ide since the Ar($O_2\cdot$)-H bond strengths will all be about the same as in the parent hydrocarbons—approximately 71 kcal/mol—and the rate of reaction 18 should not vary significantly for the three systems. If breaking of the second carbon-hydrogen bond is to determine the proportion of organic peroxide, then bond breaking must occur at the point where the bond strength varies, i.e., reaction 19, not reaction 18.

The heats required for the formation of naphthalene from the correspond radicals are very similar to those required for the formation of cyclohexene from its corresponding radicals. However, the oxidation of cyclohexane, unlike that of dihydronaphthalene, gives no evidence of olefin formation, even at 100°, in spite of the fact that the AR-H· bond strengths are the same. Here the lack of olefin in the cyclohexane oxidation is related to the stronger ArH-$O_2\cdot$ bond, which reduces the tendency of reaction 17 to reverse and prevents reaction 19 from competing.

Acknowledgments. This research has been carried out as part of the SRI Oxidation Studies, which was supported by a group of petroleum and chemical companies.

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Chemically Induced Dynamic Electron and Nuclear Polarization. VII. Simultaneous Contributions of the Radical Pair and Photoexcited Triplet Mechanisms in the Photolysis of Pyruvic Acid

K. Y. Choo and J. K. S. Wan*

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada. *Received March 10, 1975*

Abstract: CIDEP and CIDNP in the photoreduction of pyruvic acid in liquid by various hydrogen donors are reported and correlated. CIDNP study included both the low-field and high-field results and the method of using plane polarized light for excitation. The experimental evidence points to the co-existence of both the radical-pair and the photoexcited triplet mechanisms in CIDEP as well as in CIDNP observations. A general scheme for the simultaneous operations of the two mechanisms in a photochemical reaction is proposed.

Since the first observations of CIDEP in 1963[1] and CIDNP in 1967,[2] we have witnessed a remarkable development of a theory toward the understanding of these interesting phenomena. The initial efforts by Kaptein and Oosterhoff[3] and independently by Closs and co-workers[4] laid the foundation of the "radical-pair" theory which has now been generally established in CIDNP studies. The radical-pair theory was subsequently modified[5] with great success to account for CIDEP observations in radical systems showing the "multiplet effect". These include the original observation of H atom polarization in radiolysis,[1] the aliphatic ketyl radicals in photochemical systems,[6] and the alkyl and aliphatic ketyl radicals in radiolytic studies.[7] When a totally emissive pattern of CIDEP in the photoreduction of aromatic carbonyl compounds was reported in 1970 by Atkins, McLauchlan, and co-workers,[8] the phenomenon was explained by an extended radical-pair theory invoking the $S-T_{-1}$ mixing mechanism.[9] The importance of $S-T_{-1}$ mixing in the radical-pair theory has been beautifully demonstrated by CIDNP studies at low fields,[10] and a possible connection between CIDEP and CIDNP has also been generally recognized.[3,5,11]

In 1972 we reported the observation of totally emissive CIDEP in photochemical quinone systems.[12] The original naive proposal[12,13] of a photochemical triplet model based on the optically spin polarized triplets of the parent quinones and their subsequent hydrogen abstraction with retention of polarization in the primary radical pair has now received considerable theoretical[14-16] and experimental support.[17,18] The use of plane polarized excitation light as a test of the photoexcited triplet mechanism[16-18] in CIDEP studies was relatively successful. In some quinone systems, we have found[18] a variation factor dependent on the orientation of the polarized light to be larger than the theoretically predicted values by Adrian.[16] In view of the recent evidence that different photochemical reaction rates may result from different spin sublevels,[19] it is conceivable that even a small variation of reaction rates in the spin sublevels could lead to a much larger factor of the polarization magnitude in the plane polarized light experiments.

In a previous attempt to correlate both the CIDEP and the CIDNP results in the photolysis of *p*-benzoquinone in 2-propanol,[20] we did not obtain any conclusive evidence of the photoexcited triplet mechanism in the CIDNP observations, nor evidence of the radical-pair mechanism in the CIDEP observations. However, Bargon and Seifert[21a] have recently established that proton and fluorine spin polarization of photoexcited *p*-benzoquinones in nonreactive solvents are results of the triplet states of the quinones. We have also obtained evidence of the triplet mechanism in the CIDNP of tetrafluoro-*p*-benzoquinone photolyzed by plane polarized light.[21b] It has been our strong belief that, in some *photochemical* systems, the primary photochemical reaction of the excited triplet state contributes to magnetic polarization via the triplet mechanism, whereas the secondary reaction of the primary radical pair contributes to polarization by the radical-pair mechanism. It is, therefore, our objective to provide experimental evidence that simultaneous contributions of both mechanisms occur in photochemical systems showing both CIDEP and CIDNP phenomena. Such a task requires the a priori knowledge of the identity and the spin multiplicity of the initial radical-pair in the photochemical system, a systematic study of the effect of varying the nature of the excited triplet states, and a detailed investigation of both the CIDEP and CIDNP phenomena in the same chemical system, preferably in the same range of magnetic field.

This paper reports the first successful correlation and evaluation of the relative and simultaneous contributions of the radical-pair and the photoexcited triplet mechanisms to CIDEP and CIDNP observations in the photolysis of pyruvic acid in hydrogen-donor solvents. The photochemistry of aliphatic α-ketoacids is relatively well known,[22] and the energy levels and reactivities of their triplet states are quite different from the aromatic carbonyl compounds.

