle$, and if the assumption holds that the nuclei conserve their spin states $|k\rangle$ during molecule formation

$$
r_k = \sum_i r'_{ik} \quad (10)
$$

eq 8, 9, and 10 represent two general master equations for CIDNP. They can be solved in principle if the various parameters of relaxation and reaction rates are known.

A formal solution of the master equations was given previously[3] using the abbreviating Solomon equations[12] for the very simple case of a molecule having as a magnetic nucleus only a single proton and arising from a radical containing this same proton by an *abstraction* reaction. If contact hyperfine coupling in the radical is neglected, the energy levels of radical and molecule are as shown in Figure 2, where the various arrows which connect the states indicate the relevant relaxation and reaction paths. With the special assumptions (1) that all r_{ik} are equal, that is, radical formation in spin-compensated pairs and neglect of any influence of nuclear spin states or spin state populations on r_{ik}, (2) that $r'_{ik} = (1/\tau)N_{ik}$, which means depopulation of $|i,k\rangle$ by first-order reaction with a universal mean lifetime of the radicals, (3) that the $w_{ik,i'k'}$ arise exclusively from intraradical electron–nuclear interactions besides an arbitrary pure electron spin relaxation w_s, and (4) that reactions and relaxations achieve at some instant a stationary state, which might be valid for the time of the CIDNP maximum, this solution is in terms of an enhancement factor of the nmr line of the molecules

$$
V_{theor} = \frac{T_1 r}{n} \left\{ 1 - \frac{(1 + \rho''\tau) + 658\sigma\tau}{(1 + \rho''\tau)(1 + \rho\tau) - \sigma^2\tau^2} \right\} \quad (11)
$$

where $T_1 = 1/2w_{+-}$ is the nuclear spin lattice relaxation time for the product proton; $r = \sum r_{ik}$ is the total rate of radical formation at the time of steady state; $n = \int_0^T \sum r'_{ik} \, dt$ is the total number of molecules formed up to this time; and
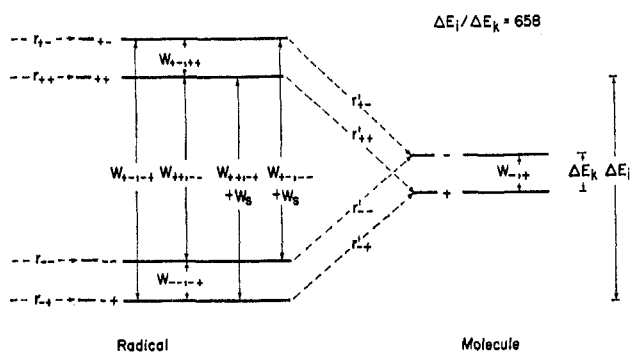
Figure 2. Energy levels of radical and product molecule.

$$\sigma = w_{+ +, - -} - w_{+ -, - +}$$

$$\rho'' = w_{+ +, - -} + 2w_{+ +, - +} + w_{+ -, - +} + w_s \quad (12)$$

$$\rho = w_{+ +, - -} + 2w_{+ +, + -} + w_{+ -, - +}$$

are combinations of relaxation probabilities of the free radical (see Figure 2) which are often used in DNP treatment.[12,13]

It can easily be shown that in eq 11 the denominator of the expression in brackets is always positive and that in the numerator $658\sigma\tau$ is the governing term for reasonable values of τ and $w_{ik,i'k'}$. Thus V can in fact be positive or negative, giving enhanced absorption or emission CIDNP according to the magnitude and sign of σ. For relaxation by dynamic scalar electron–nuclear interactions in the radical, σ is negative[12,13] and enhanced absorption will occur. For relaxation by dynamic dipolar interaction, σ is positive[12,13] and emission is possible. Thus eq 11 predicts the observed effects. Further, as is anticipated from the general picture (see introduction), eq 11 shows that, for $\tau \to 0$, $V \to 0$, and that, for $\tau \to \infty$, $V \approx 0$. In the first case no DNP develops in the radical because of lack of time, and in the second the DNP decays in the radical before it is transferred to the product. Finally, eq 11 explains the frequency dependence of the CIDNP for the benzene emission since the $w_{ik,i'k'}$ decrease with increasing frequency,[12,13] and it allows for the influence of paramagnetic ions which make w_s and ρ'' the leading relaxation probabilities.

