

# Chemically Induced Dynamic Magnetic Polarization in Photochemistry

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Both ESR and NMR spectroscopy are now commonly used to follow photochemical reactions in solutions because the transient free radicals<sup>1-3</sup> and diamagnetic intermediates<sup>4-7</sup> are easily detected and identified. The most effective experimental arrangement to study these short-lived species is to photolyze the solution directly within the ESR cavity or the NMR probe. However, spectra recorded under these conditions often exhibit "polarizations" which arise from the electron spin states of the radicals and the nuclear spin states of the diamagnetic products being populated in a non-Boltzmann manner.<sup>8</sup> These polarizations are referred to as chemically induced dynamic electron (nuclear) polarization, [CIDE(N)P].

It is now well established that both CIDEP and CIDNP have their origins in the formation and removal reactions of free radicals.<sup>7-15</sup> As a result of this, it is now possible to gain information not normally obtained from magnetic resonance studies for those photochemical reactions which show CIDE(N)P. An example of this is those photochemical reactions in which the two primary radicals react immediately to regenerate the starting compounds.<sup>16,17</sup> These regenerated compounds may show CIDNP, and this is often the only evidence that this reaction has occurred. As a general rule, CIDEP studies gather information from those radicals which escape the primary photochemical cage, whereas CIDNP provides information primarily about the "in-cage" radical reactions.

Since our last Account on chemically induced dynamic electron polarization, the controversy surrounding the origins of CIDEP has largely been resolved. In this Account, we shall briefly summarize these mechanisms and then illustrate how CIDEP and CIDNP together can be used in the study of photochemical reactions. No discussion of the theory of conventional CIDNP will be given here, as this has been treated in many excellent reviews published over the last few years.<sup>7,8,13-15</sup>

## CIDEP

In the conventional ESR experiment, it is automatically assumed that the electronic spin states of an ensemble of radicals are populated in a Boltzmann manner:

$$n_{\beta}/n_{\alpha} = \exp(g\mu_B H/kT) \quad (1)$$

where  $n_{\beta}$  and  $n_{\alpha}$  are the populations of the lower and

upper spin states, respectively,  $g$  is the electronic  $g$  factor,  $\mu_B$  is the Bohr magneton,  $H$  is the applied magnetic field,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. Since the intensity of an ESR transition is proportional to the population difference between the spin states, it is easily seen that the intensity ( $S$ ) is also proportional to the number of radicals ( $n_{\beta} + n_{\alpha}$ ), i.e.

$$S \propto (n_{\beta} + n_{\alpha})g\mu_B H/2kT \quad (2)$$

It is this relationship between intensity and radical concentration which has formed the basis for kinetic measurements on radicals. However, when CIDEP is present, eq 1 is no longer valid, which in turn invalidates eq 2.

The polarization of an ESR line is measured in terms of an enhancement factor ( $V$ ) which is defined as

$$V = (S - S_0)/S_0 \quad (3)$$

where  $S$  is the observed signal height and  $S_0$  is what the height should have been if all the spin states were populated according to the Boltzmann distribution.

In photochemically generated radicals, there are two readily recognized types of spectral polarization, each arising from quite different mechanisms and having distinctly different consequences on the spectrum.<sup>3,18-22</sup> These two polarizations may be described as "initial

- (1) H. Zeldes and R. Livingston, *J. Phys. Chem.*, **74**, 3336 (1970).
- (2) O. P. Chawla and R. W. Fessenden, *J. Phys. Chem.*, **79**, 2693 (1975).
- (3) P. B. Ayscough, T. H. English, G. Lambert, and A. J. Elliot, submitted to *J. Chem. Soc., Faraday Trans. 1*.
- (4) B. Blank, A. Henne, G. P. Laroff, and H. Fischer, *Pure Appl. Chem.*, **41**, 475 (1975).
- (5) S. Rosenfeld, R. S. Lawler, and H. R. Ward, *J. Am. Chem. Soc.*, **89**, 5518 (1967).
- (6) D. A. Hutchinson, H. M. Vyas, S. K. Wong, and J. K. S. Wan, *Mol. Phys.*, **29**, 1767 (1975); H. M. Vyas, S. K. Wong, B. B. Adeleke, and J. K. S. Wan, *J. Am. Chem. Soc.*, **97**, 1385 (1975).
- (7) H. D. Roth, *Mol. Photochem.*, **5**, 91 (1973).
- (8) See references in "Chemically Induced Magnetic Polarization", A. R. Lepley and G. L. Closs, Ed., Wiley, New York, N.Y., 1973.
- (9) P. W. Atkins and G. T. Evans, *Mol. Phys.*, **27**, 1633 (1974); *Adv. Chem. Phys.*, **35**, 1 (1976).
- (10) J. H. Freed and J. B. Pedersen, *J. Chem. Phys.*, **58**, 2746 (1973); **59**, 2869 (1973); **62**, 1706 (1975); *Adv. Mag. Resonance*, **8**, 2 (1976).
- (11) F. J. Adrian, *J. Chem. Phys.*, **54**, 3918 (1971); **57**, 5107 (1972).
- (12) N. C. Verma and R. W. Fessenden, *J. Chem. Phys.*, **65**, 2139 (1976).
- (13) H. R. Ward, *Acc. Chem. Res.*, **5**, 18 (1972).
- (14) R. G. Lawler, *Acc. Chem. Res.*, **5**, 25 (1972).
- (15) G. L. Closs, *Adv. Mag. Resonance*, **7**, 157 (1974).
- (16) K. A. Muszkat and M. Weinstein, *J. Chem. Soc., Perkin Trans. 2*, 1073 (1976).
- (17) B. B. Adeleke, Ph.D. Thesis, Queen's University, 1976; B. B. Adeleke and J. K. S. Wan, to be published.
- (18) J. B. Pedersen, C. E. M. Hansen, H. Parbo, and L. T. Muus, *J. Chem. Phys.*, **63**, 2398 (1975).
- (19) K. Y. Choo and J. K. S. Wan, *J. Am. Chem. Soc.*, **97**, 7127 (1975).
- (20) B. B. Adeleke and J. K. S. Wan, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1799 (1976).
- (21) P. B. Ayscough, G. Lambert, and A. J. Elliot, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1770 (1976).
- (22) A. J. Dobbs, *Mol. Phys.*, **30**, 1073 (1975).
- (23) J. K. S. Wan, S. K. Wong and D. A. Hutchinson, *Acc. Chem. Res.*, **7**, 58 (1974).