Experimental Section

Pyruvic acid and 2-ketobutyric acid were supplied by Aldrich. 2-Propanol, ethanol, carbon tetrachloride, perdeuteriobenzene, and benzene were all of spectrograde. Hydroquinones (Aldrich) were recrystallized from ethanol.

CIDNP studies were carried out using a Bruker HX 60 NMR spectrometer with a modified probe to allow sample irradiation via a reflecting mirror and lens assembly. The source was a 1-kW super pressure mercury lamp (Oriel) with Pyrex water filter. All spectra were recorded using either benzene or Me_4Si as internal locks depending on the positions of the signals. An auxiliary 4 in. electromagnet was used for low-field studies. The auxiliary magnet has an adjustable field strength of from 5 to 8000 G, monitored by a gaussmeter. Samples were irradiated at the lower magnetic field for 5 sec and then immediately transferred to the spectrometer for CIDNP observation. The transfer time was kept at 4 sec. An adiabatic condition during the transfer was confirmed by the reproducibility of the CIDNP signal, regardless of the relative orientation of the external and the spectrometer magnetic fields.[23]

ESR spectra were recorded with a Varian E-3 spectrometer with 100-kHz modulation. CIDEP time resolved studies were carried out in a Varian 4502 X-band spectrometer modified with a 2-MHz modulation unit. An Avco 20-kW pulse nitrogen laser with a pulse width of 3-5 nsec was used as the light source. A Biomation 610B transient recorder with a time resolution of 100 nsec per address was used to record the CIDEP curves, and the data were fed into the Nicolet 1074 computer for time averaging.

All NMR and ESR studies were at room temperature. Samples were degassed under high vacuum and sealed off. In plane polarized light experiments, the linear polarizer supplied by Oriel has a 2 in. diameter and about 35% transmission in the uv range. To show that reflection, scattering, etc. by the use of the cylindrical NMR tubes did not cause major variations on the transmission of the polarized light, several conventional NMR tubes of different size and materials (such as quartz and Pyrex) were used in control experiments. No significant changes in the experimental observations were detected. It has also been established[21b] by actual monitoring of light absorbed intensities that the difference in light absorbed intensity by the sample in a long, narrow NMR tube, when the electric vector of the excitation light was either parallel or perpendicular to the spectrometer magnetic field, was less than 0.5%. Furthermore, it has been conclusively demonstrated[18] by CIDEP experiments, in which ESR tubes of similar geometry were used, that the effect of polarized light is consistent with the well-known dependence of the electronic transition moment axis of the molecules. In the latter experiments, two quinone molecules with different polarization axes were specifically chosen to test the real effect of polarized light.

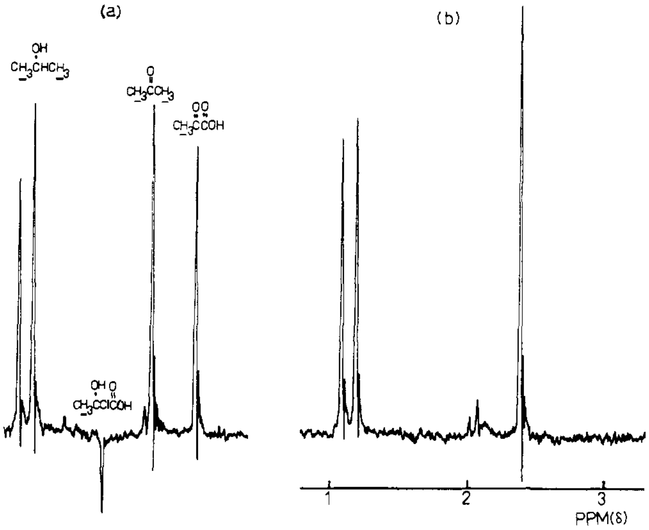


Figure 1. CIDNP spectra (a) during and (b) after irradiation of pyruvic acid and 2-propanol in carbon tetrachloride.

Results

The photoreduction of pyruvic acid in various hydrogen donor solvents such as methanol, 2-propanol, chloroform, and benzhydrol has been studied by Leermakers and Vesley.[24] Depending upon the solvent used, the $n\pi^*$ singlet–singlet transition in pyruvic acid lies in the region between 3200 and 3500 Å. In all cases, the major product of the photoreduction was found to be dimethyl tataric acid formed by the combination of the primary ketyl radicals, $CH_3\dot{C}(OH)COOH$.

1. High-Field CIDNP Study. Photolysis of a benzene solution containing 0.1 *M* of pyruvic acid alone did not give any CIDNP signal. In the presence of added 2-propanol (about 0.2 *M*), the product acetone exhibited CIDNP in the enhanced absorption mode. When ethanol was used instead of 2-propanol, the corresponding product acetaldehyde showed a mixed CIDNP pattern with the methyl protons in enhanced absorption and the aldehydic proton in emission. The relatively poor signal-to-noise ratio in this case prevented a detailed analysis of the multiplet pattern superimposed upon by the net effect.

