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The Cage Effect in the Photolysis of (*S*)-(+)-α-Methyldeoxybenzoin: Can Triplet Radical Pairs Undergo Geminate Recombination in Nonviscous Homogeneous Solution?

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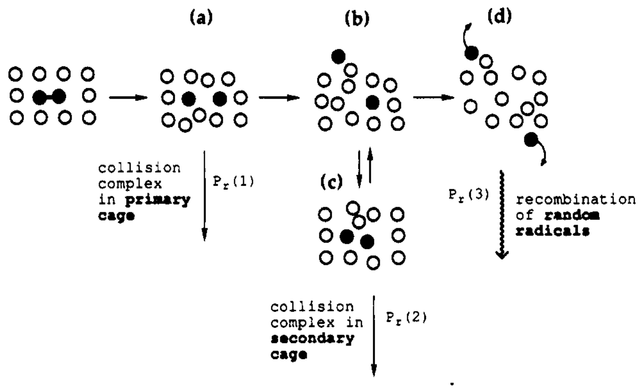
The photolysis of (*S*)-(+)-α-methyldeoxybenzoin ((*S*)-(+)-MDB) in benzene at room temperature causes a small decrease in enantiomeric purity of the starting ketone recovered after photolysis. The photoracemization of (*S*)-(+)-MDB, measured by circular dichroism (CD), can be related to the geminate recombination probability, P_r, of benzoyl/*sec*-phenethyl triplet radical pairs (RP) formed during photolysis. The probability, P_r, is determined from chemical yields of the products only; is is not a quantum yield and does not require the measurement of photon intensity. The experimental value of P_r is found to be ca. 0.04. The racemization of (*S*)-(+)-MDB remaining in a partially converted sample can be completely suppressed by the addition of relatively low concentrations of radical scavengers such as dodecanethiol and a stable nitroxide radical (TEMPO). Since, at low concentrations employed, the scavengers effectively eliminate only free radicals, the absence of products of recombination of triplet benzoyl/*sec*-phenethyl RP under conditions of complete scavenging is consistent with the absence of geminate cage recombination of this RP. The observed value of ca. 0.04 for P_r in the absence of scavenger results from the combination of radicals which have made diffusive excursions out of the primary solvent cage, i.e., random radical pairs. This conclusion is supported by CIDNP data, since the ^{1}H polarization of starting ketone and the geminate recombination product, along with polarizations of benzaldehyde and styrene and the products of the reaction of disproportionation of benzoyl/*sec*-phenethyl RP, are all completely eliminated by the addition of dodecanethiol.

Introduction. Radical Pair Concepts

When a pair of potentially reactive radicals encounter for a finite period of time, the solvent molecules serve as a "cage" which causes collisions between the radicals in the pair to occur in "sets"; i.e., the partners of the radical pair undergo more than one collision in a solvent cage per encounter.[1,2]

When a molecule is dissociated into two radicals in the liquid phase, in the absence of radical scavengers, the reactive fragments of an initial pair will eventually undergo recombination reactions (for simplicity we include combination and disporportionation reactions under the term recombination) in competition with diffusive displacements which result in reencounters or the formation of free radicals. Eventually, "recombination reactions" may be classified as those occurring between partners that were born together (geminate recombination) or between radicals produced from different dissociation events (random combination).

Scheme I



According to the Noyes model,[2] a radical pair (RP) produced by bond dissociation of a molecule may undergo recombination reactions in one of three conceptually distinct ways (Scheme I) which differ in time, space, and atomic radical pair compositional correlation: (1) recombination of geminate pairs may occur in the primary cage in which they are created with a probability $P_r(1)$; (2) recombination of geminate pairs may occur in a secondary cage formed after short diffusive excursions with a probability $P_r(2)$; or (3) combination of random pairs may occur in secondary cages which form after extensive diffusive excursions resulting in the statistical or random positioning of the pair in the liquid with a probability $P_r(3)$. In the last case, encounters lead to combination in cages containing random pairs, i.e., cages containing radical partners which were generated from separate molecular dissociations. The primary recombination and cluster of secondary geminate recombinations of the original partners are usually termed "geminate cage" or more simply "cage" recombinations, and the random combinations are termed random or free-radical cage combinations.

From this paradigm P_r is a theoretical parameter connecting the radical pair model to experimental observations of recombination at each of the three stages: $P_r(1)$ = the fraction of geminate pairs which undergoes recombination in a primary cage; $P_r(2)$ = the fraction of geminate pairs which undergoes recombination in a secondary cage; and $P_r(3)$ = the fraction of random pairs which undergoes free-radical combination. Naturally, $P_r = P_r(1) + P_r(2) + P_r(3)$. The "cage effect" may now be defined as the sum of the fraction of primary and secondary geminate pairs which undergo geminate cage recombination $[P_r(1) + P_r(2)]$. In principle, mathematical models can be devised and the individual values of $P_r(i)$ can be computed and compared with the experimental values of P_r. It is important to note that P_r is not a quantum yield. The value of P_r (see eq 2 below) is determined by the measurement of

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[†] Columbia University.

