Tetrahedron Vol. 37, No 19, pp 3411 to 3420, 1981
Printed in Great Britain.

0040-4020/81/193411-10$02.00/0
Pergamon Press Ltd

MEASUREMENT OF RATE PROCESSES OF FREE RADICALS IN HOMOGENEOUS AND MICELLAR SOLUTIONS BY CIDNP

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(*Received in USA April* 1981)

Abstract—CIDNP is used to study rate processes of free radicals in both homogeneous and micellar solution. An estimate of the lifetime of the phenyl-acetyl radical at ambient temperature ($\tau_{CO} \geq 10^{-7}$ sec) produced during photolysis of dibenzyl ketone is made based on quantitative CIDNP measurements and computer simulations. Observation of CIDNP in micellar solution is shown to be consistent with an isotropic medium which restricts diffusion on a short time scale, allowing for an increased tendency toward cage reaction. In the case of t-butyl/pivaloyl radical pairs, escape of the radical fragments from the micelle is shown to be competitive with decarbonylation of the pivaloyl radical. Likewise, CIDNP is consistent with product yield results which show the enhanced tendency of triplet born benzyl radical pairs to undergo cage reaction when they are sequestered in a micelle.

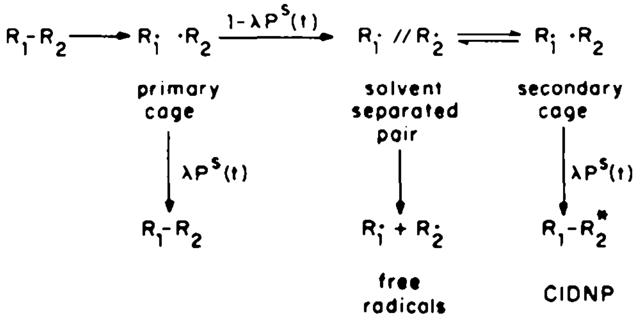
Use of CIDNP in rate measurements of radical pair and micellar processes

The radical pair theory[1] provides the basis for understanding not only the CIDNP phenomenon, but also the magnetic isotope effect[2] and the enhanced cage effect observed in micellar solutions.[3] The theory results from a consideration of the effects of nuclear spin states on the reactivity of pairs of free radicals in recombination and disproportionation reactions. The important kinetic processes which take place during the lifetime of the radical pair[1] are outlined in Scheme 1.

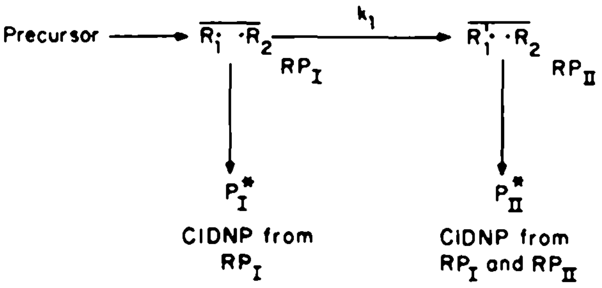
The initially formed radical pair is surrounded by a solvent cage which acts to hold the pair together. This primary radical pair has a probability $P^s(t)$ to react from the singlet electronic state to form cage product R_1R_2. In general, the triplet electronic state will be repulsive and no reaction will occur. Competitive with cage reaction are the forces of diffusion, which tend to separate the radical fragments. As this occurs, the electron spin on each fragment assumes a precessional frequency highly dependent on the structure of the fragment, but independent of its partner radical. If the radical possesses magnetic nuclei which are coupled to the electron by hyperfine interactions, then the precessional frequency is dependent on the nuclear spin state of the magnetic nuclei as well. Since the rate of mixing between singlet and triplet radical pairs is dependent on the difference of the precessional frequencies of the two unpaired electron spins[1], the mere presence of magnetic nuclei increases the rate of intersystem crossing.

Statistical analysis of diffusion[4] indicates that a pair of radicals which were together at $t = 0$, and have diffused apart, still have a fairly high probability of a reencounter after several diffusive steps. When this occurs, the radical pair forms a secondary cage pair, distinguished from the primary cage pair by the simple act of diffusive separation and by its location in time. During the lifetime of the secondary cage pair, a second chance at reaction from the singlet state is possible. Pairs which have either intersystem crossed to the triplet state or have remained in the triplet state are unreactive and tend to diffuse into the bulk solution. When the radical pair is enclosed in a micelle, the process of diffusion beyond several angstroms is severely limited.[5] The effect of the micelle on the radical pair, therefore, is to increase the probability of *multiple reencounters*, and with them to increase the probability of cage reaction. While it is not clear that diffusion within a micelle can be described as a three dimensional random walk[4] similar to that in homogeneous solution, such an assumption at least provides a preliminary basis for understanding the effects of micelles on radical pair reactions.

Pair substituent effects. The process of diffusion, intersystem crossing, reencounter and reaction described above takes place in homogeneous solution in a time span on the order of 1 to 100 ns.[6] Radical processes which are competitive with S–T mixing and/or secondary recombination may therefore affect the observed CIDNP intensities[7]. As a result, many processes involving either chemical reaction,[7] exchange[8] or rotational motion[9] may



Scheme 1.

