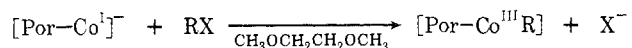Alkyl and acyl complexes of cobalt porphyrins have been formed by oxidative addition to the appropriate Co(I) complex.[35] A second method, using a

$$[Por-Co^I]^- + RX \xrightarrow[CH_3OCH_2CH_2OCH_3]{} [Por-Co^{III}R] + X^-$$

Grignard reagent, has been used to prepare alkyl and aryl cobalt porphyrin complexes by a nonoxidative route.[35] The two alkyl iron porphyrins reported[35] as

$$[Por-Co^{III}(py)(Br)] + RMgBr \longrightarrow$$
$$[Por-Co^{III}R] + MgBr_2 + py$$
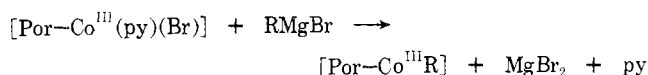
forming from iron(III) porphyrin and a Grignard reagent are less well characterized, the presence of alkyl ligands being based entirely on C, H, and N analyses.

An oxidative addition has also been used to prepare methyl rhodium porphyrin.[27] In this case the methyl group comes from an *N*-methylporphyrin (in a presumably intramolecular transfer) rather than from an alkyl halide. In addition, rhodium porphyrins have been reported to form acyl complexes, again by an intramolecular route.[72,73]

$$H^+[Por-Rh^I] \longrightarrow [Por-Rh^{III}] + HN(CH_3)_2$$

$$[Por-Rh^{III}(Cl)(CO)] \longrightarrow [Por-Rh^{III}Cl]$$
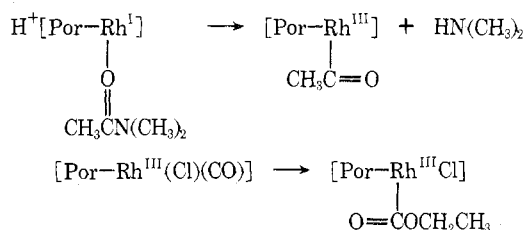
The significance of alkyls of cobalt and rhodium porphyrins lies in their similarity to vitamin B_{12}, another compound forming metal–alkyl bonds from an M(I) species.[74] This resemblance is shared by several bidentate ligands,[75] pairs of which can assume a square-planar coordination geometry, and by a number of less well known macrocycles.[33]

Schrauzer[75] has ascribed the stability of these alkyls to the strong, planar ligand field of the porphyrin or porphyrin-like ligand. Consistent with this theory, Busch[33] found cobalt alkyl bonds to be stable only in the presence of macrocycles with greater than a certain minimum ligand field strength. Clearly nothing in these arguments should limit organometallic porphyrins to those of cobalt and rhodium. Nor is it obvious that rhodium porphyrins cannot undergo intermolecular addition and cobalt porphyrins, intramolecular addition. More work will be necessary to discover the scope of carbon–metal bonding in metalloporphyrins.

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Chemically Induced Dynamic Electron Polarization of Transient Radicals

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One important application of electron spin resonance in chemical studies is in obtaining information on transient species produced in chemical reactions. A renewed and increasing interest in the field of free radical chemistry during the last decade can be attributed partly to the rapid development of electron spin resonance spectroscopy. Today esr has been developed to a point where much of the theoretical and experimental background material for chemists is readily available.

The first comprehensive and elegant demonstration of esr studies of transient radicals in liquid radiation chemical systems was by Fessenden and Schuler[1] in 1963. In that classic paper, the authors studied among other hydrocarbons the irradiation of liquid methane and deuteriomethane and reported the observation of both hydrogen and deuterium atoms. They noted that in both cases the low-field lines in the esr spectra are inverted compared to the corresponding high-field lines. This indicated that the low-field lines were not in the normal absorption

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mode and were emissive. Those authors had made the first discovery of an effect now known as the chemically induced dynamic electron polarization (CIDEP) phenomenon.

In the meantime, a related chemically induced dynamic nuclear polarization (CIDNP) effect was independently discovered by Bargon, Fischer and Johnson[2] and by Ward and Lawler.[3] Because of the wider application of nuclear magnetic resonance in chemistry, the CIDNP effect immediately caught considerable theoretical and experimental attention, and a theory of radical-pair models has been advanced to account for the effect. The current status of the CIDNP studies has been discussed in detail in a number of excellent reviews.[4-8]

The remarkable development of the CIDNP theory brought cross-fertilization to the then lesser known CIDEP phenomenon. By the late 1960's, more experimental observations of esr emission were reported, including esr emission from polarized organic triplet states. These studies generated much theoretical interest in CIDEP, but the true mechanisms of the dynamic electron polarization in various chemical systems remain controversial and unresolved. The present Account is intended as an introduction to the basic features of the CIDEP study.