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polarization"<sup>23</sup> and "emissive-absorptive (E-A) polarization".

With initial polarization, there is a net polarization of the electronic spin system which affects all transitions equally and in the same manner. This means all the lines in an ESR spectrum have the same enhancement factor.

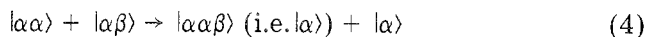
The characteristic of E-A polarization is that the magnitude and sign of  $V$  are dependent on the hyperfine energy ( $\sum A_I M_I$ ) associated with the line. Those lines to the lower magnetic field side of the center of the spectrum have emissive components ( $V < 0$ ), while those to the higher field have absorptive components ( $V > 0$ ). Also the absolute magnitude of  $V$  increases with  $\sum A_I M_I$ . In marked contrast to the initial polarization, E-A polarization develops after the formation of the radicals through the same "radical-pair" mechanism that generates CIDNP. Furthermore, the observation of E-A polarization is not restricted to photochemically generated radicals and is often present when radicals are generated by other means such as radiolysis<sup>12,24</sup> or in  $Ti^{III}/H_2O_2$  flow systems.<sup>25</sup>

The spectrum of the durosemiquinone radical, shown in Figure 1, is an example of a spectrum which shows the effects of both E-A and initial polarization. The difference in the height of the two groups of lines marked 2, 2' etc. reflects E-A polarization (both groups normally should be of equal height). The sharp increase in the height of the time profiles of the peaks when the light is turned off is indicative of the initial polarization relaxing with the  $T_1$  ( $\sim 10 \mu s$ ) of the radical.

**Initial Polarization.** Since the publication of the last Account on CIDEP,<sup>23</sup> the controversy<sup>26</sup> surrounding the origins of initial polarization has been resolved. The mechanism which invoked S- $T_{-1}$  mixing within a radical pair at high magnetic fields could not rationalize the observed dependence of the magnitude of the polarizations on the orientation of the electric vector of the photoexciting light<sup>27,28</sup> nor the dependence on quencher concentration.<sup>24-31</sup> The triplet mechanism originally proposed in this laboratory<sup>32</sup> predicts both dependencies.<sup>9,26</sup> The presence of an S- $T_{-1}$  mechanism in these systems has been further excluded by a detailed field-dependent CIDNP study<sup>6</sup> which confirmed that S- $T_{-1}$  mixing is not efficient at high magnetic fields (ESR is observed at a field  $\sim 300$  mT).

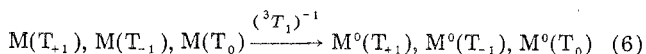
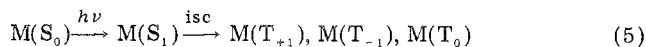
The triplet mechanism of initial polarization requires that the radicals are produced via an electronically excited molecule in a triplet state. The polarization arises from the differences in the rates of intersystem crossing (isc) from the photoexcited singlet [ $M(S_1)$ ] to the three triplet sublevels [ $M(T_i)$ ] within the absorbing molecule [ $M(S_0)$ ]. Provided these spin-polarized

triplet-state molecules react (by hydrogen abstraction or electron transfer) with spin conservation and within the longitudinal relaxation time ( ${}^3T_1 \sim 10^{-8}$ - $10^{-9}$  s) of the triplet, the difference in the populations of the  $T_{+1}$  and  $T_{-1}$  states will be carried over to the radicals produced. The ESR spectra of all the radicals generated in this reaction will be polarized in the same sense. This is easily seen if one considers a molecule in a  $T_{+1}$  state (described by the spin function  $|\alpha\alpha\rangle$ ) reacting with a diamagnetic molecule ( $|\alpha\beta\rangle$ )



The net result is the formation of two radicals with a  $|\alpha\rangle$  spin state. Likewise a molecule in the  $T_{-1}$  ( $|\beta\beta\rangle$ ) state will produce two radicals with  $|\beta\rangle$  spins, and a  $T_0(1/2^{1/2}(|\alpha\alpha\rangle - |\beta\beta\rangle))$  state will form an equal number of radicals with  $|\alpha\rangle$  and  $|\beta\rangle$  spin states. Hence, if either the  $T_{+1}$  or  $T_{-1}$  state has a population in excess of the Boltzmann distribution, all the radicals generated will have the same net polarization.