Using carbon tetrachloride as solvent, the photoreduction of pyruvic acid with 2-propanol led to additional CIDNP observation of the second product $CH_3C(OH)ClCOOH$ with the methyl protons in the emissive mode. Acetone remained in the enhanced absorption mode, and it can also be observed that the methyl protons of 2-propanol during photolysis showed an AE multiplet pattern as well as the secondary proton in 2-propanol also giving an AE pattern. Pyruvic acid itself appeared to give CIDNP in the emissive mode, as a diminished absorption of its methyl protons was observed during irradiation. Some of these CIDNP results are shown in Figure 1.

These CIDNP observations can be readily accounted for by the radical-pair theory with Scheme I. Protons exhibiting CIDNP are indicated by an asterisk. In the triplet pair, the *g* values of $CH_3\dot{C}OHCOOH$ and $CH_3\dot{C}OHCH_3$ are 2.0037[25] and 2.0032, respectively. For simple aliphatic

Scheme I

$$CH_3COCOOH + h\nu \longrightarrow {}^1(CH_3COCOOH) \longrightarrow {}^3(CH_3COCOOH) \quad (1)$$

$${}^3(CH_3COCOOH) + CH_3CHOHCH_3 \longrightarrow {}^{T}\overline{CH_3\dot{C}OHCOOH \quad CH_3\dot{C}OHCH_3} \quad (2)$$

$$\downarrow$$

$$CH^*_3COCOOH + CH^*_3CH^*OHCH^*_3 \quad (3)$$

$$\qquad\qquad\qquad\qquad\qquad\quad \mathbf{1}$$

$$CH_3\dot{C}OHCOOH + CCl_4 \longrightarrow \underset{\mathbf{2}}{CH^*_3COHClCOOH} + \dot{C}Cl_3 \quad (4)$$

$$CH_3\dot{C}OHCOOH + CH_3COCOOH \longrightarrow \underset{\mathbf{3}}{CH^*_3COCOOH} + CH_3\dot{C}OHCOOH \quad (5)$$

$$CH_3\dot{C}OHCH_3 + CH_3COCOOH \longrightarrow \underset{\mathbf{4}}{CH^*_3COCH^*_3} + CH_3\dot{C}OHCOOH \quad (6)$$

radicals, it is reasonable to assume that the hyperfine coupling constants are positive for β-protons and negative for α-protons. Using Kaptein's rule,[26] the methyl protons are expected to give emission in the escaped product (**2**) and enhanced absorption in the escaped product (**4**). In the cage reaction (eq 3), both the methyl and the methyne protons in **1** are expected to have an AE pattern.[26] These agree with the experimental observations.

The CIDNP effect of the pyruvic acid itself is more interesting. In the cage reaction (eq 3), the methyl protons of the cage product pyruvic acid are expected to show enhanced absorption. On the other hand, they are expected to give emission when pyruvic acid is formed as an escaped product (**3**) in reaction 5. Since the actual experimental observation is a diminished absorption during irradiation, it is concluded that the overall CIDNP is emission. To account for this by the radical-pair theory alone would require that the contribution from the escaped product be much greater than that from the cage product. However, the net emissive CIDNP of pyruvic acid could be accounted for by a simultaneous contribution of the photoexcited triplet mechanism.

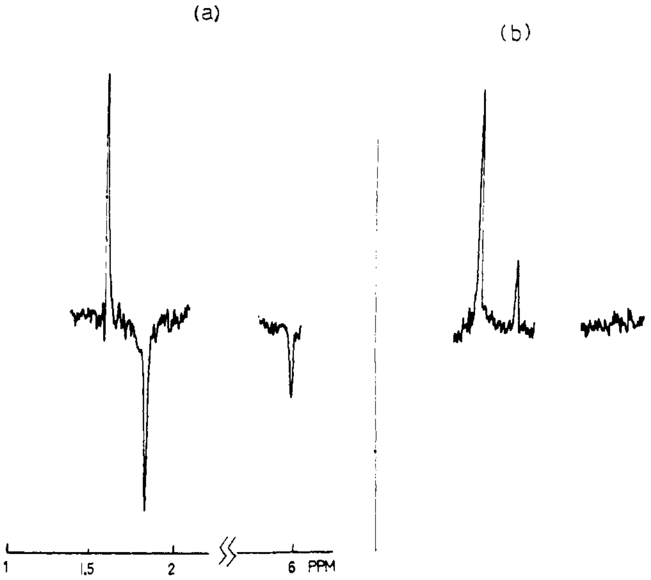


Figure 2. CIDNP spectra (a) during and (b) after irradiation of pyruvic acid and 2,5-di-*tert*-butyl-*p*-hydroquinone in benzene. In spectrum a, the absorption is due to the di-*tert*-butyl protons, the strong emission is due to the methyl protons of pyruvic acid, and the emission at about 6 ppm is due to the aromatic protons in the hydroquinone.

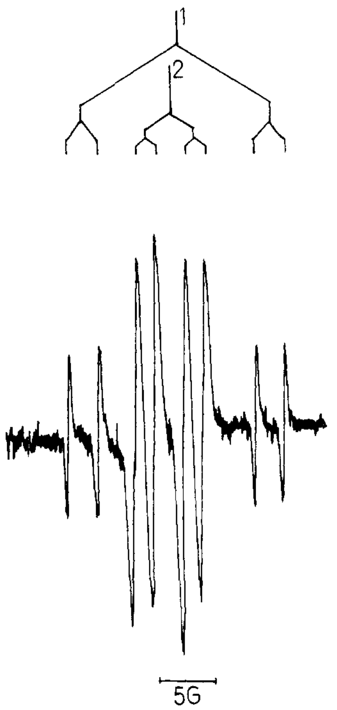


Figure 3. ESR spectrum obtained during the photolysis of pyruvic acid and 2,5-di-*tert*-butyl-*p*-hydroquinone in acetic acid. The middle four lines are due to radical 2, the semiquinone radical, and the outer lines are part of the radical 1 ($CH_3\dot{C}(OH)COOH$) spectrum.