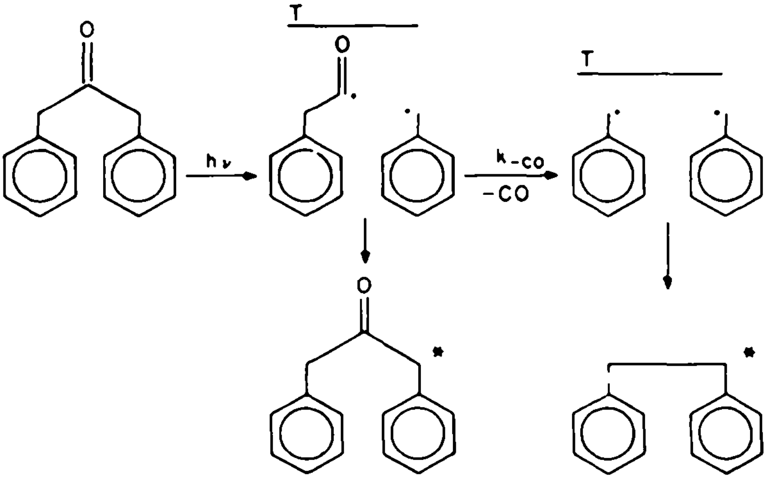


Scheme 2.

be analyzed by careful consideration of quantitative CIDNP spectra.[10] Consider for example a radical pair, RP_I, formed at t = 0, which undergoes a reaction to form the new radical pair, RP_{II}, which is competitive with secondary recombination, as shown in Scheme 2. The bar over each radical pair implies all of the attendant processes necessary for the generation of CIDNP as shown in Scheme 1. Polarization which is developed during the lifetime of RP_I may be transferred to RP_{II} with a rate given by k_1. The most important cases of this type of effect involve pairs in which RP_I has $\Delta g \neq 0$, and therefore result in net CIDNP, and RP_{II} has $\Delta g = 0$, and therefore may result only in multiplet CIDNP. In these cases, net polarization developed during the lifetime of RP_I is transferred by reaction to RP_{II}, and results in net polarized P_{II}. Since RP_{II} is itself incapable of producing net effects in P_{II}, this process has been termed[7] the "cooperative" or "pair substitution" effect. The relative magnitude of the polarization of the same nuclei in P_I and P_{II} is dependent on the properties of RP_I and RP_{II} and, most importantly, on k_1. Clearly this results from the ability of the pair substitution reaction to compete with the formation of P_I from RP_I. Two examples of the application of this method have resulted in the estimation of rate constants for the decarboxylation of benzoyloxy and acetoxy radicals during the thermal decompositions of acyl peroxides.[7] Below we describe a similar determination of the rate constant for the decarbonylation of phenylacetyl radical during the photolysis of dibenzyl ketone as shown in Scheme 3.

Micelle effects. As mentioned above, when a molecule suffers bond homolysis in homogeneous solution, the resulting radical fragments may either react with one another (i.e., cage reaction) or diffuse apart to become free radicals. In micellar solution the process of diffusion is restricted by the chemical potential of the micelle-water interface[5], thus making cage reaction more probable. The rate of intermicellar exchange of radical fragments relative to the rate of intersystem crossing for triplet born radical pairs is therefore important for optimizing the cage effect.[3] Exit rate constants for various probe molecules from micelles have been estimated in the range of 10^3–$10^7\ sec^{-1}$ for moderate to small size molecules, while re-entry rate constants of neutral hydrophobic molecules are generally close to diffusion controlled[11], in the range of 10^8–$10^{10}\ M^{-1}\ sec^{-1}$. Thus, the rate of intermicellar exchange of typical organic free radicals is governed by their rate of exit from the micelle.

Measurement of unknown rates relative to that of known rate processes is a standard tool in the chemist's arsenal. A potential method of measuring the exit rates of simple radicals from micelles is to relate this to the rate of a rearrangement or fragmentation reaction of the radical. While direct measurement of product yields is possible in some cases, an alternative method is based on the observation of CIDNP. During the photolysis of many ketones, acyl/alkyl radical pairs are formed by type I cleavage reactions.[12] Since the rate of decarbonylation of many acyl radicals are known,[13] we may



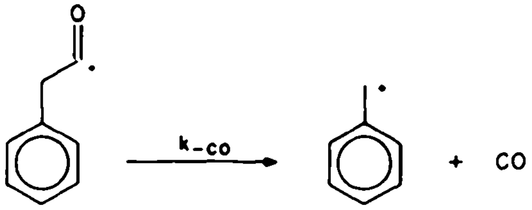
* denotes CIDNP

Scheme 3.

use these reactions as internal clocks for estimating rate processes of the radical pair. By observing the CIDNP in micelles in the presence and absence of aqueous free radical scavengers, we may assess the contribution of those radical pairs formed after intermicellar exchange.