To illustrate what factors influence the magnitude of the polarization for initial polarization, it is instructive to consider the simplified reaction scheme given by eq 5-8a. Reaction 5 describes the formation of the po-



larized triplet-state molecules. Reaction 6 indicates that the polarized triplets are relaxing toward their thermal equilibrium with a rate constant of  $({}^3T_1)^{-1}$ . Reaction 7 represents the quenching by a hydrogen donor (HD) of the triplet states, the rate constant of quenching being  $k_q$ . Reactions 8 and 8a describe possible fates of the counterradical D in that it may transfer an electron to a ground-state molecule,  $M(S_0)$ , or may simply add to  $M(S_0)$ .

Neglecting reaction 8 for the moment, it is the competition between the thermalization of the triplet-state populations (reaction 6) and the chemical quenching of the triplet state (reaction 7) which determines the enhancement value of the polarization. This can be expressed as in eq 9, where  $V_0$  is the en-

$$V = V_0 k_q [HD] / (({}^3T_1)^{-1} + k_q [HD]) \quad (9)$$

hancement factor of the radicals at infinite quencher concentration. To measure  $V$ , an intermittent light source is required so that the height of the ESR signal in the presence of light and in darkness can be measured. (The time profile of the signal is normally obtained by time-averaging.) Provided the  $T_1$  for the radical is very much faster than its chemical decay rate, the enhancement factor (eq 3) can be measured from S, the height of the "light-on" signal, and  $S_0$ , which is determined by extrapolating the peak height from the "light-off" period.<sup>22</sup> For experimental systems where the length of the light pulse and the spectrometer response time are an order of magnitude less than the  $T_1$  of the radical, the value of  $V$  obtained measures the intrinsic polarization of the radical. However, if a conventional 100-kHz spectrometer (response time

(24) R. W. Fessenden, *J. Chem. Phys.*, **58**, 2489 (1973).

(25) H. Paul and H. Fischer, *Z. Naturforsch. A*, **25**, 433 (1970).

(26) F. J. Adrian, *J. Chem. Phys.*, **61**, 4875 (1974).

(27) B. B. Adeleke, K. Y. Choo, and J. K. S. Wan, *J. Chem. Phys.*, **62**, 3822 (1975).

(28) A. J. Dobbs and K. A. McLauchlan, *Chem. Phys. Lett.*, **30**, 257 (1975).

(29) S. K. Wong, D. A. Hutchinson, and J. K. S. Wan, *Can. J. Chem.*, **52**, 251 (1974).

(30) P. W. Atkins, A. J. Dobbs, G. T. Evans, K. A. McLauchlan, and P. W. Percival, *Mol. Phys.*, **27**, 769 (1974).

(31) P. W. Atkins, A. J. Dobbs, and K. A. McLauchlan, *Chem. Phys. Lett.*, **29**, 616 (1974).

(32) S. K. Wong and J. K. S. Wan, *J. Am. Chem. Soc.*, **94**, 7197 (1972); S. K. Wong, D. A. Hutchinson, and J. K. S. Wan, *J. Chem. Phys.*, **58**, 985 (1973).

(~100–500  $\mu\text{s}$ ) is utilized in conjunction with a rotating-sector chopped light source or a pulsed lamp (light-on period ~1–10 ms), the radicals generally reach a steady-state concentration and the observed enhancement factors,  $V_{\text{ss}}$ , have to be corrected for the radical half-life ( $t_{1/2}$ ) and spin thermalization during the light pulse in order to yield  $V^{24}$  (eq 10). To obtain

$$V = V_{\text{ss}} t_{1/2} / T_1 \quad (10)$$

accurate measurements of  $V$  by this method it is necessary to arrange conditions such that the radical half-life is considerably longer than the fall time of both the spectrometer and the light. This can normally be adjusted by altering the viscosity of the solvent.<sup>21</sup>

Equation 9 can be rearranged into a form which is more convenient to use (eq 11). Equation 11 provides

$$1/V = 1/V_0 + 1/(V_0^3 T_1 k_q [\text{HD}]) \quad (11)$$

the key to obtain values for  $V_0$ ,  ${}^3T_1$ , and  $k_q$ . This, of course, assumes that the linear relationships predicted by the equation are valid. This has been confirmed for a number of systems both by Atkins and coworkers<sup>30,31</sup> and in this laboratory.<sup>33</sup> Figure 2 illustrates a plot of eq 11 for the polarization observed when 2-methyl-1,4-naphthoquinone was photoreduced in the presence of different concentrations of phenol.