We shall give a brief description of the current theories underlying CIDEP as evolved from recent experimental observations. Potential applications of CIDEP in a variety of chemical and physical problems will also be considered. They include applications to the dynamics and mechanism of intersystem crossing in organic triplet-state photochemistry and to determination of the spin–lattice relaxation times of transient radicals in solution.

Dynamic Electron Polarization

Under normal conditions, when an esr spectrum is taken, it is usually assumed that the electron spin system attains thermal equilibrium. This is particularly true for systems of "stable" radicals having short electron spin–lattice relaxation time and when low microwave power is used. Electron polarization is here defined as any deviation from the thermal equilibrated spin populations. Thus, for a doublet system ($S = \frac{1}{2}$), the ratio of the population of the lower state (N_β) to that of the upper state (N_α) is not equal to the Boltzmann factor, *i.e.*

$$N_\beta/N_\alpha = \exp(g\beta_e B_0/kT) \qquad (1)$$

where g is the electron g factor, β_e is the electron Bohr magneton, B_0 is the applied magnetic field, k is the Boltzmann constant, and T is the absolute temperature. Generally, it is convenient to express the polarization in terms of the population difference, $n = N_\beta - N_\alpha$, since the observed esr intensity at low microwave power is proportional to n. At room temperature and using an X-band spectrometer

$$n_0/(N_\alpha + N_\beta) \approx g\beta_e B_0/2kT \approx 0.075\% \qquad (2)$$

where n_0 is the population difference at thermal equilibrium. A polarization factor f may now be defined as

$$f = n/n_0 \qquad (3)$$

If $N_\alpha > N_\beta$, f is negative and esr emission will be observed. When f is positive and greater than unity, enhanced absorption will be expected. For a positive value of f less than unity, polarization is still defined, but the esr is in a "diminished" absorption mode. Finally, when f is equal to zero, no esr will be observed, even if the concentration of the radicals is relatively high.

In esr studies of transient radicals produced chemically in liquid systems, at some critical stages of reaction a spin selection process may result. The populations of the radicals are thus initially non-Boltzmann and the "polarization" decays to the corresponding thermal equilibrium value in a time related to the spin–lattice relaxation time. During this spin relaxation time, the transient radicals may also decay chemically. However, since the spin relaxation in liquid systems normally occurs very quickly (in the order of 10^{-4}–10^{-6} sec), it is possible to assume that the chemical decay rate is negligible during the spin relaxation and the initial polarization may be observed with a time-resolved esr spectrometer.

As early as 1964, Fessenden[9] recognized that static detection systems are not suitable for esr rate studies and modified the static systems for "intermittent radical production" using pulsed radiolysis. Smaller and coworkers[10] have since developed a 2-MHz modulation unit leading to an esr response time in the microsecond range. Atkins, McLauchlan, and coworkers,[11,12] using a 2-MHz detection unit coupled with a 20-nsec laser flash, have demonstrated beautifully the photo-CIDEP for the ketyl radical from benzophenone in paraffin solvents. At present, only the pulse radiolysis and the laser flash photolysis enjoy the advantage of a short and intense pulse at a rapid repetition rate. Nevertheless, Wong and Wan[13] have demonstrated that, under favorable chemical conditions, photo-CIDEP of some semiquinone radicals in alcohol solvents can be observed with a commercial spectrometer having a 100-kHz modulation unit and a custom-designed rotating sector giving light pulses with width as long as a few hundred microseconds. A typical time dependence of the esr signal intensity at constant magnetic field of the photoproduced naphthosemiquinone radical in 2-propanol is shown in Figure 1. Since the commercial spectrometer has a response time not better than 150 μsec, the observed initial polarization is only qualitative and the interconversion of the signal from emissive to absorptive mode observed here does not represent the true spin–lattice relaxation time. Using a similar rotating sector technique, Livingston and Zeldes[14] have also observed polarization of the acetyl radical in 2-propanol.