RESULTS

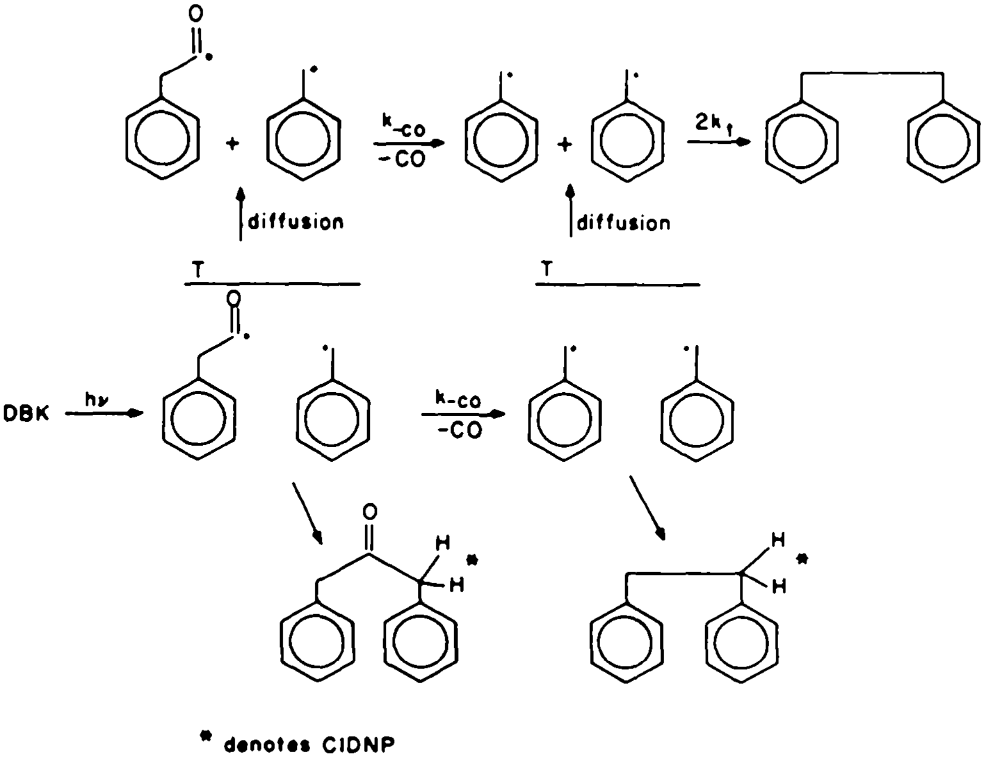
The rate of decarbonylation of the phenylacetyl radical. Previous determinations of the rate of decarbonylation of the phenylacetyl radical by steady state ESR methods[14] at low temperatures result in an estimate of $k_{-CO} = 10^7–10^8\ \text{sec}^{-1}$ at ambient temperatures. When this radical is formed by photolysis of dibenzyl ketone (DBK) at room temperature, the rate of decarbonylation is expected to be competitive with intersystem crossing of the primary triplet radical pair and secondary recombination, and, therefore, can be studied by quantitative CIDNP methods.



$$k_{-co} = 10^{13} \exp\left[-7300 \frac{\text{cal}}{\text{mole}} / RT\right] \text{sec}^{-1}$$

Previous examinations[14b,15] of the mechanism of the photoreaction of DBK in homogeneous solution indicate that α-cleavage takes place from the excited triplet state. The initially formed triplet radical pair may then, according to Scheme 1, undergo nuclear spin dependent intersystem crossing and cage reaction to reform DBK or diffuse apart to become free radicals. According to Kaptein's phase rule,[16] DBK formed in this way will exhibit emissive CIDNP in the benzylic methylene protons ($\Delta g = 1.8 \times 10^{-3}$, $A_{CH_2} = -16.3$ G),[14] while the benzyl radicals which eventually undergo second order termination will carry with them complimentary absorptive polarization. Since decarbonylation is expected to be competitive with S-T mixing and cage recombination, net emissive polarization should be transferred to geminate benzyl/benzyl radical pairs and end up as emissive CIDNP in the methylene protons of diphenyl ethane (DPE). However, since in the absence of scavengers the escaped benzyl radicals eventually recombine to give the same product, the total CIDNP intensity of the methylene protons of DPE should be the sum of emissive and absorptive effects from geminate and random recombination.

These predictions are verified by the CIDNP spectrum obtained during the photolysis of DBK in benzene[17] shown in Fig. 1. Strong emissive CIDNP is observed in the methylene protons of starting ketone at 3.6 ppm, while the methylene protons of DPE at 3.0 ppm are observed in enhanced absorption. In addition, a complex pattern of absorption and emission in the aromatic region (7.0–7.25 ppm) and a weak emission at 5.0 ppm are observed. This latter peak is assigned to the tautomer of the isomeric *p*-methyl phenyl benzyl ketone. While *p*-Me-phenyl-benzyl ketone has not been found pre-



Scheme 4.

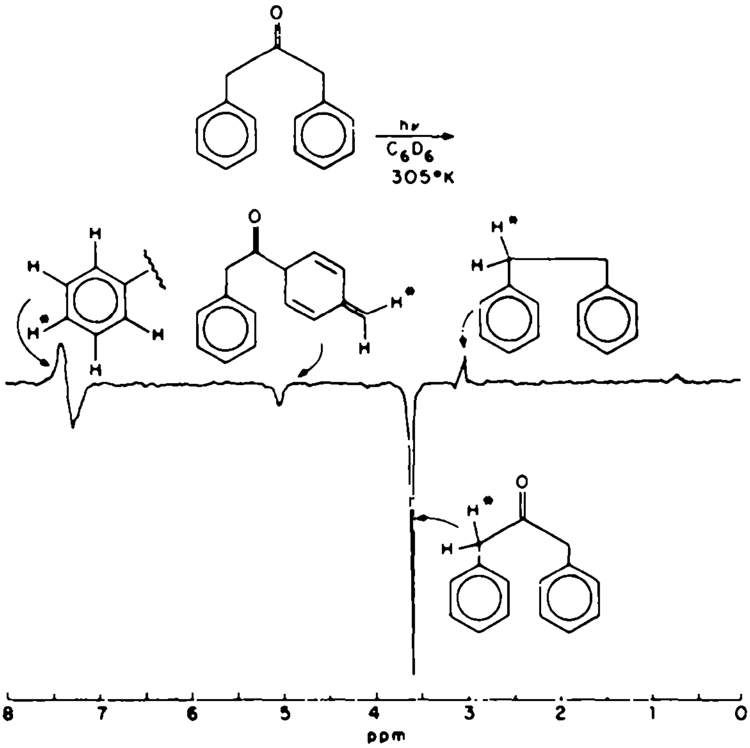
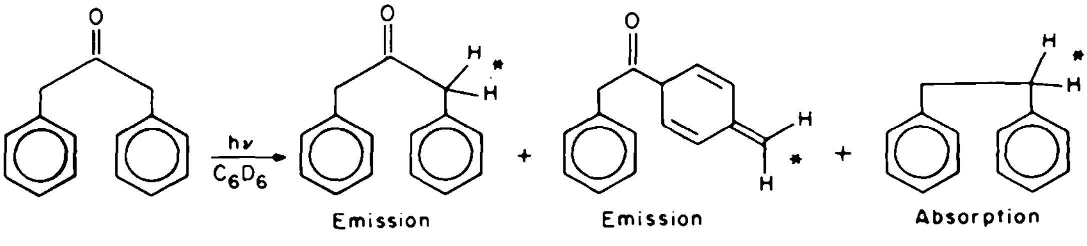