From a plot of  $1/V$  against  $1/[\text{HD}]$ , the value of  $1/V_0$  can be obtained from the intercept when  $1/[\text{HD}] = 0$  (see Figure 2). This value of  $V_0$ , which is the enhancement factor for the free radicals, can be converted to the enhancement factor  $V_0^T$  of the triplet state by allowing for the different thermal spin population distributions between the free radical and the triplet-state molecule.<sup>9</sup>

$$V_0^T = (3V_0 - 1)/4 \quad (12)$$

In the above discussion we have purposely neglected reaction 8. However, in many photochemical systems the radical formed from the hydrogen donor reacts to form another MH.<sup>34,35</sup> If this occurs after some thermalization of spins in the donor radical, an error will be introduced in the measurement of  $V_0$ .<sup>35</sup>

To date, few measurements have been made of  $V_0^T$ , the quantity which characterizes the inequality of the intersystem crossing rates to the different triplet sublevels. Atkins et al.<sup>31</sup> have determined a  $V_0^T$  of -50 to -85 for duroquinone in a number of different alcohols. We have measured, in a 15 vol % toluene-2-propanol solvent, the  $V_0^T$ 's ( $\pm 10\%$ ) for duroquinone (~-75), 2,5-dimethyl-1,4-benzoquinone (~-115), 2,5-dimethyl-1,4-benzoquinone (~-130), 2-methyl-1,4-benzoquinone (~-150), 1,4-benzoquinone (~-190), and 2-methyl-1,4-naphthoquinone (~-250).<sup>33</sup> Some of these values are near the maximum predicted from theoretical considerations by Pedersen and Freed.<sup>10</sup>

Atkins and co-workers<sup>31</sup> have determined experimentally the triplet relaxation time for duroquinone using eq 11. The values for  ${}^3T_1$  were found to increase from 2.7 to 17 ns over the viscosity range 0.6 to 57 cP. These results represent the first measurements of  ${}^3T_1$

in liquids. The  $T_1$  of the radical was determined directly from the decay of the polarization, and it was found that the ratio of  ${}^3T_1$  to  $T_1$  was essentially constant over the viscosity range studied, indicating that both relaxation times depend on the same molecular motion.

Perhaps the most important development in the final acceptance of the triplet mechanism as the origin of the initial polarization was the theoretically predicted<sup>26</sup> and experimentally<sup>27,28</sup> found dependence of  $V$  with the orientation of the electric vector of plane polarized light. Adrian<sup>26</sup> has predicted that, when the plane of the polarized light is rotated from perpendicular to the magnetic field to parallel, there should be a variation of 10 or 20% in the enhancement factor depending upon whether the transition dipole of the molecule lies perpendicular or parallel to its principal axis. Confirmations of Adrian's two predictions have been obtained by using substituted benzoquinones<sup>27,28</sup> for the first case and anthraquinone<sup>27</sup> in the second case.

It is also possible from CIDEP studies to obtain semiquantitative information about the rate constants of the chemical quenching of triplet states. This can be achieved in two ways. If different quenchers are used but the rest of the system is kept the same, then  ${}^3T_1$  and  $V_0$  will be constant. Hence for two different quenchers the ratios of the slopes of a plot of  $V^{-1}$  vs.  $[\text{HD}]^{-1}$  (eq 11) will give the ratio of the quenching rate constants. The alternative method is a competitive technique where two quenchers are present but only the concentration of one is varied. Hence when the concentration of one quencher is high, the plot of eq 11 is linear, but at lower concentrations deviation will occur due to the competition between the two quenchers. From this deviation it is a relatively simple matter to get  $k_{q1}/k_{q2}$ .<sup>33</sup>

If addition reactions such as (8a) occur, it is sometimes possible to roughly estimate the rate of this reaction ( $k_{8a}[\text{M}(\text{S}_0)]$ ). If MD shows some initial polarization, the rate of addition must be faster or comparable to  $T_1$  of the donor radical  $\dot{\text{D}}$ . Hence, if the concentration of  $\text{M}(\text{S}_0)$  is known, then an estimate of  $k_{8a}$  can be made. Ayscough et al.<sup>3</sup> have used this method to estimate how fast radicals derived from alcohols add to maleimide.

**E-A Polarization.** For many years the presence of E-A polarization has been obvious in the spectra of many short-lived radicals,<sup>36</sup> yet it has received little detailed experimental examination. Unlike initial polarization, there was little controversy as to the general mechanism<sup>10,11</sup> responsible for its formation since the analogous NMR polarization arises through the same radical-pair process.<sup>7,8,13,14</sup> Until recently the situation was such that theoretical investigators had virtually no quantitative experimental data with which to test their conclusions. However, over the last few years some experimental data have been published.<sup>3,12,20,21,24,25,37,38</sup>

This polarization arises from the diffusive encounters of radicals to form a radical pair in which a non-Boltzmann distribution is induced in the populations of the electronic-nuclear spin states by mixing the S and the  $T_0$  states.<sup>11</sup> This gives rise to spin selective

(33) A. J. Elliot and J. K. S. Wan, to be published.