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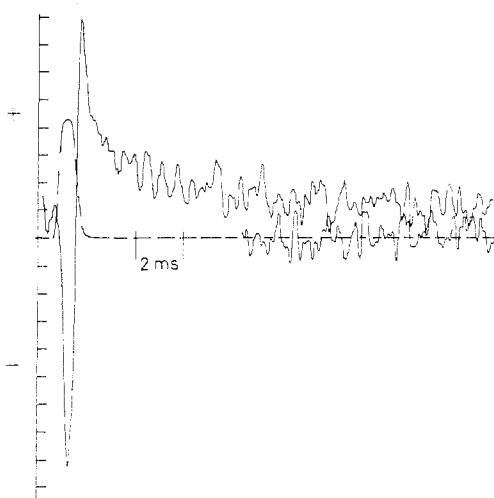(14) R. Livingston and H. Zeldes, *J. Magn. Res.*, 9, 331 (1973).

Figure 1. Time dependence of the esr signal intensity at constant magnetic field of the photoinduced 1,4-naphthosemiquinone radical. Also shown (dotted line) is the shape of the light pulse. The initial negative (−) signal indicates emission. The signal then converts to positive (+), indicating absorption at the end of the light pulse. The conversion is due to spin-lattice relaxation. The absorption signal then decays to zero due to radical self-reaction. For the sake of clarity, only *part* of the zero line is shown on the right-hand side

Experimental CIDEP results reported to date are still relatively rare compared to CIDNP studies. No doubt, part of the reason is the greater difficulty of performing CIDEP experiments. In CIDNP studies, one is dealing with spectra of stable reaction products and the nuclear spin-lattice relaxation times are usually much longer than the electron spin. Thus a sophisticated rapid-response time-resolved nmr spectrometer is not required for CIDNP experiments. In this respect, it is encouraging that recent CIDEP experiments[13,14] showed that less sophisticated and commercial spectrometers readily available in many esr laboratories may be used as a tool to study CIDEP in chemical applications.

Despite the scarcity of available CIDEP experimental results, Kaptein and Oosterhoff[15] in 1969 proposed the first CIDEP theory while attacking the CIDNP problems. Their first attempt has now formed the foundation of the so-called "radical-pair theory" which has been widely tested and generally accepted in nuclear polarization studies. An independent theoretical study of the CIDNP phenomenon has also been undertaken by Closs and coworkers.[16,17] Although the radical-pair theory was initially accepted to account for CIDEP results, it has not been tested experimentally to any vigorous degree. In the following section we outline the basis of the radical-pair theory and some of the most recent developments.

The Radical-Pair Theory

The radical-pair model assumes that a radical pair formed in an initial stage of a chemical reaction (e.g., molecular dissociation into two fragments, a bimolecular abstraction of a hydrogen by an excited molecule), or two independently generated radicals upon collision, may not react chemically immediate-

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ly but instead they may separate into a region where the singlet-triplet splitting ($2J = E_S - E_T$) of the radical pair is comparable to its magnetic energy. In this region, mixing of the singlet (S) and triplet states (T_{-1}, T_0, T_{+1}) of the radical pair by the magnetic interactions ($\mathcal{H}^M$) may lead to a growth of electron spin density on one radical and a corresponding decrease of electron spin density on the other radical in the pair. Only the mixing of S and T_0 is being considered here, and the mixing of S, T_{+1}, and T_{-1} is thought to be unimportant, particularly in the presence of a strong external magnetic field because of the large energy gap.[15-17] This assumption will be modified in later discussion.

According to the formulation by Adrian,[18] the time-dependent Schrodinger equation for the evolution of the radical-pair wave function is

$$[\mathcal{H}^M - J(2\mathbf{s}_1\mathbf{s}_2 + \tfrac{1}{2})]\Psi(t) = i[\partial\Psi(t)/\partial t] \qquad (4)$$

where $\mathbf{s}_1$ and $\mathbf{s}_2$ are the electron spins of the two radicals in the pair and the exchange interaction $2J$ is the singlet-triplet splitting. The magnetic Hamiltonian $\mathcal{H}^M$ has the usual isotropic terms and the anisotropic terms are neglected, since the radicals are in liquid systems.