Fig. 1. Saturation recovery CIDNP spectrum[18] (τ = 10 sec) during the photolysis of 5.0 mM DBK in C_6D_6 at 305 K, 30 scans over 60 seconds, pulse width = 30.

viously among the products in homogeneous solution, it has been isolated as a product from photolysis of DBK in micellar solution.[18] CIDNP observations in homogeneous solution may, therefore, give clues to the formation of radical pairs products which may be enhanced by micellization. We have recently observed that photolysis of either *d,l* or *meso* α,α'-dimethyl-dibenzyl ketone in homogeneous solution results in CIDNP in both diastereomers regardless of which is initially present.[26] Isolation of the starting ketone however indicates that no measurable isomerization occurs. When the photolysis is conducted in micellar solution, the recovered ketone product shows significant isomerization.[26] Thus, the micelle enhances the "internal return" of geminate triplet radical pairs by restricting diffusion beyond several angstroms.

The overlap of absorptive CIDNP in the methylene protons of DPE from random termination with the emissive effect expected from the cage product can be eliminated by the addition of free radical scavengers. Addition of sufficient n-butyl thiol leads to the trapping of free benzyl radicals as toluene. Quantitative CIDNP spectra obtained by the saturation-recovery method of Barbara and Lawler[10] during the photolysis of DBK in benzene in the presence of n-butyl thiol are shown in Fig. 2. As the concentration of thiol increases, the absorptive polarization in the methyl group of toluene, 2.3 ppm, increases with a corresponding decrease DPE polarization. Above 0.25 M n-butyl thiol no polarized DPE signal is observed, and even at 1.5 M thiol no emissive signal is observed at 3.0 ppm. Thus, the rate of decarbonylation must be slow enough so as not to be competitive with recombination of this radical pair system.

A quantitative estimate of the rate constant for decarbonylation may be determined by a detailed simulation of the expected CIDNP as a function of k_{CO}. The theoretical framework for calculation of CIDNP spectra with "cooperative" or "pair substitution" effects has been previously established by Schwertzl *et al.*,[7a] and by den Hollander[7b]. Using a CIDNP simulation program modified to take such effects into account,[19] we have simulated the relative polarization of the methylene protons of DBK and DPE as a function of k_{CO}. The parameters used in these simulations are given in Fig. 3, and the results are presented in Figs. 4 and 5.



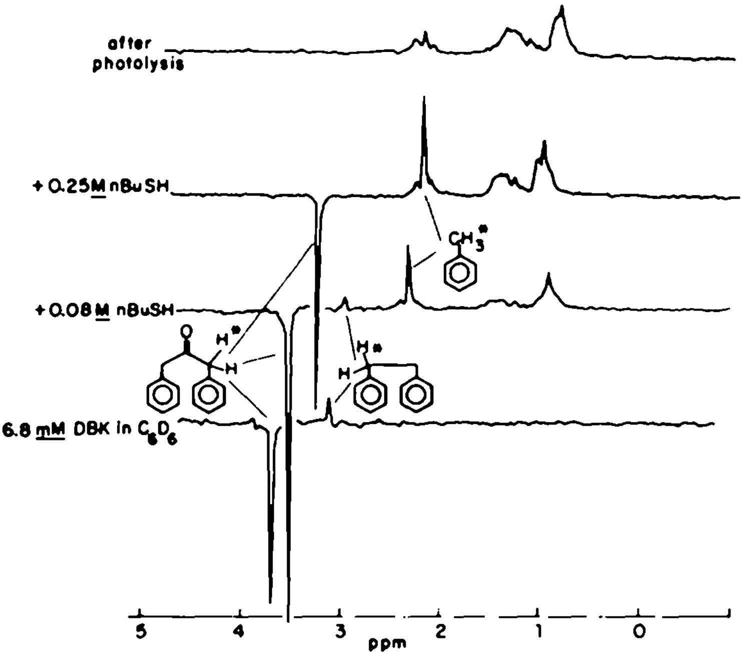
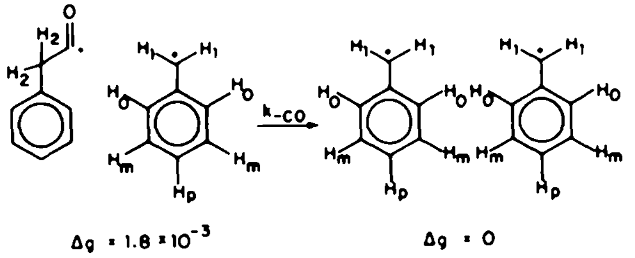


Fig. 2. Saturation recovery CIDNP spectra[10] (τ = 1.0 sec) during the photolysis of DBK in C_6D_6 in the presence of nBuSH at 305 K. 30 scans over 60 seconds, pulse width = 30°.