A series of experiments was carried out to establish the nature and the mechanisms of the CIDNP of pyruvic acid. Figure 2 shows the CIDNP spectrum of pyruvic acid photoreduced by 2,5-di-*tert*-butyl-*p*-hydroquinone in a benzene solution. Using C_6F_6 or C_6D_6 as solvent did not alter the CIDNP spectrum, which shows a strong emission of the methyl protons of pyruvic acid and an emissive signal of the hydroquinone protons. The ESR spectrum (Figure 3) obtained during photolysis of this solution shows the presence of both primary radicals $CH_3\dot{C}(OH)COOH$ and the semiquinone radical with the g value of the semiquinone radical being greater than that of the ketyl radical. This is the reverse of the g value difference in the triplet pair in reaction 2 in which the 2-propanol radical has a g value smaller than the pyruvic acid radical. Thus, if one assumes the same explanation for the 2-propanol system that the major contribution to the CIDNP of pyruvic acid comes from the escaped product, the present experiment with hydroquinone would lead to enhanced absorption as the overall effect on the CIDNP of pyruvic acid. The experimental observation here is clearly the opposite. However, such an experimental test is not conclusive because one can argue that, in different 2-propanol and hydroquinone systems, the relative chemical reactivities of the triplet pairs may be very different. To test the triplet mechanism, we have chosen a system using various silanes (including phenyl-, diphenyl-, methyldiphenyl-, and dimethylphenylsilanes) to replace 2-propanol as the hydrogen donor. The g values of the silyl radicals are almost identical with that of the 2-propanol radical, but the hydrogen abstraction from Si-H bond is known to be relatively much more efficient than that from C-H bonds. The experimental results from all silane experiments show very strong emission of the pyruvic acid compared with the reduced absorption shown by using 2-propanol. We attribute

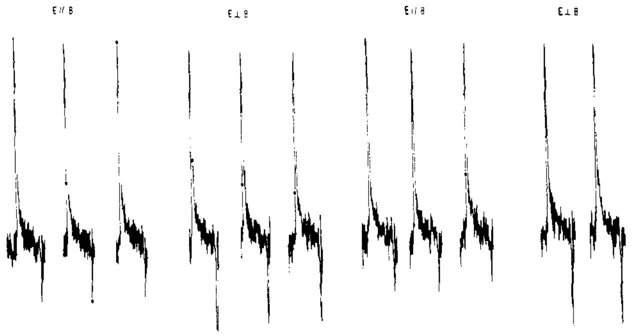


Figure 4. Dependence of the CIDNP emission intensity of the methyl proton in pyruvic acid on the orientation of the polarized exciting light in the photolysis of pyruvic acid and 2,5-di-*tert*-butyl-*p*-hydroquinone in benzene. *E* is the electric vector of the light, and *B* is the external magnetic field.

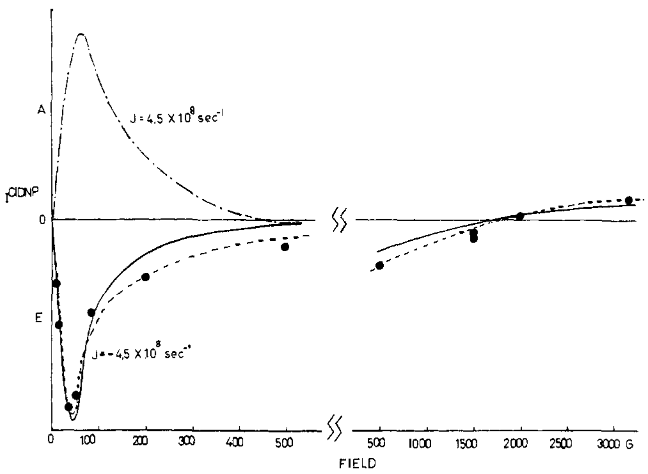


Figure 5. Field dependent CIDNP intensity of the protons in product acetone formed during low-field photolysis of pyruvic acid and 2-propanol in benzene. The dotted line is the experimental data; the — line is the calculated result using a negative *J*, and the —·— line is the calculated result using a positive *J*.

the difference in polarization magnitude to the significant different abstraction rates by the triplet pyruvic acid molecule in the two different systems.

A second experiment was also carried out with a photochemical system containing pyruvic acid and lactic acid in a benzene solution. Here the primary photochemical abstraction leads to a pair of *identical* radicals and hence $\Delta g = 0$ in the triplet pair. The S–T_0 mixing in this case would not lead to any net effect in CIDNP observation. The experimental result, however, is a diminished absorption of the pyruvic acid, again suggesting the CIDNP is emission. It should be pointed out that the pyruvic acid–lactic acid system would give a net polarization if S–$T_\pm$ mixing occurs efficiently in the spectrometer magnetic field of 14000 G. From some of the low-field CIDNP studies, it is obvious that efficient S–$T_\pm$ mixing at such a field of 14000 G would be very unlikely.