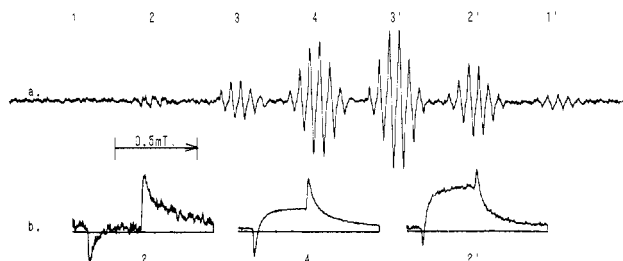
(34) P. B. Ayscough and R. C. Sealy, *J. Chem. Soc. Perkin Trans. 2*, 543 (1973).

(35) K. A. McLauchlan and R. C. Sealy, *Chem. Phys. Lett.*, **39**, 310 (1976).

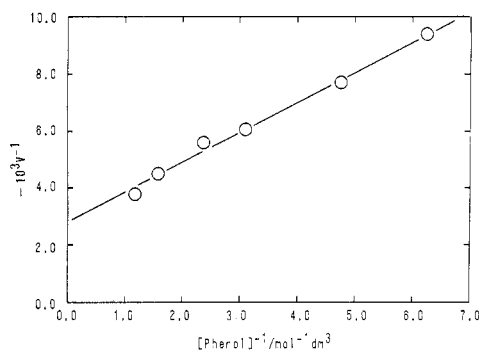
(36) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **47**, 4173 (1967).

(37) P. B. Ayscough, T. H. English, G. Lambert, and A. J. Elliot, *Chem. Phys. Lett.*, **34**, 557 (1975).

(38) H. Paul, *Chem. Phys.*, **15**, 115 (1976).



**Figure 1.** (a) The ESR spectrum of durosemiquinone radical formed when a 15 vol % toluene-1-propanol solution containing  $0.09 \text{ mol dm}^{-3}$  duroquinone and  $1.45 \text{ mol dm}^{-3}$  phenol was photolyzed at  $0^\circ\text{C}$ . Groups of lines indexed 2, 2' etc. should be of equal height. Peak 4 is the center of the spectrum. (b) The time profiles of a representative peak within groups 2, 4, and 2' obtained when the light beam used in (a) was chopped by a rotating sector. The downward spike in the trace is the "light-on" point and the upward spike is the "light-off" point. The on-duration was about 11 ms.



**Figure 2.** The plot of reciprocal enhancement factor vs. reciprocal phenol concentration for the 2-methyl-1,4-naphthosemiquinone radical. The radical was generated by photolyzing a 15 vol % toluene-1-propanol solution containing  $0.06 \text{ mol dm}^{-3}$  2-methyl-1,4-naphthaquinone in the presence of varying concentrations of phenol at  $0^\circ\text{C}$ .

reactions, the rates of which depend on the electronic and nuclear spin state of the radical.<sup>10,24</sup>

Theoretically<sup>10,11</sup> it has been predicted that, for an ensemble of two different radicals undergoing diffusive encounters (for illustrative purposes we are only considering here encounters between different radicals, not those between similar radicals), the enhancement factor of a peak indexed  $a$  is given by eq 13,<sup>22</sup> where  $a$  and  $b$

$$V_a^{\text{EA}} \propto \sum_b^{\text{all states}} n_b \frac{\mathcal{H}_{ab}}{|\mathcal{H}_{ab}|} |\mathcal{H}_{ab}|^\epsilon \quad (13)$$

index the nuclear spin states in the radical pair and  $n_b$  is the multiplicity of the state  $b$ . For radicals 1 and 2

$$\mathcal{H}_{ab} = \frac{1}{2} \mu_B H (g_1 - g_2) + \frac{1}{2} \sum_n A_{1n} M_{1n}^a - \frac{1}{2} \sum_m A_{2m} M_{2m}^b \quad (14)$$

where  $M_{1n}^a$  is the magnetic nuclear quantum number of the  $n$ th nucleus in radical 1 in an overall spin state characterized by  $a$ .  $A_{1n}$  is the isotropic hyperfine coupling constant of nucleus  $n$  in radical 1, etc. Adrian<sup>11</sup> has predicted a value of  $\epsilon$  of 0.5, whereas Pedersen and Freed<sup>10</sup> have suggested  $\epsilon$  is viscosity dependent, but for the viscosities normally encountered in ESR experiments  $\epsilon$  is close to 0.5.<sup>21,37</sup>

Equation 14 defines the polarization dependence on both the  $g$  factor difference of the two radicals in the

radical pair, and on the isotropic hyperfine coupling constants of the radicals. It can be seen from eq 14 that for two radicals which have identical  $g$  factors there is no net polarization, i.e.,  $\sum V_a^{\text{EA}} = 0$ . This is because the peak (a) associated with  $|\sum A_n M_n|$  to the low magnetic field side of the spectrum center will have an emissive polarization which is exactly compensated for by an absorptive polarization of the high-field peak associated with  $|\sum A_n M_n|$ . If the spectrum contains a center peak, it will have no polarization. However, if the radicals present have  $g_1 > g_2$ , then the ESR spectrum of radical 1 will display net emissive polarization and the spectrum of radical 2 will display an equal but opposite net absorptive polarization.<sup>11,24</sup> For organic radicals where the differences in  $g$  factors are small compared to the hyperfine terms, the effect of changing the sign of this  $\Delta g$  term cannot readily be demonstrated by monitoring only one of the radicals in the pair. In a systematic study of quinone-phenol systems, Adeleke and Wan<sup>20</sup> have confirmed the effect of the sign of the  $\Delta g$  on the polarization of the semiquinone and the phenoxy radicals as dictated by eq 14.