If we assume that J is time independent, namely J is zero at all times except during the very brief intervals when the radicals encounter each other, eq 4 is then readily solved into eq 5, where $|S\rangle$ is the singlet

$$\Psi(t) = [C_{S,ab}(t)|S\rangle + C_{T,ab}|T_0\rangle]\phi_{ab}^N \qquad (5)$$

wave function $2^{-1/2}(\alpha\beta - \beta\alpha)$ and $|T_0\rangle$ is the triplet wave function $2^{-1/2}(\alpha\beta + \beta\alpha)$. ϕ_{ab}^N is a nuclear spin function and the nuclear spin states a and b refer to radicals 1 and 2, respectively. C_S and C_T are the coefficients for the singlet and triplet states. The unpaired electron spin density at radical 1 is given by eq 6, where s_{1z} and s_{2z} are the components of $\mathbf{s}_1$ and

$$\rho_{1,ab}(t) = \langle\Psi^*(t)|\mathbf{s}_{1z} - \mathbf{s}_{2z}|\Psi(t)\rangle \qquad (6)$$

$\mathbf{s}_2$, respectively, in the direction of the external magnetic field. Since the electron spin is parallel to the external field in the upper Zeeman level, $\rho_{1,ab} > 0$ corresponds to an emission mode in the esr of radical 1, and $\rho_{1,ab} < 0$ corresponds to an absorption mode. Equation 6 can be expanded into

$$\begin{aligned}\rho_{1,ab}(t) = [C_T(0)C_S{}^*(0) &+ C_T{}^*(0)C_S(0)] \times \\ [\cos 2\omega t &+ 2(\mathcal{H}_{ab}^M/\omega)^2 \sin^2 \omega t] + \\ (iJ/\omega)[C_T(0)C_S{}^*(0) &- C_T{}^*(0)C_S(0)] \sin 2\omega t + \\ (2\mathcal{H}_{ab}^M J/\omega^2)[|C_S(0)|^2 &- |C_T(0)|^2] \sin \omega t \quad (7)\end{aligned}$$

Here $\omega = [(\mathcal{H}_{ab}^M)^2 + J^2]^{1/2}$ and $C_S(0)$ and $C_T(0)$ are the coefficients of the initial singlet and triplet states. The Hamiltonian $\mathcal{H}_{ab}^M$ has the form

$$\mathcal{H}_{ab}^M = \tfrac{1}{2}\beta_e B_0(g_1 - g_2) + \tfrac{1}{2}\sum_n A_{1n}M_{1n}{}^a - \sum_m A_{2m}M_{2m}{}^b \qquad (8)$$

where $M_{1n}{}^a$ is the magnetic quantum number of the nth nucleus of radical 1 in the overall nuclear spin state a, and $M_{2m}{}^b$ is the magnetic quantum number of the mth nucleus of radical 2 in the overall nuclear spin state b.

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It can be shown that the last term on the right-hand side of eq 7 can lead to electron spin polarization in the radicals, but none of the other terms in the equation can induce polarization following the first encounter of the radicals. During the initial encounter, the radical pair may be in either a pure singlet or a pure triplet state. It may also have the spins uncorrelated. In the first case, the terms $C_T(0)$ and $C_S(0)$ are obviously zero. In the latter case of uncorrelated spins, both the magnitude and phase of the singlet and triplet components in the radical-pair wave functions are at random, and the term $C_T^*(0)C_S(0) \pm C_T(0)C_S^*(0)$ will vanish when averaged over the random phase factor.

The initial radical-pair theory is developed to explain the esr spectra of mixed emission and absorption patterns. Let us consider the simplest example of a pair of a H atom (radical 1) and radical 2, both having identical g factor. The resonance magnetic fields for the two hyperfine lines of the esr spectrum of the H atom at a constant microwave frequency ν will be

$$B_{res}(M_1) = (\nu - A_1 M_1)/\beta_e g_1$$
$$\mathcal{H}_{ab}{}^M = \frac{1}{2} A_1 M_1 \qquad (9)$$

If the radical pair is formed by the dissociation of the molecule HX in an excited state, J will either be greater or less than zero depending on the excited state being either a singlet or a triplet, respectively. In either case, however, the product $J[|C_S(0)|^2 - |C_T(0)|^2]$ will be positive and therefore the sign of $\rho_{1,ab}$ will be determined by the sign of the term $A_1 M_1$. For the low-field hyperfine line, $A_1 M_1$ is positive and thus the line will be in an emission mode. For the high-field line, $A_1 M_1$ is negative and the line will be absorptive. The theory is thus in agreement with the experimental observations of the mixed pattern on the H atom.[19] For radicals with more than two hyperfine lines, similar treatment will lead to a mixed-pattern esr spectrum, provided that the matrix element $\mathcal{H}_{ab}{}^M$ is primarily determined by the hyperfine interactions rather than by the electron Zeemen interactions. The radical-pair theory also accounts for the relative intensities of the esr lines observed in some experiments.[19]

This theory will also explain totally emissive esr spectra, provided that the electronic g factors of the two radicals in the pair are significantly different, causing the heavier contribution of the electronic Zeeman interactions to the matrix element of $\mathcal{H}_{ab}{}^M$. In such a case and $g_1 > g_2$, the esr spectrum of radical 1 will be totally emissive while the spectrum of radical 2 will be correspondingly absorptive.