Further conclusive evidence of the triplet mechanism in the CIDNP observation of pyruvic acid was obtained by the plane polarized excitation light test. The reduced intensity from the plane polarized light source made it difficult to study systems that do not exhibit very strong CIDNP phenomenon. Because of the very strong emission of the pyruvic acid in the photoreduction with hydroquinone, we studied the dependence of the emission magnitude of pyruvic acid on the orientation of the exciting plane polarized light. The results are shown in Figure 4, which clearly indicates the dependence of the emission magnitude on the light orientation. In the photoreduction of pyruvic acid with 2-propanol, the escaped product acetone in reaction 6 also exhibited strong enhanced absorption. However, it was found that the CIDNP intensity of acetone was not dependent upon light orientation.

2. Low-Field CIDNP Study. In order to probe the relative S–T_0 and S–T_{-1} mixings in the photoreduction of pyruvic acid systems, we have studied the pyruvic acid–2-propanol photoreduction in a benzene solution at low fields. Since all our CIDEP studies are at about 3000 G, it is also desirable to have CIDNP data at comparable fields.

When the photolysis was carried out at fields below 2000 G, the observed CIDNP of the product acetone changed from enhanced absorption to emission. Figure 5 shows the field dependence of the acetone CIDNP in the photoreduction of pyruvic acid with 2-propanol. The crossover is consistent with the radical-pair theory that S–T_{-1} mixing becomes dominant at low fields. The field (about 2000 G) at which the crossover occurs is relatively much higher than in the quinone[20] and other systems.[10] From the field-dependent study, the approximate magnitude and sign of the J value can be deduced.[27] Following our previous theoretical treatment on the low-field CIDNP study which included all triplet levels in the calculation,[27] we have calculated the field dependence of the pyruvic acid–2-propanol system by using the triplet pair in reaction 2 and taking into account the six equivalent methyl protons in the 2-propanol radical which is the precursor of the product acetone. The parameters used in the calculation (plotted alongside with the experimental results in Figure 5) are listed below:

$$J = -0.45 \times 10^9 \text{ sec}^{-1} \qquad A_H = 0.35 \times 10^9 \text{ sec}^{-1}$$

$$\Delta g = -0.0005 \qquad \tau_S = 0.25 \times 10^{-4} \text{ sec}$$

$$\tau_D = 0.1 \times 10^{-10} \text{ sec}$$

Here τ_S is the scavenging life time and τ_D, the cage lifetime. For the purpose of comparison, the calculations using $J = +0.45 \times 10^9 \text{ sec}^{-1}$ were carried out and plotted in Figure 5.

3. CIDEP Study. Photolyses of pyruvic acid and 2-ketobutyric acid in various hydrogen-donor solvents, such as cyclohexanol, 2-butanol, 2-propanol, and lactic acid, were studied by ESR. Both the pyruvic acid radical $CH_3\dot{C}(OH)COOH$ and the butyric acid radical $CH_3CH_2\dot{C}(OH)COOH$ were identified by their well-resolved hyperfine structure. For $CH_3\dot{C}(OH)COOH$, $A_{CH_3} = 17.0$ G and $A_{OH} = 2.2$ G. For $CH_3CH_2\dot{C}(OH)COOH$, $A_{CH_2} = 12.2$ G, $A_{CH_3} = 1.0$ G, and $A_{OH} = 2.3$ G. These values are in good agreement with those reported in literature.[25]

A typical ESR spectrum obtained during the photolysis of pyruvic acid in lactic acid (identical primary radicals are formed) is shown in Figure 6. The noticeable anomalous intensity distribution in the spectrum is real with the low-field lines weaker than the corresponding high field lines. This anomaly could be due to some CIDEP effect.

The CIDEP phenomenon was confirmed by the time-resolved experiment carried out for each individual hyperfine line. Figure 7a shows a typical CIDEP decay curve of the transient radical $CH_3\dot{C}(OH)COOH$. At low power, the spin–lattice relaxation time of the radical could be estimated from the decay of the polarization which is about 5 μsec. Figure 7b presents a constructed ESR spectrum of the transient radical obtained from similar CIDEP decay curves on each of the hyperfine lines. Contrary to the well-known aromatic ketyl or semiquinone radicals showing totally emissive signals,[8,12] the pyruvic acid radical $CH_3\dot{C}(OH)COOH$ clearly exhibits a multiplet effect. After correcting for the

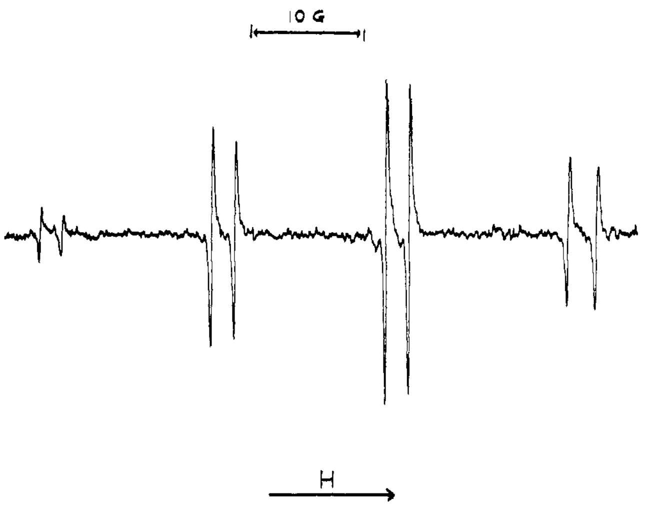


Figure 6. ESR spectrum obtained during steady irradiation of pyruvic acid in lactic acid. The quartet spectrum should have a normal 1:3:3:1 intensity distribution. The observed anomaly in intensity can be attenuated by slightly increasing microwave power level.