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chemical yields only; thus, the measurement of P_r can be measured with good precision and does not require any actinometry.

The RP paradigm is important for an understanding of chemically induced magnetic polarization (CIDNP), magnetic isotope effects, and magnetic field effects.[3] The radical-pair paradigm was combined with the magnetic resonance paradigm by Closs,[3a–c] Kaptein, and Oosterhoff.[3d,e] This paradigm assumes that caged triplet RPs are unreactive toward recombination, whereas caged singlet RPs are extremely reactive toward recombination reactions and connect the time scales of intersystem crossing of magnetic pairs to the time scales of RP diffusional dynamics. Employing conventional values for diffusional displacements in a nonviscous solvent such as benzene, Noyes[2] suggested that the time scale of dissociation of the primary cage is ca. 10^{-11} s (time for two radicals originally in contact to separate ca. 5 Å, the size of a benzene molecule) and that secondary cages, formed by reencounters of a geminate pair, may last for up to 10^{-9} s (time for two radicals to have diffused to statistical separations). An important issue which merits experimental analysis is the validity of these estimates and whether the differentiation of the predicted three stages of recombination can be distinguished experimentally.[4]

The range of random excursions of a radical pair may be estimated from the equation for a three-dimensional random walk (eq 1), where D is a coefficient of self-diffusion of a radical; in nonviscous organic solvents such as benzene $D \approx 10^{-5}$ cm^2 s^{-1}. For a value of intersystem crossing time for a RP $\tau_{\mathrm{ISC}} = 10$ ns (which is considered typical for a geminate pair of carbon centered radicals), one can estimate the average separation of RP, according to eq 1, to reencounter in the singlet state to be of the order of 55 Å. Referring to Scheme I, it is evident that the larger the distance between radicals of RP at the solvent separation stage (b), the smaller the probability they will reencounter as a geminate pair [stage (c)] and the higher the probability that the individual fragments of the pair will encounter a radical from an uncorrelated dissociation.

$$\langle r^2 \rangle = 6D\tau \qquad (1)$$

CIDNP is commonly observed in the products of type I cleavage of triplet ketones.[5] Such results place constraints on the efficiency of geminate cage recombination. The observation of CIDNP requires that a finite fraction of the primary geminate triplet RP eventually undergoes hyperfine induced intersystem crossing (ISC) after diffusional excursions outside of the primary solvent cage. Since the rate of hyperfine induced ISC for RP from typical ketones investigated can be estimated to be ca. 10^8 s^{-1} according to the RP paradigm and the estimates of the Noyes model for the lifetime of geminate pairs in a nonviscous solvent, the efficiency of *secondary* geminate cage reaction should be of the order of several % (approximate ratio of the "lifetime" of secondary geminate pairs, ca. 10^{-10} s, to the "lifetime" of ISC, ca. 10^{-8} s). On the other hand, the efficiency of *primary* geminate cage recombination should be of the order of 1% or less (approximate ratio of the "lifetime" of primary geminate pairs, 10^{-11} s, to the "lifetime" of ISC, ca. 10^{-8} s).

The paradigm of molecular photochemistry relates the rate of ISC of triplet RPs produced by α-cleavage and rates of the three stages of pair recombination (primary geminate pairs, secondary geminate pairs, and random pairs) to the relative reaction probabilities in the presence and absence of scavengers. For example, if the rate constant for scavenging of the most reactive of the radicals of the pair is ca. 10^9 M^{-1} s^{-1}, then for concentrations of scavenger of ca. 0.01–0.1 M (effective initial scavenging rate ca. 10^7–10^8 s^{-1}), only combination products of random pairs should be removed from the reaction products, but geminate (both primary and secondary) cage recombination would be unaffected by the scavenger (unless the geminate pair lifetime is considerably longer than that expected from the Noyes model).[4]

From these orders of magnitude estimations, it seemed to us that the reported efficiency of cage recombination of 33% from the photolysis of (S)-(+)-α-methyldeoxybenzoin ((S)-(+)-2-phenylpropiophenone in the original paper)[6] was higher than expected. The experimental basis for this conclusion was the measurement of the racemization of optically active (S)-(+)-α-methyldeoxybenzoin in the presence of radical scavengers. It was reported[6] that 33% of the racemization could not be interrupted by a thiol scavenger, and the cage effect was computed from these data.[6] These results suggest that 33% of the primary geminate triplet pair produced by type I cleavage undergo cage recombination. That a significant primary cage effect could occur was consistent with the general observation that the quantum yields for disappearance of ketones which react exclusively by type I cleavage are rarely equal to unity.[7] A significant primary cage effect is conceivable if a significant fraction of the α-cleavage occurs from the singlet state of the aryl ketone or if a spin-orbit induced ISC of the order of ca. 10^{10}–10^{11} s^{-1} occurred for the primary triplet RP. However, the occurrence of significant α-cleavage from the singlet state of an aryl alkyl ketone is unprecedented to our knowledge and for α-methyldeoxybenzoin, in particular, is in contradiction to the quenching[7] and CIDNP[8,9] literature data.