A_1 = −16.3G, A_2 = 0.4G, A_o = −5.2G, A_m = 1.8G, A_p = −6.2G

Characteristic time for a diffuse step, $\tau_d = 10^{-12}$ sec

Fig. 3. ESR and NMR parameters used in the simulation of the CIDNP arising during the photolysis of DBK.

As shown in Figs. 4 and 5, the polarization ratio DBK*/DPE* is quite sensitive to the magnitude of the decarbonylation rate constant over the range 10^7–10^9 sec^{-1}. A plot of this ratio vs τ_{-CO}, the lifetime of the phenylacetyl radical, is relatively linear for $\tau_{-CO} \geq 10^{-9}$ sec. Since the net effects arise solely from interactions in the first radical pair ($\Delta g = 1.8 \times 10^{-3}$), we would predict that the total polarization intensity (DBK* + DPE*) should increase with the lifetime of the first radical pair. This is clearly borne out by the simulations shown in Fig. 4.

From a comparison of the observed and simulated results, we estimate k_{-CO} to be $\leq 10^7$ sec^{-1} at 31°. While this value is lower than the value estimated by steady state ESR methods,[14] the previous determinations were calculated relative to order of magnitude estimates of second order termination rate constants for which no experimental determination was available. We are extending our studies of this reaction in the area of nanosecond resolved flash photolysis with hopes of observing this process directly.

Estimation of the exit rate of t-butyl/pivaloyl radicals from HDTc micelles: Generally,[17] measurements of exit rates from micelles are obtained by observing the luminescence lifetime of the probe as a function of aqueous quencher concentration. Such methods offer high sensitivity and precision, but are limited to fluorescent or phosphorescent probes. CIDNP can, however, be used in some cases to obtain estimates of exit rates of simple free radicals which would otherwise not be available.

The rate of decarbonylation of the pivaloyl radical has been studied by kinetic ESR methods at various temperatures and yields a rate constant given by[13f] $k_{-CO} = 7.94 \times 10^{11} e^{-(9300/RT)}$. We can, therefore, estimate the rate constant for decarbonylation of the pivaloyl radical at 31°C as ~ 10^6 sec^{-1}.

Generation of this radical by photolysis of di-t-butyl ketone results in the formation of an initial triplet (T) radical pair with a t-Bu radical.[13f] Since the lifetime of the pivaloyl radical at ambient temperature is > 1 μs, we expect that the products of cage reaction will be derived

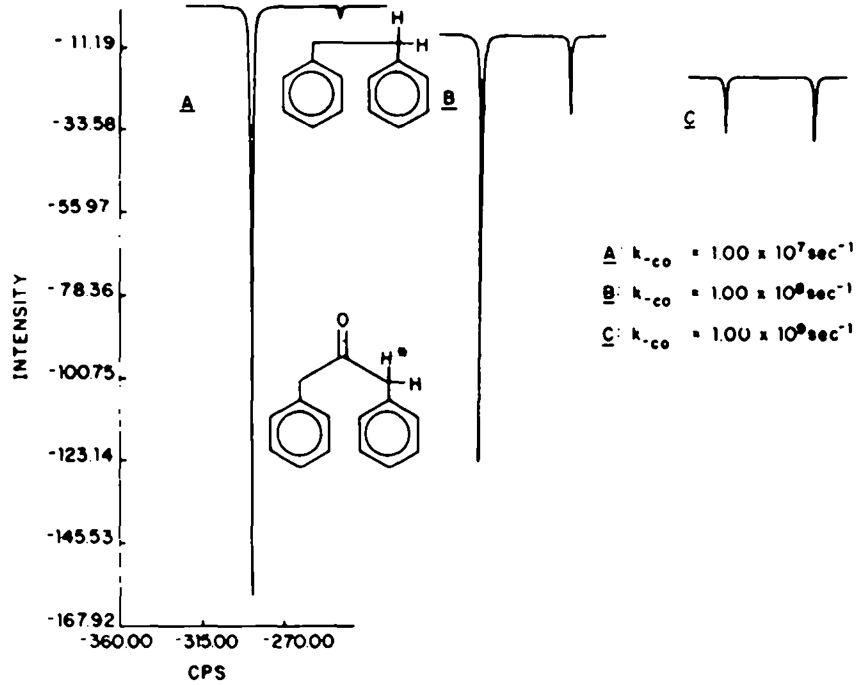


Fig. 4. CIDNP simulations of the net polarization of the methylene protons of DBK and DPE as a function of k_{-CO}.

from recombination and disproportionation reactions of pivaloyl and t-Bu radicals. Pivaloyl radicals which diffuse into the bulk of the solution, however, will decarbonylate prior to encountering other t-Bu radicals in free radical (F) pairs (Scheme 5). Thus, in homogeneous solution we observe[20] net CIDNP in the products of the initial triplet pairs ($\Delta g \neq 0$) and multiplet CIDNP in the products of the secondary free radical pairs ($\Delta g = 0$) as shown in Fig. 6a. When this photolysis is performed in HDTCl micellar solution, an essentially identical CIDNP spectrum is observed, as shown in Fig. 6b.