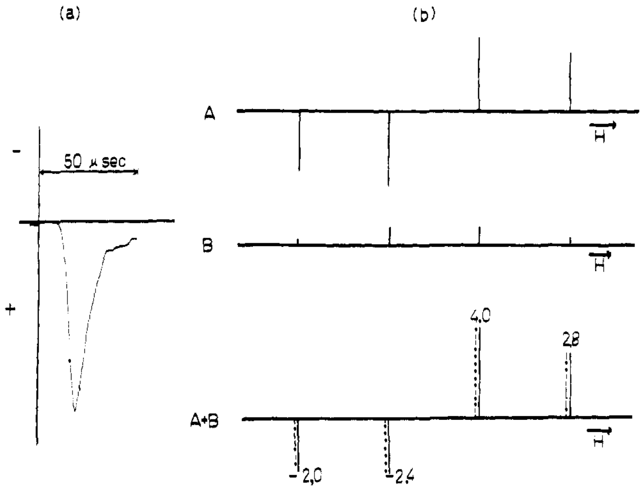


Figure 7. (a) The typical time dependence of electron polarization of $CH_3\dot{C}(OH)COOH$ radicals immediately after the pulse-laser photolysis of pyruvic acid in lactic acid. (b) The reconstruction of the total CIDEP spectrum: A is the pure multiplet effect; B is the net enhanced absorption; A + B is the total overall spectrum as compared with the experimental results given in dotted lines.

normal absorption, a small additional enhanced absorption mode superimposed on the multiplet pattern can be observed. This analysis is shown in Figure 7b.

Similar CIDEP observations showing multiplet effect were obtained for the butyric acid radical $CH_3CH_2\dot{C}(OH)COOH$.

Discussions

1. The Co-Existence of the Radical-Pair and the Photoexcited Triplet Models. The CIDEP intensities based upon the radical-pair model can be approximated according to Adrian's formulation:[11]

$$\langle \rho_{1,\mathrm{ab}} \rangle = 0.085(\mathcal{H}_{\mathrm{ab}}{}^{\mathrm{M}}J/|\mathcal{H}_{\mathrm{ab}}{}^{\mathrm{M}}J|)(\mathcal{H}_{\mathrm{ab}}{}^{\mathrm{M}}/\tau_{\mathrm{D}})^{1/2} \times [|C_{\mathrm{S}}(\mathrm{O})|^2 - |C_{\mathrm{T}}(\mathrm{O})|^2] \quad \text{(I)}$$

Here $2J$ is the singlet-triplet splitting, and $C_S(O)$ and $C_T(O)$ are the coefficients of the initial singlet and triplet states. The Hamiltonian $\mathcal{H}_{ab}{}^{M}$ has the form

$$\mathcal{H}_{\mathrm{ab}}{}^{\mathrm{M}} = \tfrac{1}{2}\beta_0 B_0(g_1 - g_2) + \tfrac{1}{2}\sum_n A_{1n}M_{1n}{}^{\mathrm{a}} - \sum_m A_{2m}M_{2m}{}^{\mathrm{b}} \quad \text{(II)}$$

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. B_0 is the external magnetic field, and β_0 is the Bohr magneton. $\rho_{1,ab} > 0$ corresponds to an emission mode of radical 1, and $\rho_{1,ab} < 0$ corresponds to an absorption mode.

Variations in g values among aromatic radicals and among aliphatic radicals are usually smaller than their hyperfine couplings. Thus, for a radical pair with small g value difference, the magnitude and the sign of the electron spin polarization depend mainly upon the multiplicity of the initial radical pair, the sign and value of J, and the magnitude of the proton hyperfine coupling constants. The CIDEP multiplet pattern does not depend upon the signs of the hyperfine couplings, although the signs are important in determining CIDNP multiplet effects. In all the CIDEP systems showing multiplet effects, the hyperfine couplings range from a very large value of 500 G in the H atom to a minimum of 17 G in the pyruvic acid radical reported here. For aromatic ketyl, semiquinone, and phenoxy radical systems, the proton hyperfine couplings are usually much smaller than 17 G. Thus, it is apparent from the eq I and II that the radical-pair mechanism contribution to CIDEP of these aromatic ketyl and semiquinone radicals would be much smaller and difficult to observe. However, our most recent study of CIDEP in quinone systems has revealed the co-existence of both the dominant photoexcited triplet mechanism and the less significant multiplet effects via the radical-pair mechanism.