Because of the equal but opposite nature of E-A polarization the enhancement factor defined earlier in eq 3 can be shown to be

$$V_a^{\text{EA}} = (S_H(a) - S_L(a)) / (S_H(a) + S_L(a)) \quad (15)$$

where  $S_H(a)$  and  $S_L(a)$  are the heights of the high- and low-field peaks (indexed by  $a$ ) which corresponds to the transitions between spin states defined by  $|\sum A_n M_n|$ .

Verma and Fessenden<sup>12</sup> have characterized E-A polarization by following the complete time profile of the polarization by generating radicals in aqueous solutions with a submicrosecond pulse of 2.8-MeV electrons and monitoring the ESR spectrum using a spectrometer with a time resolution of less than a microsecond. The radicals were formed with an equal number of  $|\alpha\rangle$  and  $|\beta\rangle$  spin states and the polarization grew in as a result of spin-selective reactions. The time dependencies of the signals were fitted to Bloch equations which were modified to account for chemical reactions and any CIDEP effects arising from these reactions.

Although Trifunac<sup>39</sup> found no dependence of  $V^{\text{EA}}$  on radical concentration, both Fessenden<sup>12,24</sup> and Ayscough et al.<sup>21,37</sup> have observed, for a number of different radicals, that the magnitude of  $V^{\text{EA}}$  increases linearly with radical concentration as predicted by Fessenden's phenomenological model.

Ayscough et al.<sup>21,37</sup> have examined the validity of eq 13 by comparing the ratio of the enhancement factors ( $V_a^{\text{EA}} / V_a^{\text{EA}}$ ) for different peaks in a spectrum to those calculated for different  $\epsilon$ . Good agreement was found between experiment and theory for  $\epsilon \sim 0.5$ , as predicted by Adrian.<sup>11</sup> For the pyruvic acid semidione radical,  $\epsilon$  was found to be rather insensitive to the viscosity of the medium over the range 0.7 to 20 cP.<sup>21</sup>

To study initial polarization in those cases where E-A polarization is also present, the E-A polarization can be canceled out by averaging the CAT traces of peaks equally disposed around the center of the spectrum. For example, if the CAT traces of 2 and 2' in Figure 1b are averaged, they replicate that of trace 4 which has virtually no E-A polarization because it is only 0.020

(39) A. D. Trifunac, *J. Am. Chem. Soc.*, **98**, 5202 (1976).

mT from the spectrum center. However, it must also be remembered that, for conventional kinetic ESR measurements, the presence of CIDEP must be accounted for before the "absolute" concentration of the radicals can be obtained.<sup>21,40</sup>

### CIDNP

The initial attempts to rationalize CIDNP after it was first discovered were in terms of electron and nuclear cross-relaxation (Overhauser effect) in the precursor radicals.<sup>15</sup> However, this mechanism could not account for the multiplet effect subsequently discovered or the very large enhancements observed. Because of this, the Overhauser mechanism was neglected in favor of the radical-pair model which accounts more than adequately for the majority of CIDNP observations.<sup>15,41</sup> CIDNP has become a useful tool to provide a great wealth of information about the nature of free-radical reactions. By the use of Kaptein's rules<sup>41</sup> it is reasonably straightforward to determine whether a product was formed by a radical-radical reaction (in-cage reaction) or by some scavenging process involving a neutral molecule (out-of-cage reaction). Kaptein's rules, which arise naturally out of the radical-pair model, have been described in a number of articles.<sup>7,15,41</sup>

In our laboratory a number of photochemical systems have been investigated,<sup>19,42,43</sup> the results of which indicate that under certain limited circumstances the Overhauser effect directly contributes to the observed CIDNP. The first example was the emissive <sup>19</sup>F NMR signals from both tetrafluoro-1,4-benzoquinone (FQ) and tetrafluoro-1,4-hydroquinone (FQH<sub>2</sub>) when FQ and FQH<sub>2</sub> were photolyzed in benzene. The radical-pair mechanism predicts no net NMR polarization as the geminate pair involves identical radicals, FQH, from the reaction of the triplet FQ abstracting a hydrogen atom from the donor FQH<sub>2</sub>. Of course it is always possible to explain the results by the presence of an "impurity" which can give rise to a radical with a different *g* factor from that of the FQH radical. However, when FQ alone was photolyzed in chloroform solution, the magnitude of the emission from <sup>19</sup>F was dependent on the orientation of the plane of polarization of the incident light with respect to the external magnetic field. This cannot be explained by the radical-pair theory and strongly implicates a triplet precursor. Another system<sup>19</sup> which also displays CIDNP dependence on the orientation of plane-polarized light is pyruvic acid photolyzed in the presence of the good hydrogen donor, 2,5-di-*tert*-butylhydroquinone. (In this case the polarization of CH<sub>3</sub>COCOOH was followed.)