Although the idea that a significant fraction of triplet geminate radical pairs undergo recombination has been widely accepted[10a] during the 1970's, more recent knowledge of the HFI constants of individual radicals enables one to calculate the rates of ISC of RPs.[10b] However, for carbon-centered radicals, ISC rates of the order of ca. 10^{10}–10^{11} s^{-1} would be unprecedented. Furthermore, ISC rates of the order of 10^{10}–10^{11} s^{-1} would be expected to quench CIDNP effectively. Thus, when viewed from the new knowledge gathered over the past decades, the observation of a primary cage effect of 33% from a triplet pair would require at least a quantitative and possibly a qualitative modification of current paradigms. As a result, we decided to reinvestigate the photoracemization of optically active (S)-(+)-α-methyldeoxybenzoin with different scavenging and analytical methods for determining the extent of racemization and to determine whether any un-

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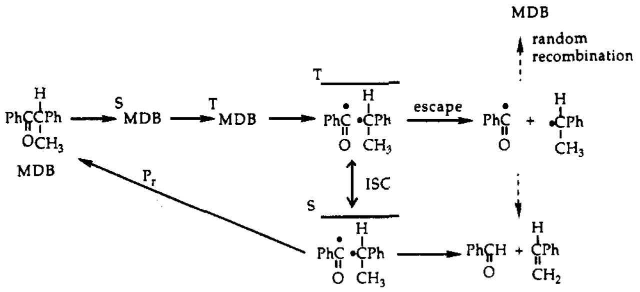
Scheme II



anticipated complications might require a reexamination of the computed primary cage effect by the methods reported earlier.

Experimental Section

Methyldeoxybenzoin (MDB) was prepared by methylation of deoxybenzoin (Aldrich).[11] (*S*)-(+)-α-Methyldeoxybenzoin [(*S*)-(+)-MDB] was prepared as in the literature.[12] 1-Dodecanethiol (Aldrich) was used as received, and TEMPO, 2,2,6,6-tetramethylpiperidinoxyl (Aldrich), was sublimed under reduced pressure. Benzene (Aldrich, spectrophotometric grade) was used as received. The concentration of (*S*)-(+)-MDB used for photolysis was 4.8×10^{-3} M. The solution was bubbled with Ar before photolysis. Photolysis of (*S*)-(+)-MDB was carried out in a Rayonet photochemical reactor (350-nm excitation); several experiments were performed with 300-nm excitation. The results were experimentally indistinguishable.

The conversion of MDB after photolysis was measured by a Hewlett-Packard 5890 capillary GC interfaced to a Hewlett-Packard 3392 electronic integrator on a 25-m HP-1 column with hexadecane as an internal standard.

Several chiral HPLC columns were employed in an attempt to separate the enantiomers of MDB, but none provided the resolution necessary for quantitative analysis. As a result, the stereochemistry of unconverted substrate was determined by the optical activity of the partially converted samples. The CD spectra of (*S*)-(+)-MDB were recorded on a JASCO J-500 A CD spectrometer without the isolation of ketone from the reaction mixture. The shape of the CD spectra did not change during the course of photolysis.

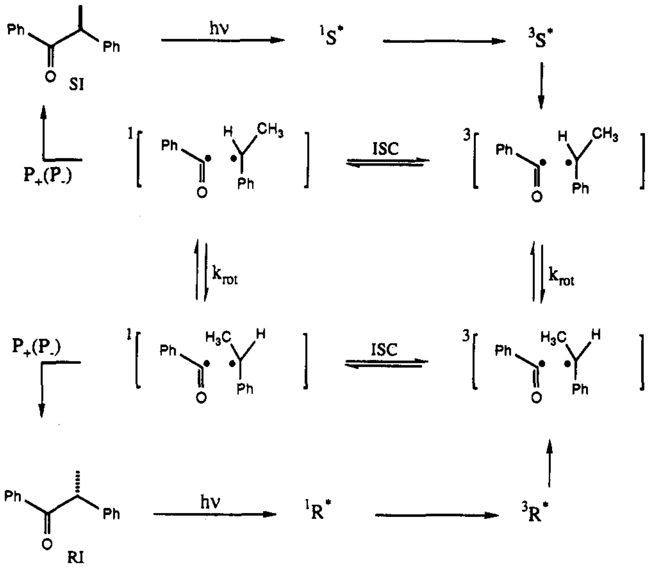
Experiments were performed isolating the unconverted starting material and measuring the CD and computing P_r. The values obtained were experimentally indistinguishable from those obtained from measurement of the CD without isolation, but the accuracy of the data was better. The reason for the better accuracy is due to the requirement in quantitative CD measurements to prepare accurately a solution of known concentration of the isolated ketone, which is extremely difficult considering the small amount of sample available after isolation. By measuring the CD without isolation the accuracy is high, since it is only required that the conversion be measured accurately, which is readily done with internal standards in GC measurements.