Kinetic Modifications of the Radical-Pair Theory

One of the weaknesses of the initial radical-pair model is that, in order to achieve the observed polarization, the radicals must remain at the separation where $J \sim \mathcal{H}^M$ for a time interval of 10^{-10} sec or longer.[15] J decreases very rapidly with increasing radical separation. Because of the correlation time of the Brownian motions in liquid being about 10^{-12} sec and the short time involved in the breaking of a chemical bond, it is thought that the required inter-

val of 10^{-10} sec or longer is quite improbable. Recent developments of the theory have been aimed mainly at solving this difficulty. Fischer[20] suggested that the wave functions of the radical pair could adiabatically follow the change of J during the lifetime of the pair to produce electron polarization. Similar considerations were entertained by Glarum and Marshall.[21]

In another approach, Adrian[18] attacked the problem by proposing that after the initial encounter the radicals of the pair diffuse apart instead of recombining and subsequently they undergo a second nonreactive encounter. Thus the pair will have much longer time to produce the polarization from the triplet mixing induced by magnetic interactions. This also brings into play the effect of the singlet–triplet splitting by the exchange interaction. With such assumptions, Adrian[18] was able to predict that polarization can also result from encounters of independently produced radicals with uncorrelated spins. Since the recombination probability of a radical pair is proportional to its singlet character, a radical pair with uncorrelated spins which has survived the initial encounter will probably have a greater than average triplet character. Thus, the radical pair with uncorrelated spins behaves just like a triplet pair.

Adrian[22] further refined his calculations by adding a consideration of the effect of the exchange interaction on the evolution of the radical-pair wave function during the entire diffusion trajectory of the pair, rather than just during a brief interval. Pedersen and Freed[23] carried the problem further and applied the stochastic Liouville method for solving the spin-density matrix equation of motion to obtain numerically the magnitude of the polarization based on the radical-pair theory. A similar method has been applied by Evans, Fleming, and Lawler[24] to both CIDEP and CIDNP problems. These calculations, adopting a more realistic diffusion model, are complex and comprehensive. Their analyses reach qualitatively the same results of the earlier models.[15,18,20] For the details of the individual treatment, the original papers by Adrian,[22] Pedersen and Freed,[23] and Evans, Fleming, and Lawler[24] should be studied.

In an experimental and theoretical study, Verma and Fessenden[25] reinvestigated the CIDEP of H atoms in the pulse-radiolysis system with a microsecond time-resolved spectrometer. They developed a kinetic model based on the Fischer and Lehnig formulation of the radical-pair theory[26] that radical combinations can be in part adiabatic for radical separations in the region where J is comparable to the hyperfine splitting. Their kinetic model fits satisfactorily the details of the observed time dependence curves, including the initial growth and the oscillatory behavior. They also argued that initial·polarization produced at the radical formation stage is inadequate to account for all the experimental results.

Before discussing "initial polarization," we note that the singlet and triplet states of the radical pair have not been consistently and precisely defined in

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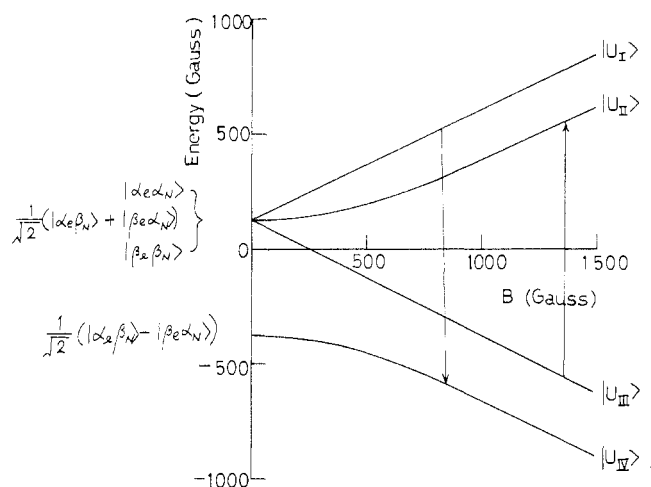
Figure 2. Energy levels for H atoms in a varying magnetic field.

the radical-pair theory. This causes some uncertainty and confusion about the signs of the singlet–triplet splitting J, i.e., whether the singlet state lies below or above the triplet state.[15-18,20-22,27] Since the sign of J often determines the nature of the polarization (emission or absorption), this uncertainty must be removed in future development of the theory.