Exit rate constants for small probe molecules from typical micelles[11] are generally in the range of 10^7–10^5 sec^{-1}. This places the rate of decarbonylation of pivaloyl in a range competitive with typical exit rates. The question then arises as to whether or not intermicellar exchange of free radicals occurs before or after

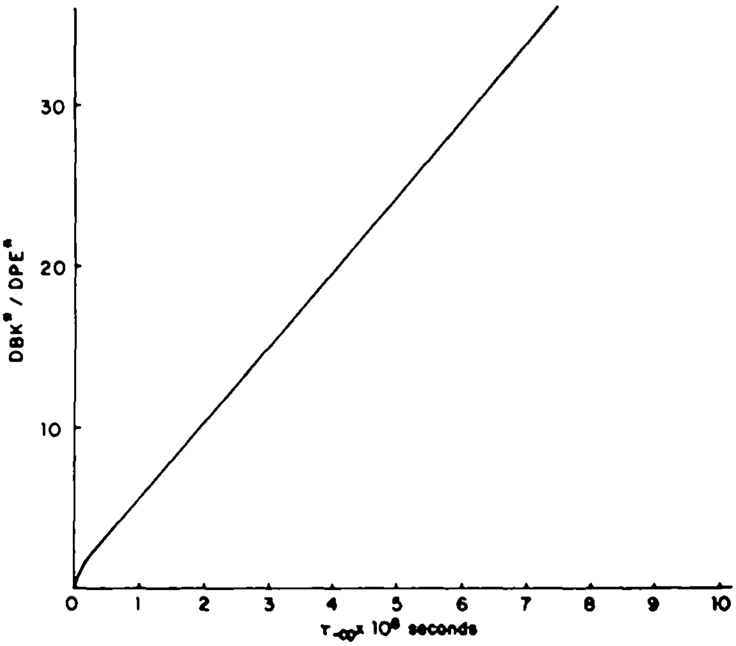
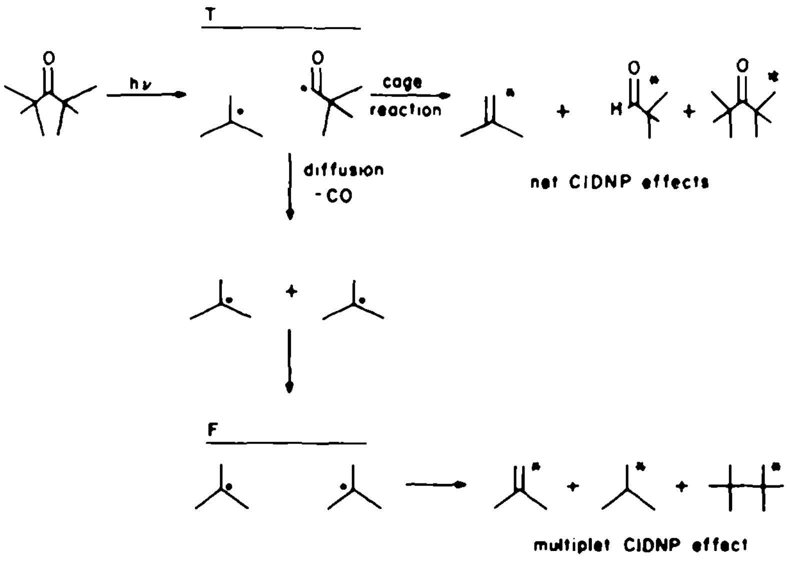


Fig. 5. Ratio of the simulated net polarization of the methylene protons of DBK and DPE as a function of the lifetime of the phenylacetyl radical, τ_{-CO}.



Scheme 5.

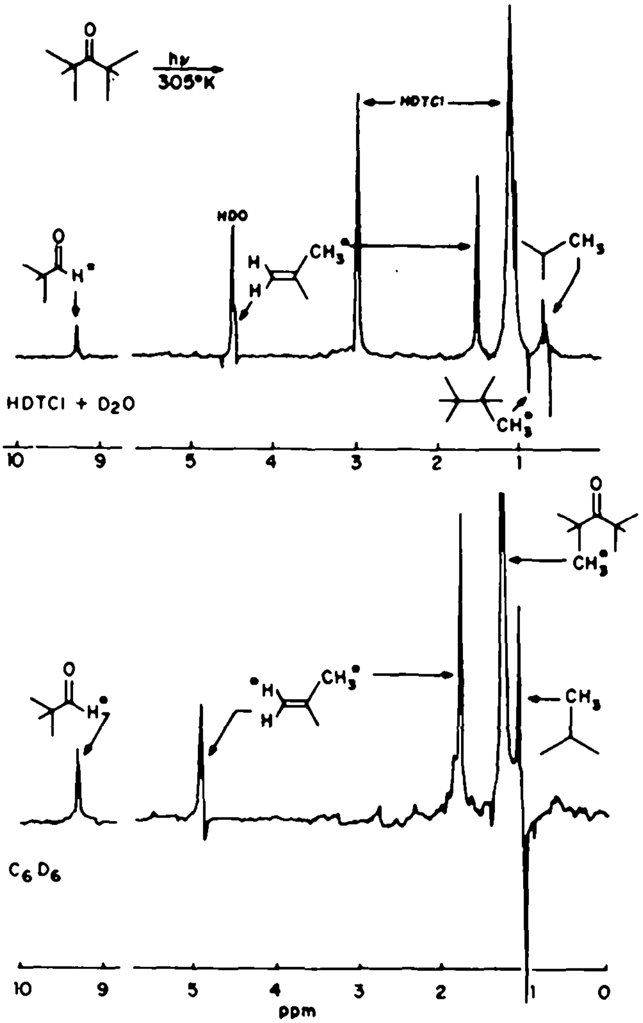
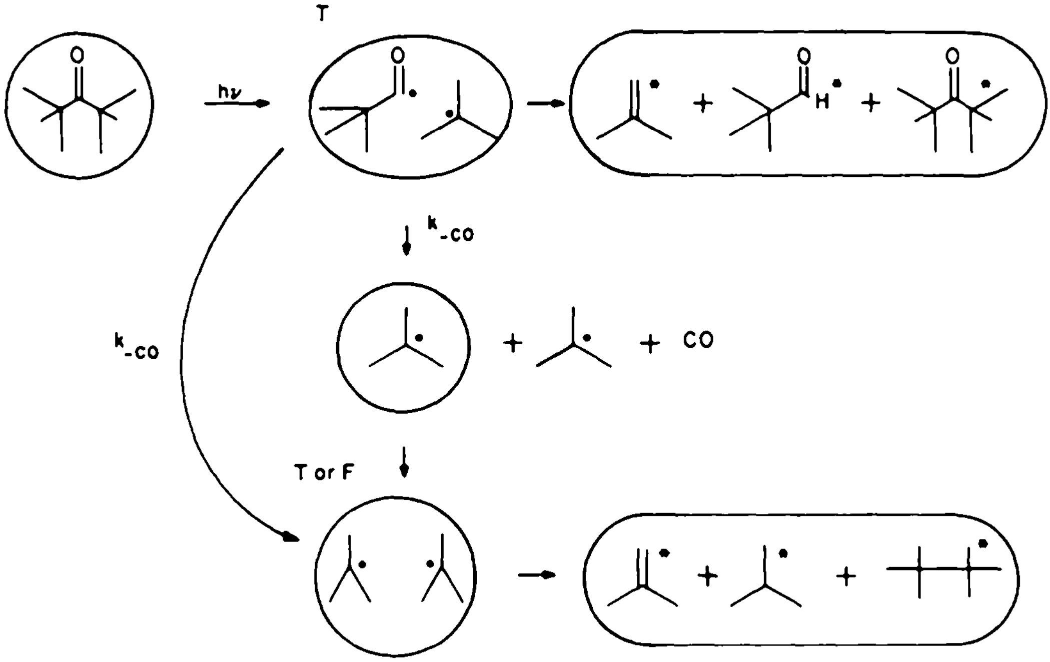