The CIDNP spectra were obtained on a Bruker WM-250 NMR spectrometer. Samples were irradiated with a Hanovia 1-kW Xe–Hg high-pressure lamp through an aqueous filter and quartz optical pipe.

Results

The initial chemical act in the photolysis of MDB (Scheme II) is the dissociation of the C–CO bond of the triplet excited state of the molecule to form ^{3}RP consisting of benzoyl and *sec*-phenethyl radicals.[7] The primary geminate ^{3}RP can separate to yield free radicals or can separate, and after completion of ISC, can reencounter and regenerate the starting molecule or can disproportionate to form benzaldehyde and styrene[7] (see Scheme II). We seek to determine experimentally the probability of geminate recombination resulting from the photolysis of (*S*)-(+)-MDB. It has been shown that this probability can be determined from measurement of the extent of stereoisomerization of (*S*)-(+)-MDB as a function of conversion.[13]

Scheme III



The photoracemization of an optically active ketone[6,13] such as (*S*)-(+)-MDB (see Scheme III) can be described by eq 2[13], where Z and Z_0 are the optical purity of the

$$\log (Z/Z_0) = \beta \log (1 - f) \qquad (2)$$

ketone after and before the photolysis, f is the conversion of the starting ketone, and β is the efficiency of photoracemization and is directly related to P_r (vide infra). The ratio Z/Z_0 is readily determined by measurement of the circular dichroism (CD) spectra of the samples without isolation of the ketone. Since the concentration of MDB decreases during the photolysis, eq 2 may be transformed to eq 3, where A_0 and A are the intensities of CD spectra at a given wavelength (usually 320 nm) before and after the photolysis, respectively, for the conversion f. The

$$\log (A/A_0) = (\beta + 1) \log (1 - f) \qquad (3)$$

probability of recombination P_r of RP, which is determined only by the properties of the RP and of the environment, and not to the efficiency of production of the pair (i.e., P_r is not a quantum efficiency), is related to the experimentally measurable efficiency of racemization, β, of the starting ketone by eq 4.[13] Equation 4 is valid under

$$P_r = \beta/(1 + \beta) \qquad (4)$$

conditions where the probabilities of the recombination of RP without P^+ and with P^- inversion of the ketone's initial configuration are equal (Scheme III). This assumption requires that the radicals are randomly oriented at the time of recombination. Under these assumptions, $P_r = P^+ + P^-$. Since the rotational correlation time of the *sec*-phenethyl radical in benzene at 20°, τ_r, is 12 ps (using ethylbenzene as a model[14]), and τ_{ISC} of ^{3}RP under consideration is calculated[10b] to be about 3–5 ns, the utilization of eq 4 for the determination of P_r is clearly justified.[13]

Figure 1 shows the data for photoracemization of (*S*)-(+)-MDB in benzene plotted in terms of eq 3. From the

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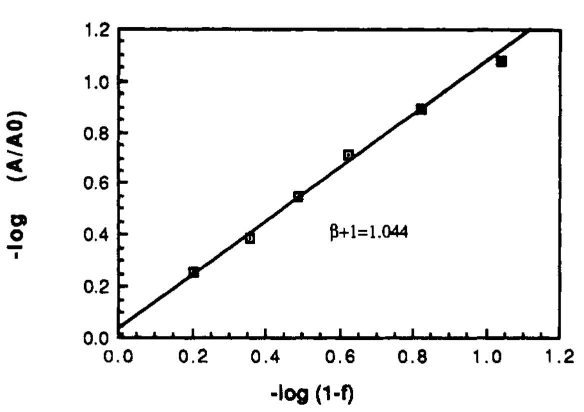

Figure 1. Photoracemization of *MDB in benzene versus conversion in the variables of eq 2.

slope of the graph, $\beta + 1 = 1.044 \pm 0.027$ and $P_r = 0.042 \pm 0.026$. Thus, within our experimental error, the true value of P_r may be as small as 2% or as large as 7%. If *all* of the combination were due to geminate pairs, the former value is within the range expected from the estimations made in the introduction, and the latter would appear to be bordering on the high side of the estimated value.