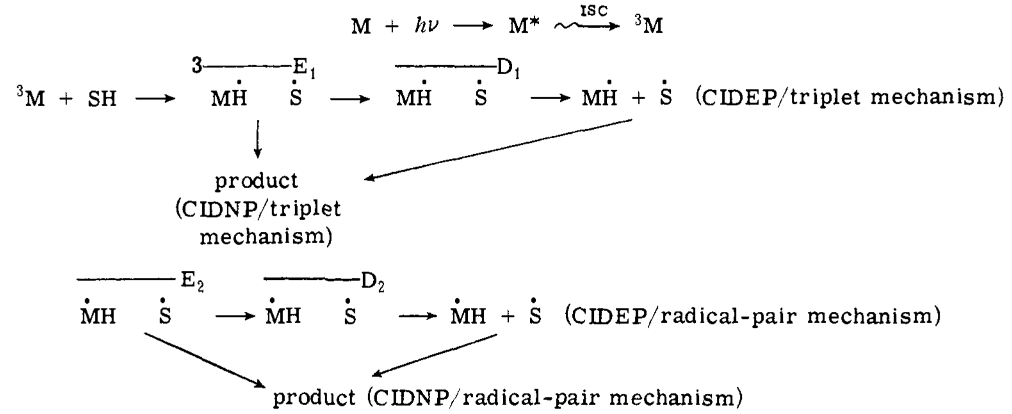
The CIDEP observation in the present photoreduction of pyruvic acid in lactic acid clearly suggests the dominance of the radical-pair mechanism. The multiplet pattern can be readily accounted for by considering $\Delta g = 0$, $J < 0$ (deduced from CIDNP low-field study), and the initial pair is a triplet. The predicted spectrum should then show low-field lines in emission and high-field lines in absorption with the lines at the outer wing more polarized than those in the center of the spectrum. The experimentally observed result was analyzed firstly in terms of this multiplet effect and it was found (Figure 7) that a complete reconstruction of the observed spectra can be obtained by allowing a small net effect of enhanced absorption to be superimposed upon the dominant multiplet effect. Since in this system the two primary radicals in the pair are identical (i.e., $\Delta g = 0$), the net effect could be either due to S–T_{-1} mixing by the radical-pair theory or the photoexcited triplet mechanism. The CIDNP results indicate that S–T_{-1} mixing is less efficient at fields higher than 2000 G, and the CIDEP was observed at about 3400 G. It is thought, therefore, that the net effect of enhanced absorption could be explained by the photoexcited triplet mechanism.

We have shown that, in the photoexcited triplet model,[13] the population in each of the spin sublevels can be approximately given by

$$P_{\pm 1} \propto (P_x + P_y - 2P_z)(D/B_0) \quad \text{(III)}$$

In order to give enhanced absorption, it is necessary that either $D > 0$ and $P_z > P_x$, P_y, or $D < 0$ and $P_z < P_x$, P_y. Here, D is an electron dipolar parameter which, together with an E value, determines the relative energy level of the zero-field triplet states. It should be mentioned that the triplet pyruvic acid has been found to abstract hydrogen with a rate similar to benzophenone triplet in various alcohols.[24]

Scheme II



The application of the photoexcited triplet model to CIDNP systems requires additional conditions. The cross relaxation (Overhauser effect) of the electron spin polarization to the nuclear system should occur before product formation, and the product formation must be fast enough to preserve the nuclear spin polarization in the radical precursor. Assuming a cross relaxation time for the pyruvic acid radical $CH_3\dot{C}(OH)COOH$ to be about 10^{-4} to 10^{-5} sec, observation of CIDNP due to the triplet mechanism would require the radical having a lifetime of between 10^{-4} and 10^{-5} sec. This is well within the experimental condition.[28]

The present study clearly demonstrated that the radical-pair and the photoexcited triplet mechanisms can operate side by side in a chemical system. They are two independent models, and their relative contributions depend upon the properties and the reaction rates of the triplet molecule. Obviously, the radical-pair mechanism can also operate in chemical systems which do not involve photoexcited triplets. Scheme II represents the simultaneous operations of the two mechanisms in a triplet photochemical system. Here E_1, E_2 are the first and second encounter pairs, and D_1 and D_2 are the first and second diffused pairs.[23,27] If the triplet molecule ^3M does not have the required properties and chemical reactivities to give polarization,[14-16] the radicals diffusing out from the cage in reaction 8 would not show any CIDEP. Otherwise, they would exhibit CIDEP due to the triplet mechanism. Simultaneously S–T mixings would occur in the second encounter pair and the radicals subsequently diffusing out of the cage in reaction 10 would show CIDEP according to the radical-pair mechanism. Similarly, products formed in the initial cage in which the triplet pair is polarized would give CIDNP via the triplet mechanism. If they are formed by radicals with electron spin-polarization which had induced sufficiently nuclear spin polarization in the radicals, the product would also exhibit CIDNP by the triplet mechanism. CIDNP of the products from all subsequent reactions can then be accounted for by the radical-pair mechanism.

2. Correlation of CIDNP and CIDEP Results. If both CIDEP and CIDNP of the chemical system can be fully accounted for by the radical-pair theory alone, the correlation between CIDNP and CIDEP data would be very simple. Analysis of the CIDEP results would yield the relative sign of J and the spin multiplicity. High-field CIDNP results would then lead to the sign of the hyperfine couplings, the multiplicity of the initial radical-pair, and the g value difference. Additional low-field CIDNP data would provide the information on the sign and approximate magnitude of J, the spin multiplicity of the initial pair, and the crossover between S–T_0 and S–$T_{\pm 1}$ mixings, if it occurs.