These results can all be reconciled with the triplet mechanism of generating initially polarized radicals in which the net electron polarization is transferred to the nuclear spin states by the Overhauser effect before the radicals thermalized and react to form diamagnetic products.<sup>43</sup> Both FQ<sup>44</sup> and pyruvic acid<sup>19</sup> produce initially polarized radicals when photolyzed in the presence of good hydrogen donors. However, if a poorer hydrogen donor is used, the radicals produced will have

less electron polarization and hence CIDNP generated from the radical-pair mechanism will predominate. Thus, in the case of pyruvic acid, when it was photolyzed in a poorer hydrogen donor such as 2-propanol, the CIDNP monitored from CH<sub>3</sub>COCH<sub>3</sub> did not show any dependence on the orientation of the plane-polarized light.<sup>19</sup>

More detailed studies<sup>43</sup> into the triplet mechanism in CIDNP have been carried out by comparing the polarization in FQ (produced by photolyzing FQ, FQH<sub>2</sub> in benzene) as a function of magnetic field to that calculated by theory. The agreement was good. Furthermore, it was demonstrated that, when benzoquinone (Q) was photolyzed in deuterated chloroform, the triplet mechanism CIDNP for benzoquinone (an emissive component) could be "exposed" by quenching the predominant radical pair CIDNP (an enhanced absorption component) by increasing the benzoquinone concentration.<sup>43</sup> This prevents the radical reencounters needed to generate the radical-pair CIDNP by transferring a hydrogen atom from the semiquinone radical (QH) which has some nuclear polarization generated by the Overhauser effect

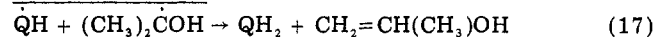


In this system, the radical pair theory cannot predict emissive polarization.

In most photo-CIDNP experiments involving protons, any CIDNP generated by the triplet mechanism is normally overshadowed by that generated from the radical-pair mechanism. Hence, it is generally quite safe to apply Kaptein's rules to the polarizations observed under these circumstances. The time scales of the above-mentioned processes support this last statement. For the electron-nuclear cross-relaxation step in the initially polarized radical, the time required is of the order of 10<sup>-4</sup>-10<sup>-6</sup> s. However, the lifetime of the radical in the cage is only of the order of 10<sup>-9</sup> s. Thus, if the radicals react in cage, they will do so before cross-relaxation can occur. Yet this is sufficient time for radical-pair polarization to develop. With fluorinated radicals the transfer of electron polarization to the nuclear states is far more efficient than in the proton analogues by virtue of the large<sup>19</sup> F anisotropic hyperfine coupling constants.<sup>43</sup>

The large signal enhancements associated with CIDNP aid in the detection of unstable diamagnetic intermediates.<sup>4-6</sup> A good example of this is the observation of the enol form of keto compounds which are formed by the disproportionation reaction of ketyl radicals which have β protons. These enols are very short-lived and readily tautomerize back to the keto form, and they are only observed by virtue of the CIDNP generated within the cage of the disproportionation reaction.

CIDNP has been observed from 2-propenol and acetone during the photolysis of benzoquinone in the presence of 2-propanol.<sup>6</sup> At high magnetic fields, application of Kaptein's rules<sup>7,15,41</sup> to these polarizations indicates that the enol was formed predominantly by the cage reaction



whereas the acetone was formed predominantly in an out-of-cage net hydrogen-transfer reaction.

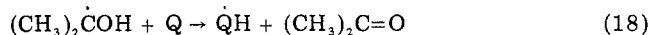
(40) G. Lambert, Ph.D. Thesis, University of Leeds, 1977.

(41) R. Kaptein, *Chem. Commun.*, 732 (1971); *Adv. Free Radical Chem.*, 5, 319 (1975).

(42) H. M. Vyas and J. K. S. Wan, *Chem. Phys. Lett.*, 34, 470 (1975).

(43) F. J. Adrian, H. M. Vyas, and J. K. S. Wan, *J. Chem. Phys.*, 65, 1454 (1976).

(44) H. M. Vyas and J. K. S. Wan, *Can. J. Chem.*, 54, 979 (1976).



Reaction 18 was further studied at various lower magnetic fields.<sup>6</sup> It was found that S-T<sub>-1</sub> mixing becomes dominant at fields below 100 mT, which agrees with the theoretical treatment<sup>6</sup> of the low-field CIDNP which includes all triplet levels in the calculation. From such a field-dependent study, the approximate magnitude and sign of the *J* value can be deduced.