To determine the contribution of geminate radicals after long diffusional walks as well as free-radical recombination to P_r values, scavenging experiments were performed. Two scavengers were used: 1-dodecanethiol (RSH) and TEMPO. On the basis of the yield of benzaldehyde, a concentration of 0.03 M RSH has been found to be sufficient for complete scavenging of all benzoyl radicals.[6] The chemical yield of benzaldehyde increased from about 6% without to 42% with 0.03 M RSH. Consistent with an earlier report[6] we did not observe any quenching of the conversion of (*S*)-(+)-MDB during the photolysis by RSH up to the highest concentration of the scavenger employed. In contrast, TEMPO reduces the rate of (*S*)-(+)-MDB photolysis, presumably as the result of triplet quenching. However, the occurrence of triplet quenching of (*S*)-(+)-MDB does not interfere with the treatment of the experimental data according to eqs 2 and 3, since the probability of geminate pair reaction is assumed to be independent of the actual efficiency of geminate pair formation. For (*S*)-(+)-MDB, photolysis in benzene with 0.014 M TEMPO and the formation of *d,l*- and *meso*-diphenylbutanes is completely suppressed (GC analysis), while their chemical yield without scavenger is about 20%. Therefore, we consider a 0.014 M concentration of TEMPO to be sufficient for complete scavenging of free *sec*-phenethyl radicals.

In Figure 2 the data for photoracemization of (*S*)-(+)-MDB photolysis in benzene with RSH (0.03 M) and TEMPO (0.014 M) are plotted in terms of eq 3. Both sets of experimental data can be fit by one line with the slope $\beta + 1 = 0.955 \pm 0.025$. The excellent fit of photoracemization of (*S*)-(+)-MDB with two different scavengers (moreover, RSH scavenges preferentially benzoyl, and TEMPO scavenges preferentially benzyl radicals) demonstrate that under these conditions photoracemization reflects only recombination of the radicals from primary cage and from short diffusional walks, while all free radicals are completely scavenged. We suspect that the slightly negative value of β (a decrease in the degree of optical rotation with photolysis is less than the rate of disappearance of the starting optically active ketone) is probably associated with some minor unidentified chemical reaction of (*S*)-(+)-MDB which induces a slight degree of optical activity in the system. For example, it is known that 1,2-dibenzoyl-1-phenylethane is one of the minor products of MDB photolysis (chemical yield depends on conditions but is less than 1%).[13] When formed from (*S*)-(+)-MDB this product should be enantiomerically pure as well and should have UV absorption in the same range as MDB. Therefore, although the starting molecule disappears during photolysis along this pathway, an enantiomeric excess of the minor by product may be created.

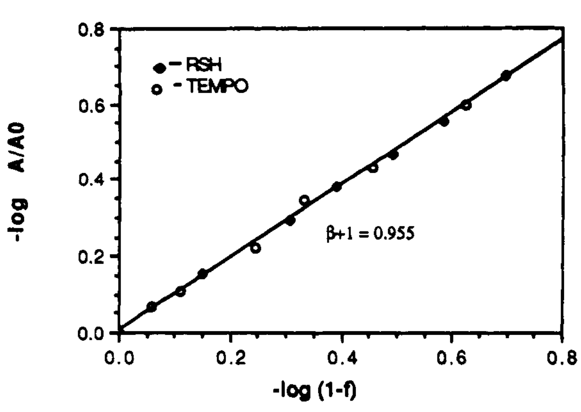

Figure 2. Photoracemization of *MDB in benzene with radical scavengers, dodecanethiol (RSH), and TEMPO versus conversion in the variables of eq 2.

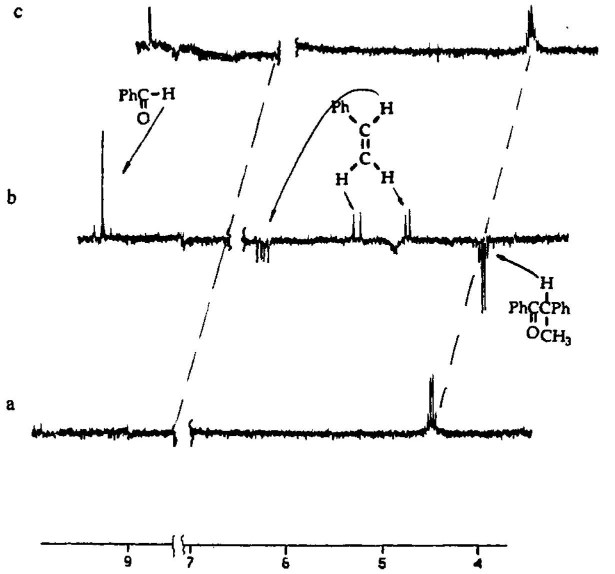

Figure 3. ^{1}H CIDNP spectra under photolysis of MDB in benzene-d_6: (a) dark spectra, (b) spectra during the photolysis, (c) spectra during the photolysis with dodecanethiol. Spectral b and c are shifted relative to a and to each other.