Fig. 6. Steady state CIDNP spectra during the photolysis of di-t-butyl ketone in (a) homogeneous C_6D_6 solution and (b) HDTCl micellar solution.



Scheme 6.

the loss of CO by pivaloyl. This is schematically represented in Scheme 6.

By adding an aqueous phase free radical scavenger such as Cu^{2+}, we may observe changes in the CIDNP spectrum due to the exchange of radicals out of the micelle. Figure 7 shows the changes in the high field region of the CIDNP spectrum as $CuCl_2$ in added to the system. The disappearance of the multiplet polarization due to isobutane and the residual net polarization of 2,2,3,3-tetramethylbutane is complete with the addition of only 0.5 equivalents of Cu^{2+}. Most importantly, the intensity of the net polarization in the methyl groups of isobutene is unaffected by the added Cu^{2+}.

Since S–T_0 mixing and secondary recombination are expected to be effective up to approximately 100 ns[6] and the lifetime of the pivaloyl radical at 31°C is ~6 μs, we

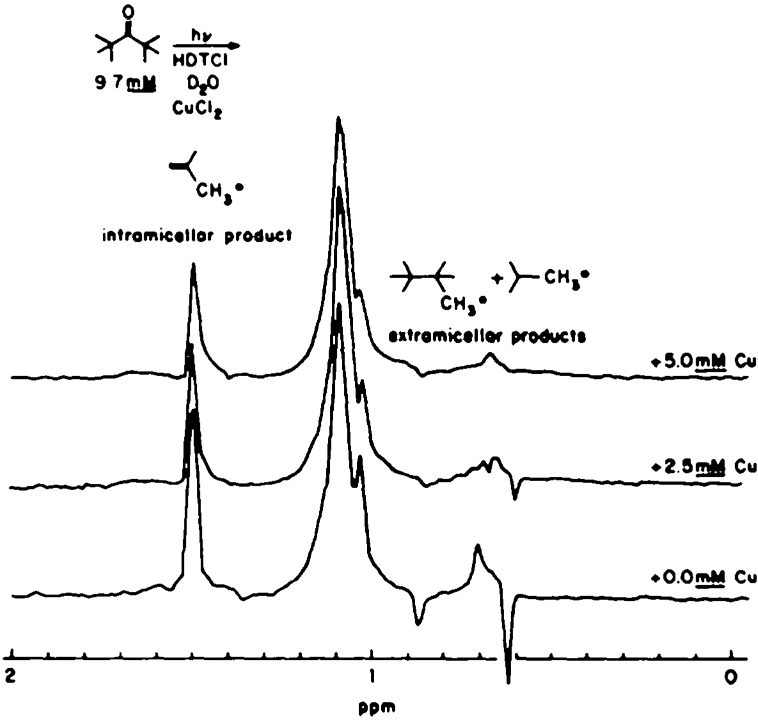


Fig. 7. Steady state CIDNP spectra during the photolysis of di-t-butyl ketone in the high field region in HDTCl micellar solution in the presence of $CuCl_2$.

can estimate the exit rate constant for a pivaloyl/t-Bu radical at 10^6–10^7 sec^{-1}. This is clearly in line with the measured exit rates of small fluorescent probe molecules from similar micelles.[5]

Demonstration of the cage effects on radical pair reactions of micellization. Perhaps the largest effect noted to date of micelles on the photoreactions of ketones is the tremendous increase in the yield of cage products of triplet radical pairs.[3] In homogeneous solution, the cage reaction of triplet born pairs is a very minor contribution to the overall product yields. When the radical pair is generated exclusively in the triplet state, the quantum yield for formation of free radicals is ususally found to be very close to 1.[21]

An example of this effect is the yields of diphenylethanes from the photolysis of benzyl-p-toluylmethyl ketone in homogeneous and micellar solution.[3] When this reaction is conducted in benzene or aqueous solution, the recovered diphenylethanes represent the statistically expected 1:2:1 mixture. When the photolysis is conducted in micellar solution, however, the yields of the symmetrical products drop substantially, indicating that the micelle-water interface restricts diffusion substantially and forces the fragments to react with one another.