Mechanisms of "Initial Polarization"

So far the radical-pair model considers only how electron polarization is produced after a pair of radicals is formed. It assumes no initial polarization of the radicals during their chemical formation stage. However, the fact that initial polarization may arise during chemical reactions has been casually mentioned by various authors.[26-31]

Recently Wan and coworkers have made some attempts[13,32-34] to probe the mechanism of initial electron polarization, without recourse to the familiar radical-pair model. In the radiolysis system of aqueous acidic solutions, electron polarization of hydrogen atoms has been observed.[30-31,35] If we assume that the formation of hydrogen atoms proceeds in two stages[36]

$$H^+ + e_{aq}^- \rightleftharpoons (H^+e^-) \longrightarrow H(^2S_{1/2}) \qquad (10)$$
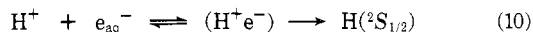
with the second step being rate determining, and the species (H^+e^-) represents a complex, probably in some higher excited states, we could argue[32] that the second step is equivalent to a cascade process presumably following the selection rule $\Delta F = 0$ or ± 1. It must be pointed out that the use of such an optical selection rule is arbitrary, similar to the random choice of the sign for J in the radical-pair theory. It

is hoped, however, that further study may justify the use of the optical selection rule.

By accepting these basic assumptions, one can readily see that the $F = 1$ triplet sublevels of the ground-state $^2S_{1/2}$ have more precursors than those of the $F = 0$ singlet sublevel. Such a preference for the $F = 1$ hyperfine level of the ground state could account for a population difference between the $F = 1$ and the $F = 0$ sublevels. The probability of formation P_r of the field-dependent state $|u_r\rangle$ is obtained through an adiabatic mixing between the $F = 1$ and $F = 0$ states by the external magnetic field (Figure 2). The results are that P_I is greater than P_{IV} and P_{III} is greater than P_{II} (see Figure 2). Thus it predicts the low-field line being emissive and the high-field line being absorptive, as observed in the experiments.[30-31,35]

The model also predicts the absolute initial magnitude of the polarization of the low-field line to be greater than that of the high-field line. On the other hand, the radical-pair theory would predict equal intensity of the two lines. This cascade model has also been applied to the case of D atoms,[32] and the results are again in qualitative agreement with the experiment.[35] Further calculations have been extended to simple organic radicals containing two equivalent and three equivalent protons.[37]

At this point, we recall that Verma and Fessenden[25] have argued that such an initial polarization produced upon the H atom formation is inadequate to account for all the experimental results. Fessenden[38] has also applied his interpretation to the radicals $\cdot CH(CO_2^-)_2$, $\cdot CH_2CO_2^-$, and hydroxycyclohexadienyl, formed in each case by reactions of OH radical. The strongest evidence in favor of a radical-pair mechanism is that the polarization persists at times longer than the spin–lattice relaxation time.[38]

It is conceivable that in a chemical system polarization can be induced simultaneously by a combination of mechanisms, including both the radical-pair and the initial polarization models. It may be just a coincidence that the cascade model happens to predict the right magnitude of polarization in simple cases such as the H and the D atoms. Nevertheless, further and specific experimental tests of these models are very much desirable. In the authors' laboratory, the approach of using an s-band spectrometer with a much lower magnetic field to test the models is being considered.

We now turn to CIDEP in photochemical systems. In 1970 Livingston and Zeldes[28] discovered a totally emissive esr spectrum in the photolysis of a tartaric acid solution. Atkins and coworkers[11] observed a totally emissive esr spectrum in the laser flash photolysis of some carbonyl compounds such as benzophenone in liquid paraffin. These authors[27] have suggested that the polarization in a totally emissive mode could be attributed to the $S_0 \leftrightarrow T_{+1,-1}$ intersystem crossings by some magnetic interactions such as hyperfine interaction and spin–rotation interaction. Their mechanism predicts that the radicals in the pair (the ketyl and the solvent radicals) will have the same sign of polarization. In other words the

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countersolvent radicals are predicted to be emissive. This is in contrast to the original radical-pair theory considering only the $S_0 \rightarrow T_0$ mixing which would lead to the prediction that the ketyl radical and the countersolvent radical have opposite sign of polarization. While the benzophenone ketyl radicals have been observed in a totally emissive mode,[11] the countersolvent radicals have eluded observation, and their sign of polarization thus is not determinable.