Figure 3 shows the ^{1}H CIDNP spectra resulting from the photolysis of MDB in benzene-d_6. The "light" spectrum (Figure 3b) shows the polarization of the recombination product of RP, starting ketone, and the products of the reaction of disproportionation, benzaldehyde and styrene. The ^{1}H CIDNP spectrum of MDB is consistent with Kaptein's rules[15] for a primary photochemical process of α-scission of ^{3}MDB to yield a primary RP of benzoyl and *sec*-phenethyl radicals.[8,9] The sign of polarization of geminate (or triplet random recombination) and escape products[9] are consistent with expectations.[7,16] The quartet centered at 4.47 ppm is assigned to the methine proton, and a doublet at 1.65 ppm (not shown) is assigned to the methyl protons of the starting ketone. The two doublets

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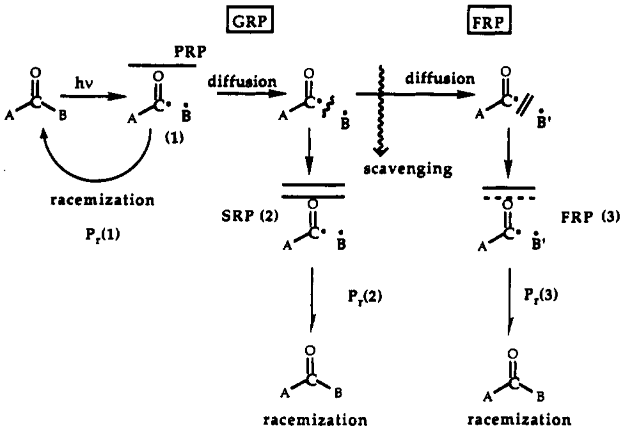
Scheme IV



$$P_r = P_r(1) + P_r(2) + P_r(3)$$

at 4.79 and 5.24 ppm are assigned to two methylene protons of styrene, and the doublet of doublets at 6.7–6.9 ppm belongs to the methine proton of styrene. The singlet at 9.82 ppm is assigned to the aldehydic proton of benzyldehyde. The addition of RSH to MDB solution in the concentration 0.03 M completely eliminates the polarization of the starting ketone and the products (Figure 3c). The small peak of observed benzaldehyde is assigned to the steady-state concentration of benzaldehyde, which is formed with high yield under the thiol scavenging conditions. The addition of TEMPO to the MDB solution in the concentration of 0.02 M induces small broadening of all peaks; however, the addition of TEMPO at this concentration completely eliminates the polarization of all the products.

Discussion

The experimental results obtained in this paper will be interpreted in terms of the general paradigm for the behavior of a dynamic radical pair (RP) formed in the photolysis of an optically active ketone in solution as shown in Scheme IV. When B is a chiral radical (the *sec*-phenethyl radical in the case of (*S*)-(+)-MDB), the paradigm suggests that since, in general, a triplet geminate radical pair (GRP) recombines much more slowly than rotational relaxation of B, the probability of selective retention of stereochemistry after formation of the pair should be small, the order of a few percent at best. The total probability of recombination, P_r, derived from the photoracemization of the starting ketone in the absence of scavengers is equal to the sum of the three recombination steps (Scheme IV) $P_r(1)$, $P_r(2)$, and $P_r(3)$, respectively. We now inquire as to how our results can be employed to decide whether the three stages of combination reaction can be separated, and, if so, if the magnitude of the individual probabilities can be determined from experimental data.

The problem of separating the two stages of geminate combination reactions and the random combination reactions has been treated theoretically by Noyes,[2] but attempts to sort out these stages by product analysis and scavenging have not been successful in distinguishing the various stages.[4,10c]

In principle, CIDNP can determine the extent of secondary geminate and random combination reactions (it is assumed that the technique is silent on the primary combination because the time scale of this process is too fast to build up nuclear polarization), since the observed nuclear polarization is sensitive to the sorting of reactions of the initial pair into geminate cage reactions and escape reactions to form free radicals. However, in the steady-state ^{1}H CIDNP spectrum of MDB (Figure 3b), the assignment of geminate and random reactions based on the sign of the polarization is ambiguous, since both triplet geminate pair (GRP) recombination and recombination due to random encounters of free radicals (FRP) are predicted to lead to emissive polarization.[15]

Perhaps the most elegant way to sort out the contribution from secondary geminate pair and random pair recombination is through time-resolved CIDNP.[17–21] Closs and Miller[17a] employed time-resolved ^{1}H CIDNP in the microsecond time domain and the scavenging technique by employing thiols as scavengers in the photolysis of deoxybenzoin in benzene in a time resolved CIDNP experiment. They found that, at the earliest time of observation, an emissive polarization of the CH_2 group of the starting ketone was observed and that this emission grew in with time up to about 100 μs. Addition of dodecanethiol (5×10^{-3} M) as a free-radical (benzoyl-radical) scavenger suppressed the growth of emission and was unable to suppress the early time emission. From these results it was concluded that the early time polarization was due to geminate recombination on the submicrosecond time scale and that the grow in between 1 and 100 μs was due to random recombination.