Formal solutions of the master equations have also been obtained with the simple one-proton model for cases where the products are not formed by radical transfer in *abstraction* reactions but by *combination* or *disproportionation* using assumptions 1, 3, and 4, and substituting for the r'_{ik} appropriate second-order rate terms. For combination and disproportionation we find that the magnitude of the CIDNP effect depends on the electron spin selection rules of the reaction.

If two radicals always react regardless of their spin states (which means that both triplet and singlet encounters lead to molecule formation), then the rates of depopulation

$$r'_{ik} = kN_{ik} \sum_{i',k'} N_{i'k'} = kN_{ik}N = \frac{N_{ik}}{\tau} \quad (13)$$

are given by expressions 13 and CIDNP occurs with eq 11 describing the enhancement factor. If, on the other hand, only singlet-type encounters lead to molecule formation

$$r'_{ik} = kN_{ik} \sum_{i'k' \neq i} N_{i'k'} \quad (14)$$

and the rate of radical disappearance from states $|i,k\rangle$ will not be pseudo first order in N_{ik} and eq 11 will no longer hold. Instead here we find with a little algebra that the molecules should not show appreciable CIDNP effects.

This result can also be anticipated from the general explanation of CIDNP. If only singlet encounters lead to molecule formation, two radicals with paired electron spins always disappear simultaneously. Thus the over-all number of downward relaxation transitions in the free radicals which give CIDNP equals the over-all number of upward transitions (cf. Figure 2) which cancel this CIDNP, and no net effect is observed.[20]

For comparison of theory with experiment, we now consider CIDNP for the special cases where molecules with only one set of equivalent protons are formed by radical abstraction reactions. It is easy to show that eq 11 should hold for these molecules if the radical precursors have the same equivalent protons. Thus eq 11 might be applicable to describe CIDNP during benzene and chlorobenzene formation if the influence of the proton added to the radicals in the abstraction reaction eq 2 is small and if we assume that in the phenyl radicals only the two equivalent *ortho* protons interact strongly with the unpaired electron. Inserting in eq 11 the parameters r, n, and τ obtained from experiment and ρ'', ρ, and σ from calculations of relaxation terms from radical structure, we in fact get enhancement factors of the correct order of magnitude. For instance, for benzene during BPO decomposition we find $V_{\text{theor}} \approx -3$ for 100 MHz, -14 for 56.4 MHz, and -20 for 40 MHz, whereas the experimental values were -2.9, -8.5, and -20, respectively.[3,4,5,21]

The difference in CIDNP for the abstraction and the combination products of the cyanoisopropyl radicals during AIBN decompositions can also be understood from theory. The abstraction product product shows CIDNP as expected, and the combination product does not, probably because it is formed exclusively in singlet encounters. Another explanation of this lack of CIDNP, that the mean lifetime of the radicals is very small because the combination products were predominantly formed in a rapid cage reaction immediately following radical production, can be ruled out since at temperatures lower than that used in our experiments (40–$67°$ vs. $110°$) the fraction of radicals escaping the cage was determined to be in the range of 40–60%.[22–24]

(20) This cancelation of CIDNP during singlet-encounter radical combination or disproportionation was pointed out to these authors by K. H. Hausser, Heidelberg, in 1967.

(21) The values of V_{theor} given here differ from the values published earlier.[3] In recalculation, a value for T_1 was used which is considered to be more appropriate.[4,5]

Application of the theory to the disproportionation products of alkyl radicals, such as the olefins treated above, however, leads to two major difficulties. These are: the olefins show CIDNP and the multiplets of the nmr transitions of nonequivalent vinyl protons show emission and enhanced absorption simultaneously.