A similar observation is found when the CIDNP spectra are obtained during this reaction.[22] Photolysis of benzyl-*p*-toluyl methyl ketone in cyclohexane-d_{12} results in the observed CIDNP spectrum shown in Fig. 8a. Only the single assymetric ketone is polarized showing by the relative magnitude of the two methylenes that α-

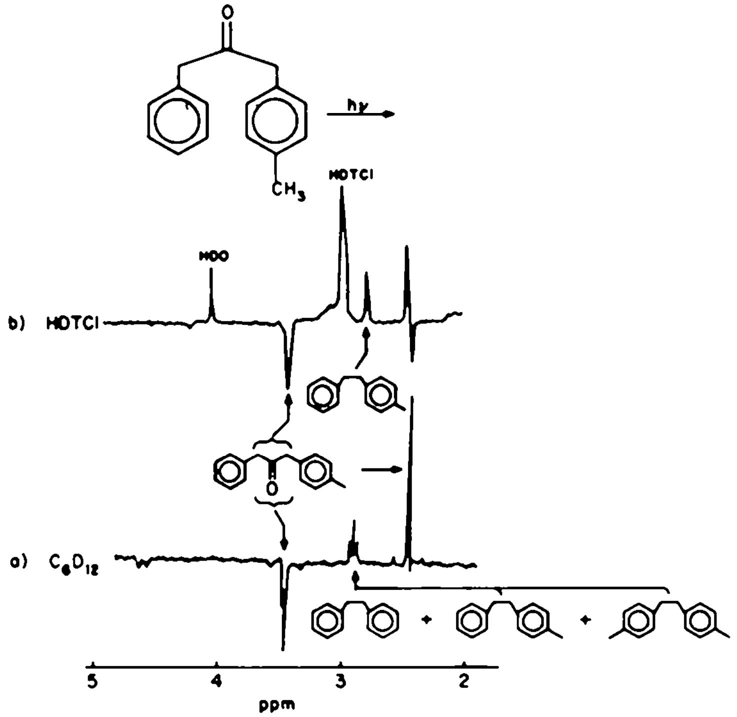
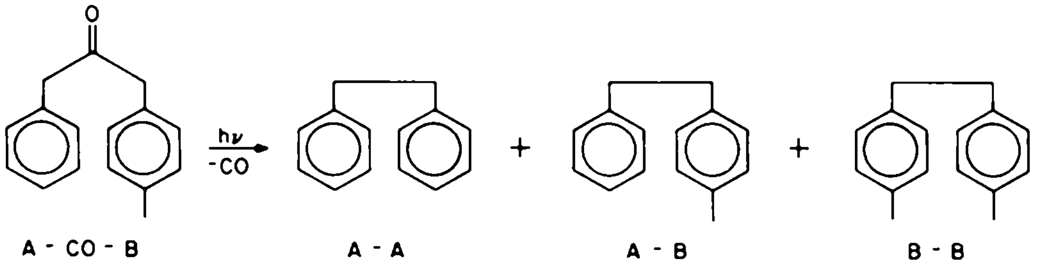


Fig. 8. Steady state CIDNP spectra during the photolysis of benzyl-p-tolyl-methyl ketone in (a) homogeneous C_6D_{12} solution and (b) HDTCl micellar solution.



		relative yields	
homogeneous solution	25%	50%	25%
micellar solution	< 1%	98%	< 1%

cleavage is preferred on the side of the *p*-methylbenzyl radical. The polarization of the methylene groups of the three diphenyl ethanes, however, appear to represent the statistical 1 : 2 : 1 ratio expected on the basis of the product yields. When the CIDNP spectrum is obtained during the photolysis is micellar solution (Fig. 8b) the same pattern of emission is observed for the present ketone, but in this case only the single asymmetric diphenyl ethane is observed with absorptive polarization. CIDNP, therefore, compliments the product yield results[3] for this photoreaction.

EXPERIMENTAL

CIDNP spectra were obtained on a Bruker WP-80 FT Spectrometer without modification. Solns in 5 mm NMR tubes were photolyzed by means of a supersil quartz light guide extended vertically down the NMR tube on which was focused the output of a 1 kw Hg/Xe high pressure lamp.[24] Excessive heating of the sample was avoided by filtering the light through 8 cm of aqueous $NiSO_4$ Soln.[25] UV wavelengths in the region $265\,nm < \lambda < 390\,nm$ were selected with a Corning 7-54 bandpass filter.

Steady state CIDNP spectra were obtained by pulsing (pulse angle = 30°) as rapidly as possible for approximately 60 sec after the light was admitted to the probe (acquisition time = 1.02 sec, number of scans = 60). Generally, the product NMR spectrum after the light was turned off indicated that 50–70% of the ketones were consumed.

Quantitative saturation recovery CIDNP spectra were obtained by the method of Barbara and Lawler.[10] Saturation of the entire proton NMR spectrum (generally not more than 7 ppm full width) could be accomplished with the unmodified homonuclear broad band decoupler in about 1 sec at full power. The decoupler was then gated off and a 30° RF pulse applied after waiting a delay time τ_d. After acquisition of the FID, the decoupler is again turned on and the cycle repeated. Thus, with the decoupler gated on for 1.0 sec, a delay $\tau_d = 1.0$ second and an acquisition time of 1.02 sec, a FID of 20 scans can be collected in approximately 60 secs.

Acknowledgements—The authors thank the National Science Foundation and the Air Force Office of Scientific Research for their generous support of this research.

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