In the steady-state ^{1}H CIDNP experiments reported here (Figure 3), the observed polarization of the starting ketone is *completely quenched* with the addition of 0.03 M of thiol or TEMPO scavenger. In the case of TEMPO, although quenching of CIDNP is observed, the interpretation of the mechanism of quenching is ambiguous, since both fast electron relaxation due to spin exchange with stable radicals or paramagnetic nuclear relaxation in the presence of TEMPO and free-radical scavenging may eliminate any CIDNP produced in the photolysis. In the case of thiol as scavenger, the result appears to be straightforward, in that no mechanisms other than chemical scavenging of benzoyl radicals is likely for the quenching of the CIDNP. It should be noted that in the time-resolved experiments some residual polarization of regenerated deoxybenzoin remained in the presence of thiol scavenger. We note, however, that the the concentration of RSH used in the time-resolved experiments with deoxybenzoin[17a] was 5 mM, which is six times lower than the value employed in our experiments. Since the fastest rate constant for scavenging of the benzoyl radical by a thiol is 10^9 M^{-1} s^{-1} (in reality we expect it to be about an order or two less than this value), the *minimum* lifetime of the scavenged radicals is of the order of 10^{-7}–10^{-8} s. From these experiments we conclude that there is no measurable extent of geminate recombination.

This conclusion is supported by P_r data. The recombination probability of benzoyl/*sec*-phenethyl RP formed under photolysis of (*S*)-(+)-MDB in benzene in the absence of scavenger, $P_r \approx 0.04$, means that only about 4% of the originally formed triplet RP recombine to starting molecule

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by geminate or random recombination (Scheme IV). The reason for such a low probability of geminate recombination in the rapid dissolution of the primary cage and in the nature of three-dimensional unrestricted diffusion in nonviscous liquids:[2,22] the probability of the secondary encounter of RP decreases with a time t as $t^{-3/2}$.

During the time required for ISC the radicals comprising triplet RP diffuse far apart, and being reactive radicals, they are readily scavenged during these long diffusive excursions. These factors result in a small value of P_r. By the addition of the scavenger it is possible to increase systematically the termination of diffusive walks of the geminate radicals. Scavengers interfere with radical recombination; the higher the scavenger concentration, the shorter the diffusional walk intercepted by the scavenger. From this point of view the effective cage size as a *dynamic* parameter depends on the concentration of the scavenger. Therefore, the value of P_r and the yields of geminate cage products depend on the scavenger concentration. Experimentally, this process can be followed, for example, by an increase of the chemical yield of benzaldehyde, the product of hydrogen donation from RSH with an increase of RSH concentration under photolysis of MDB in benzene.[6] If all the free benzoyl radicals are scavenged, the total combination probability of free radical to form MDB becomes 0. Since this value was measured in the photoracemization experiment of (S)-(+)-MDB in the presence of scavengers, we conclude that $P_r(1) + P_r(2) = 0$ (Scheme IV). Thus, for triplet RPs, probabilities of both primary and secondary geminate recombination in nonviscous solvent are equal to 0, within the experimental error. Evidentally, the participation of geminate recombination inferred from the time-resolved experiments[17a] is too small to resolve by chemical scavenging. The measured value of P_r of ca. 4%, we conclude, is due to random pair combination, so that $P_r = P_r(3)$, within the experimental error.

There are means of enhancing the probability of triplet geminate pair recombination. According to the dynamic radical pair paradigm, the value of P_r of triplet RP can be increased by decreasing the rate of diffusion by increasing the viscosity of the solvent (decreasing D, as one could expect from eq 1) or changing the nature of the diffusion of RP, i.e., imposing spatial restriction to long diffusional walks on the GRP as happens when they are dissolved in a micelle. We are unaware of data on direct measurements of P_r of RPs in viscous solvents, but indirect data are available. The efficiency of $^{13}C/^{12}C$ isotope selection, α, induced by magnetic isotope effect (MIE) under the photolysis of dibenzyl ketone increases with the increase in the viscosity of the solvent.[23,24] The magnitude of α is determined by P_r of RP with ^{12}C and P_r of RP with ^{13}C, and the dependence of α versus viscosity has a maximum ca. 2400 cP.[24] For the recombination of the ketyl/phenoxyl RP formed during photoreduction of benzophenone in *p*-cresol/glycerol mixture, the value of the cage effect determined according to Noyes[2] from the kinetics of geminate recombination increases about three times with increasing the viscosity of the solvent (by changing the temperature) from 600 to 10^4 cP.[25]