The first result may be explained if the disproportionation reactions occur without spin selectivity, so that triplet-state transition complexes are at least allowed. To our knowledge this has not been shown so far to be possible, although some remarks of Benson[25] may be understood to indicate triplet states during alkoxy radical disproportionation.

Secondly, the multiplet effect, which however is not unique for disproportionation products, is still more difficult to understand. Even if the general master equations 8 and 9 are used and if the reaction parameters and the relaxation terms are varied as far as at all reasonable, the effect is not revealed by the theory[8,26] unless special assumptions concerning the populations of the free-radical states are introduced. These assumptions are that the rates of population of the electron spin states $|i\rangle$ in the radicals depend on the associated nuclear spin states $|k\rangle$. If, for instance, in a radical with two nonequivalent protons the relation

$$r_{+,++} = r_{-,--} \neq r_{+,+-} = r_{+,-+} = r_{-,+-} = r_{-,-+} \quad (15)$$

is obeyed by the rates of population, then the two nmr multiplets of a corresponding abstraction or transfer product could show the multiplet effect, the detailed features depending on the type of inequality in eq 15 and on the type of electron–nuclear interaction in the radical.

Though there seems no foundation for eq 15 available at present, it may be mentioned that this relation does not mean a buildup of net electron spin or nuclear spin polarization on radical formation. It does mean, however, that the esr spectra of the radicals should show simultaneously emission and absorption lines immediately after radical formation. This transient behavior should be observable until electron spin relaxation, for instance by electron–nuclear coupling, has lead to the normal thermal equilibrium, that is, during a time of 10^{-6} to 10^{-5} sec after radical formation. Fessenden and Schuler,[27] and quite recently Smaller, et al.,[28] have observed just such transient emission and absorption esr signals; thus eq 15 and the multiplet effect in CIDNP might be related to their findings.

To summarize these conclusions, it is obvious that for CIDNP experiment and theory are both in only a preliminary stage. Much more experience and information on the details of radical relaxation and on radical reactions, especially on the behavior and development of spin states, is needed before the effect can be completely understood. However CIDNP may well be a valuable new tool for the investigation of these topics.[29]

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(24) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).

(25) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964).

(26) H. Metzler and H. Fischer, unpublished calculations.

(27) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

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(29) NOTE ADDED IN PROOF. R. Kaptein (private communication, to be published) has considered an explanation for the multiplet effect in the nmr of abstraction products which is similar to that proposed here. He also found a mechanism for the unequal population of the free radical states (eq 15) and for the esr emission effects.[27,28] It agrees with a tentative theory of these authors, and is based on spin state changes in intermediate radical pairs by the simultaneous action of hyperfine and exchange interaction. Thus for several abstraction reaction products the multiplet effect may in fact be caused by CIDNP. For the disproportionation reaction products especially for those of alkyl halide–lithium alkyl radical reactions[6-11] a CIDNP explanation of the multiplet effect is unlikely, however. Esr experiments on these systems (H. Fischer, to be published) show that the lifetimes of the corresponding alkyl radicals are longer than the electron–nuclear relaxation times, thus the spin state populations are in thermal equilibrium before product formation occurs. It is suggested that in these and similar cases the multiplet effect is due to spin state changes during radical encounters similar to the ones responsible for the esr emission effect. For recent experimental examples on the multiplet effect see also: H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Am. Chem. Soc.*, **91**, 746 (1969); A. R. Lepley and R. L. Landau, *ibid.*, **91**, 748 (1969); A. R. Lepley, *ibid.*, **91**, 749 (1969); A. R. Lepley, *Chem. Commun.*, 64 (1969).

Intermolecular Electron Exchange

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It is known that processes which involve a change in spin multiplicity proceed appreciably faster in the presence of paramagnetic materials. The lowest triplet states of molecules containing light atoms can be very long living because the transition to the singlet ground state is spin forbidden and spin–orbit coupling is very weak. On the other hand, when these triplet molecules can collide with paramagnetic species a rapid quenching occurs. Porter and Wright[1] have studied this triplet quenching by flash photolysis and found efficient

(1) G. Porter and M. R. Wright, *Discussions Faraday Soc.*, **27**, 18 (1959).