Recently Wong and Wan[39] have extended the study to investigate the photochemical reaction of triplet benzophenone with 2,6-di-*tert*-butylphenol in acetic acid solvent. They found that the counterradical, the phenoxy, indeed showed a totally emissive character. They further established that the magnitude of polarization is dependent upon the concentration of the phenol as the reactant, a fact which cannot be accounted for by the modified radical-pair theory. Nevertheless, these experiments[11,39] clearly established that the photochemical reaction of the triplet benzophenone leads to a ketyl radical and a counterradical, both being in the emissive mode.

Wong and Wan[13] also observed totally emissive esr of the 1,4-naphthosemiquinone radicals produced in the pulsed photolysis of the parent quinone in 2-propanol. Subsequently, they established that when 2,6-di-*tert*-butylphenol was used as the reactant both the semiquinone radical and the phenoxy counterradical are totally emissive.[33] They approached the polarization problem by considering a "photochemical" mechanism leading to "initial polarization." It was proposed that the dynamic electron polarization is due to the optically spin polarized triplets of the parent quinones and their subsequent hydrogen abstraction reaction with retention of polarization in the resultant semiquinone and phenoxy radicals. Obviously the chemical rate of the hydrogen abstraction reaction must be comparable to, or greater than, the spin–lattice relaxation rate of the triplet quinone (*i.e.*, depolarization).

Atkins and coworkers[27] have briefly mentioned such a possibility as a mechanism to induce polarization in their photochemical systems, but they discarded it because some of the hydrogen abstraction rates of known triplet molecules are too slow[40] to compete with the spin relaxation rate. On the other hand, Wong and Wan[13] argued that in some cases, *e.g.*, the excited triplet *p*-benzoquinone, the molecules could have a hydrogen abstraction rate comparable to, or greater than, the spin relaxation rate. Furthermore, spin polarization of the lowest triplet during photoexcitation of organic molecules has been well established by esr experiments,[41] by pmdr studies,[42] and by triplet–triplet absorption measurement at zero field.[43] The extremely useful pmdr technique, which provides most of the information on such optical spin polarization of triplet molecules, has recently been reviewed by El-Sayed.[44]

A formal theoretical development of the "photochemical" theory to account for the polarization in the quinone photochemical systems was given by Wong, Hutchinson, and Wan.[34] If the intersystem-crossing probabilities P_x, P_y, and P_z, from the photoexcited singlet to the zero-field triplet sublevels T_x, T_y, and T_z, are unequal (x, y, z here refer to the molecular axes), the calculations show that the randomly oriented triplet molecules in a finite magnetic field are spin polarized. The actual spin states are the linear combinations of infinite high-field spin states: $T_1 = |\alpha\alpha\rangle$, $T_0 = 2^{1/2}(|\alpha\beta\rangle + |\beta\alpha\rangle)$, and $T_{-1} = |\beta\beta\rangle$. If the hydrogen abstraction occurs before the triplet spin depolarization takes place, the resultant radicals will be initially populated in a manner that is mainly determined by the triplet polarization; *i.e.*, $|\alpha\alpha\rangle + |\alpha\beta\rangle \rightarrow |\alpha\alpha\beta\rangle + |\alpha\rangle$ and $|\beta\beta\rangle + |\alpha\beta\rangle \rightarrow |\beta\beta\alpha\rangle + |\beta\rangle$. The calculations further show that when the excited triplet molecules have *either* $D > 0$ and P_x or $P_y > P_z$, *or* $D < 0$ and $P_z > P_x$ and P_y, the resultant radicals will both have totally emissive character. Here, D is an electron dipolar parameter which, together with an E value, determines the relative energy level of the zero-field triplet states.

That a spin polarization may arise in excited triplet molecules in liquid (random) systems appears to contradict one's intuition and the understanding that the tumbling of the molecules ultimately averages any polarization to zero, if only because of the relaxation mechanism that arises from rotational modulation of the zero-field splitting. As an analogy to the nmr pseudocontact shift phenomenon in liquid, Weissman[45] has suggested that, in the present CIDEP systems, the P_x, P_y, and P_z anisotropy and the dipolar interaction may fluctuate together in a correlated way under random reorientation. The average over their cross-term does not vanish, and spin polarization of the triplet molecules may result. Weissman[45] also pointed out that it would be very interesting to consider the limiting behavior at very fast rotation when the spins *do not* follow the molecular orientation.