The correlation between CIDEP and CIDNP resulting from the photoexcited triplet mechanism is not as simple. For CIDNP, the transfer of electron spin polarization to nuclear spin can occur in two mechanisms. The scalar relaxation mechanism would lead to polarization opposite to the electron polarization, while the dipolar relaxation mechanism would yield the same polarization as the electron spin. For β-protons in alkyl radicals, the isotropic hyperfine interactions are modulated by the rotation of these protons relative to the 2p orbital. This leads to a more probable scalar cross relaxation.[11a] If the radicals exhibit a net effect in the enhanced absorption mode, the products formed after the cross relaxation within the radicals will show CIDNP in the emissive mode.

The photoexcited triplet model can therefore account for part of the correlation of CIDEP and CIDNP results in the pyruvic acid system. Here the CIDEP results indicate that the triplet mechanism is responsible for the small net effect of enhanced absorption in the pyruvic acid radical. Assuming the cross relaxation is predominantly by the scalar mechanism, the products formed in reaction 9 should give CIDNP in the emissive mode. Experimentally we have observed that, in the photoreduction of pyruvic acid by 2,5-di-*tert*-butyl-*p*-hydroquinone, both the pyruvic acid and the hydroquinone exhibit emission during irradiation. This can be accounted for by the triplet mechanism. Conclusive evidence of the contribution of the photoexcited triplet mechanism is established by the plane polarized excitation light experiment.

The present study of the photoreduction of pyruvic acid represents the first clear demonstration that the CIDEP and CIDNP of the system can be correlated and fully accounted for by the co-existence of the radical-pair and photoexcited triplet mechanisms. Work now in progress in this laboratory will attempt to provide quantitative assessments of the relative contributions of these two mechanisms in photochemical systems showing CIDEP and CIDNP phenomena. It is our hope that such further investigation will lead to better understanding of the dynamics and mechanism of intersystem crossing and the reactivity of organic triplet states in photochemistry.

Acknowledgments. This research is supported by a special grant from the National Research Council of Canada. We thank Mr. H. M. Vyas for some technical assistance.

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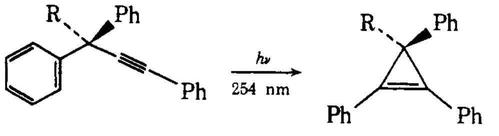
The Photochemistry of Phenylpropenyl Allenes. Suppression of the Di-π-methane Rearrangement in an Acyclic Allenic System through Involvement of the Triplet Excited State[1a,b]

D. C. Lankin, D. M. Chihal, N. S. Bhacca,[1c] and G. W. Griffin*

Contribution from the Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70122. Received October 15, 1974

Abstract: The photochemistry of *cis*- and *trans*-7-phenyl-2,5,5-trimethylhepta-2,3,6-triene was studied in order to extend the synthetic utility and mechanistic understanding of the di-π-methane reaction. A systematic variation of the hybridization at various reactive centers in the migrating π-moiety is in progress. In this paper we describe the effect of introducing an sp hybrid center one carbon removed from the migrating terminus. The requisite cis and trans allenic di-π-methane substrates were synthesized and subjected to direct and sensitized irradiations. It has been observed, upon *direct* irradiation of the trans isomer, that 2-isopropylidene-*anti*-3-phenyl-5,5-dimethylbicyclo[2.1.0]pentane is the major photoproduct. The anticipated trans vinylcyclopropane, namely *trans*-3,3-dimethyl-2-(3′,3′-dimethylallenyl)-1-phenylcyclopropane, as well as the noncyclized alternate cis geometric isomer is observed as minor photoproducts formed by way of competing processes. The allenic cis di-π-methane substrate was observed to undergo primarily cis-trans isomerization with subsequent rearrangement of the trans isomer to a bicyclo[2.1.0]pentane and trans cyclopropane. *Sensitized* irradiations of both isomeric allenic substrates give bicyclo[2.1.0]pentane formation as well as cis-trans isomerization. No di-π-methane rearrangement to cyclopropanes is observed. Quenching studies indicate that the triplet state of *cis*- and *trans*-7-phenyl-2,5,5-trimethylhepta-2,3,6-triene is the chemically significant excited state in the formation of the bicyclo[2.1.0]pentane. The suppression of the di-π-methane rearrangement is discussed.

It is now recognized that di-π-methane rearrangements constitute a basic class of photochemical transformations and considerable effort has been devoted to defining the scope and limitations of this intriguing reaction.[2] An area of considerable interest to us relates to the effect induced on the photochemical behavior of di-π-methane substrates by altering hybridization at various centers of the migrating group. Of initial concern has been the photochemistry of di-π-methane systems in which at least one of the π-moieties is a substituted acetylene.[3] For example, we have found that the photorearrangements of **1a** and **1b**, where one π-moiety is acetylenic in character and the other is incorporated within an aromatic ring afford the cyclopropenes **2a** and **2b**, respectively, as the *primary* photoproducts[3c] (eq 1).



(1)

1a, R = Ph
b, R = OMe

2a, R = Ph
b, R = OMe

More recently, our studies[3a-c] of the photochemistry of the isomeric acetylenes **3a** and **3b** have revealed that the acetylenic cyclopropanes **4a** and **5a** as well as **4b** and **5b**, respectively, are the major photoproducts detected. Interestingly *no* cyclopropenes were observed although they constitute potential rearrangement products of **3a** and **3b** (eq 2). This work confirms that the formation of the cyclopropanes is highly stereospecific; i.e., **3a** affords **4a** and **5a**, while **3b** gives **4b** and **5b**. In this respect, the stereochemical course of the reaction of **3a** and **3b**, determined at low con-

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