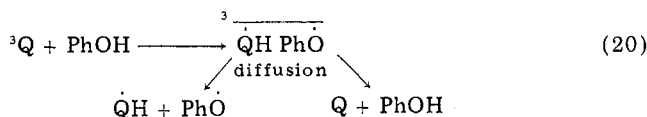
When the photolysis of benzoquinone in 2-propanol is studied by ESR spectroscopy the benzosemiquinone radical is observed, and this decays by second-order kinetics presumably by reaction 19. In this system, the



(CH<sub>3</sub>)<sub>2</sub>ĊOH radical is not observed because its lifetime is too short, due to reaction 18. The ESR results also indicate that the semiquinone radicals are initially polarized and hence confirm that the triplet state of benzoquinone was involved in their formation. However, all the ESR results are obtained on radicals which have escaped or are formed outside the primary cage and as such provide only one side of the story. The CIDNP experiment indicates the presence of the in-cage disproportionation reaction 17. Unfortunately in this case it cannot provide any quantitative results as to which proportion of radicals undergo reaction 17 because the enol tautomerizes to acetone.<sup>4</sup>

For a large number of photochemical reactions involving phenols as hydrogen donors, it appears that the two radicals formed following hydrogen abstraction disproportionate to regenerate the starting compounds.<sup>16,17,41</sup> For example, when biacetyl and phenol are photolyzed together there is no depletion of the biacetyl. Yet phosphorescence from the biacetyl triplet state is quenched.<sup>45</sup>

In our laboratory, substituted phenols have been used extensively as hydrogen donors in CIDNP studies on the photolysis of quinones because the phenoxy radicals formed are relatively long-lived, enabling primary radicals to be studied.<sup>19,20,26,41</sup> A number of quinones in the presence of alkyl-substituted phenols were photolyzed in the NMR probe. All the proton results obtained could be explained in terms of the radical-pair theory, although the radical intermediates are known to be initially polarized.<sup>17</sup> A general reaction scheme which explains the results is given by eq 20. The ESR



experiments only "see" those radicals which escape the cage, while the CIDNP observed arises predominantly from the initial pair in the primary cage. No out-of-cage CIDNP will be observed because the radicals are sufficiently long-lived that any nuclear polarization generated in the cage would have thermalized. The absence of NMR signal due to QH<sub>2</sub> (polarized or unpolarized) suggests that QH predominantly decays by disproportionation with the phenoxy radical in the cage. An important point to note here is that CIDNP provides information on those reactions which regenerates

starting compounds. Without the polarization in NMR signals, there is no NMR evidence that the reactions have even taken place. Recently a number of other systems in which reversible hydrogen abstraction occurs have been studied by CIDNP.<sup>5,18</sup>

Another area in which CIDNP appears to be able to provide mechanistic data is in the stereoselectivity of free-radical reactions. In a recent publication Livant and Lawler<sup>46</sup> have shown that in the disproportionation of two cyclohexyl radicals it is the pseudoequatorial β hydrogen that is transferred. Schollkopf et al.<sup>47</sup> and Baldwin et al.<sup>48</sup> have followed the retention of conformation in molecular rearrangement by CIDNP. In our laboratory, Adeleke and Wan<sup>17</sup> have observed what appears to be an orientation dependence in the disproportionation of anthrasemiquinone and benzo-semiquinone radicals within the primary cage.

### Conclusion

In the past 3 years the development of the triplet mechanism and the establishment of the coexistence of the radical-pair and the triplet mechanisms in photochemically induced magnetic polarization represent a major advance in the understanding of these phenomena. This has been brought about by a concerted international effort by a number of workers in various laboratories. The better understanding of the mechanisms involved in the magnetic polarization permits the combination of CIDEP, CIDNP, and the conventional ESR and NMR techniques to be a powerful tool with which to study organic photochemistry involving excited triplet states and free-radical reactions.

The most promising area to which electron polarization studies can contribute in the future is that of probing the time scales of the various events in a photochemically induced reaction. It has been shown that CIDEP can provide data on the differences in the rate of intersystem crossing to various triplet sublevels (i.e., V<sub>0</sub><sup>T</sup>), longitudinal spin-relaxation times (<sup>3</sup>T<sub>1</sub> and T<sub>1</sub>), and also triplet-quenching rate constants. The rate of radical addition or electron transfer to diamagnetic molecules can also be estimated. In reactions where an initially polarized primary radical rearranges to form a second radical, the extent of polarization in the secondary radical can give an estimate of the rearrangement time scale. The nuclear polarization study of these reactions will, in general, provide the other half of the story as the CIDNP can yield detailed information for the "in-cage" reactions.

Before completing this Account we should add that we believe there are still other classes of radical reactions which may produce electron polarization and which are awaiting to be discovered. A possible mechanism which would produce polarized radicals is one where the three triplet sublevels of an excited molecule abstracted hydrogen at different rates.

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(46) P. Livant and R. G. Lawler, *J. Am. Chem. Soc.*, **98**, 6044 (1976).

(47) U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Lett.*, 3415 (1969).

(48) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1969).

(45) N. J. Turro and R. Engel, *J. Am. Chem. Soc.*, **91**, 7113 (1969).