Experiments have recently been designed in the authors' laboratory to test the applicability of both the radical-pair and the photochemical theory. We have established[33] that, in the photochemical reaction of triplet quinone with phenol, the magnitude of the polarization depends on the phenol concentration. Such a dependence is implied in the photochemical theory dealing with hydrogen abstraction rates but cannot be satisfactorily accounted for by the current radical-pair theory. The original radical-pair model using only the $S \leftrightarrow T_0$ mixing mechanism fails even to account for the totally emissive behavior of both radicals. The effects of temperature and magnetic field on the magnitude of polarization in these systems have also been observed.[33] It is expected that the temperature will affect both the hydrogen abstraction rate and the spin–lattice relaxation rate. According to the photochemical theory, the polarization will indeed be dependent on the interplay of these two rates. The magnetic field effect, on the other hand, is not a simple one. Further stud-

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ies, including the possible use of an s-band spectrometer, will be required before the effect can be reasonably understood.

It goes without saying that there are inadequacies in the photochemical theory also. It is our hope that the proposed theory will stimulate further refinement and development of an ultimate theory for the CIDEP phenomenon. Indeed, it has just been brought to our attention that Atkins, McLauchlan, and coworkers,[46] who contributed much to the development of the current radical-pair theory, have obtained some experimental evidence against the radical-pair model. They have studied the photolysis of duroquinone in the presence of various amines and observed a totally emissive behavior of the durosemiquinone radical anions. The counter amine radical cations were not detected. They found that the magnitude of the polarization depends on the nature of the amine, the concentration of the amine, and the solvent. The current radical-pair theory is not able to account for these observations.

Atkins, McLauchlan, *et al.*, also presented some experimental evidence which cannot be satisfactorily explained by the photochemical theory. For example, they measured the triplet duroquinone lifetime by conventional nanosecond flash photolysis and have argued that it is not in line with the magnitude of polarization observed by esr. They proposed that an exciplex mechanism is operative in this system (eq 11). The electron polarization is produced in the ex-

$$DQ + h \longrightarrow {}^3DQ \xrightarrow{R_3N}$$
$$[DQ^- .. R_3N^+] \longrightarrow DQ^- + R_3N^+ \quad (11)$$
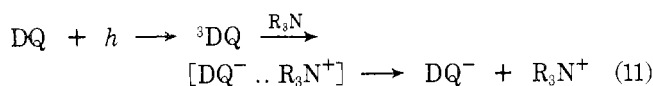
ciplex step where the $S \leftrightarrow T_{-1}$ mixing can be achieved with a strong electrostatic interaction holding the cation and anion close together for a sufficiently long period of time. Nevertheless, these authors[46] concluded that such a mechanism would not be completely satisfactory. Perhaps their conclusion echoes our beginning statement that the mechanisms of the dynamic electron polarization in various systems remain controversial.

Potential Applications of CIDEP

Future developments of CIDEP theories will require more quantitative experimental data in a variety of chemical systems. Given the necessary technical and financial support, it is conceivable that rapid-response time-resolved submicrosecond or even nanosecond spectrometers could be developed to probe the mechanism of initial polarization.

When a better understanding of CIDEP is acquired, the data can be applied to obtain spin–lattice relaxation times of radicals or triplet molecules in solution, to obtain further information on the complex intersystem crossing phenomenon in organic photochemical systems, and to obtain information on reaction mechanisms. For example, Atkins and coworkers[12] have demonstrated that CIDEP can provide a new tool for the direct determination of electron spin–lattice relaxation times of radicals in liquid. Wong and Wan[39] have suggested the potential application of photo-CIDEP to intersystem-crossing study of benzophenone.

The importance of organic triplet states in photochemistry has been well recognized in the past decade. The fact that the repopulation of the lowest excited singlets can result from the thermal equilibrium existing in the triplet states has led many to question[47] whether the photochemical reactivity in some organic systems originates directly from the triplet states. With the development of a better photochemical CIDEP theory, such questions can be at least partially answered by a direct observation of esr emission of the resulting radical. CIDEP experiments can also be extended to investigate energy-transfer mechanisms in triplet photosensitization reactions.

The radical-pair theory can provide direct insight into the nature of the radical–radical reactions and their dependence on nuclear spin states. Information about rate constants, the multiplicity of the precursor radical pair, and the exchange interaction J can also be obtained. The theory dealing with initial polarization can provide some details of the mechanism of the radical formation and the nature of the precursors. Given a rapid-response time-resolved experimental capability, the initial polarization theory will lead to a very simple method of determining the spin–lattice relaxation time of the radicals directly from the interconversion or the decay of the polarization.

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