Another means of enhancing the fraction of geminate combination reactions is to isolate spatially the GRP by adsorbing the ketone and the pair produced by photolysis in a micelle. The diffusion of RP within a micelle is restricted spatially by the micellar boundary, and the rate of radical escape from micelles is small enough (usually an order of 2×10^6 s^{-1} or less[21,26]) to compete with the ISC rate. Indeed, in micellar systems P_r may reach substantial values. For example, for the RP from (S)-(+)-MDB, $P_r = 0.51$ in SDS micelles[13] and $P_r = 0.48$ in CTACI micelles.[27]

Green[28] and Kopecky[29] employed stereoisomerization to investigate the geminate recombination reactions induced by the thermolysis of optically active compounds[30] involving *sec*-phenethyl radicals. A small degree (few %) of retention of stereochemistry was found in the coupling of *secondary* pairs (formed from loss of nitrogen from the primary pairs) in both studies. These results differ from those reported here in that the geminate pair precursors are produced in the singlet state and recombination occurs after loss of a nitrogen or carbon dioxide molecule, which may separate the pair in a manner similar to a solvent molecule. In contrast to the situation for a triplet GRP, the fraction of recombination in a primary cage for a singlet GRP may be an important factor in determining the extent of racemization.

One important conclusion from the results reported here is that the reason for the quantum yields of α-cleavage of some benzyl phenyl or phenyl alkyl ketones[6,7] is significantly less than unity is not likely to be due to fast cage recombination of primary or secondary triplet GRP, but rather to other radiationless processes. One possible reason has been suggested by Arnaut and Formosinho[31] in terms of a Salem diagram and is associated by a surface-avoided crossing[32] and a jump from the trajectory corresponding to the dissociation of $^3n\pi^*$ excited ketone directly to the S_0 state potential surface passing the state of RP formation. This mechanism is essentially a radiationless transition and does not require the formation of a RP and therefore should not result in any racemization of the starting ketone. Another possibility[33] is that some unusually effective spin–orbit coupling interaction causes triplet pairs to undergo rapid ISC. For example, a fraction of the triplets may undergo α-clevage to produce a linear acyl fragment, which due to its inherently stronger internal spin–orbit coupling and spin relaxation mechanisms, can undergo intersystem crossing at a rate that is not anticipated by the conventional paradigm. It is commonly stated in the photochemical literature that an observed rate of deactivation which is much faster than that for a model must be due to a chemical process because no "known" radiationless process is expected to proceed with such a rapid rate. However, it may be that the very chemistry that is absent in the model provides an interaction at a surface crossing which creates an opportunity for radiationless deactivation which is lacking in the model.

Conclusions

The recombination probability, P_r, of the triplet benzoyl/*sec*-phenethyl RP in benzene was measured by

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monitoring the photoracemization of (*S*)-(+)-MDB as a function of conversion. The small experimental value of $P_r \approx 0.04$ means that only about 4% of initially formed triplet RPs which go on to products eventually recombine by any mechanism to reform starting ketone. In order to estimate the contribution of geminate pairs and free pairs to P_r, the photolysis of (*S*)-(+)-MDB in benzene was carried out in the presence of radical scavengers. Photoracemization of the starting ketone is completely suppressed even at a modest concentration of dodecanethiol. This result shows that even the small observed value of $P_r \approx 0.04$, obtained under the absence of scavengers, corresponds to the recombination of RP which have undergone extensive diffusive walks, i.e., have become random radicals. We thus conclude that triplet geminate recombination is negligable in nonviscous homogeneous solution.

In support of this conclusion, the ^{1}H CIDNP of the starting ketone and other products of the triplet benzoyl/*sec*-phenethyl RP observed under photolysis of MDB in benzene is completely suppressed by the addition of modest concentrations of dodecanethiol. This means that all the nuclear spin selective recombination of the radicals is taking place after diffusive walks by FRP and that there is no geminate cage recombination of triplet GRP.

In contrast to the difficulty in distinguishing between the various stages of combination reactions in solution, such experimental discrimination has recently been reported for the restricted reaction space of a zeolite[34] and a micelle.[35]

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Registry No. (*S*)-(+)-MDB, 951-85-9; TEMPO, 2564-83-2; $CH_3(CH_2)_{11}SH$, 112-55-0; PhCHO, 100-52-7; PhCH=CH$_2$, 100-42-5.

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Kinetics and Mechanism of the Aminolysis of 4-Nitrophenyl Dithioacetate

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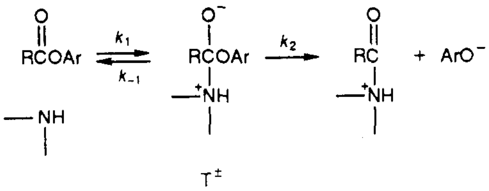
The reaction of the title substrate with a series of secondary alicylic amines has been the subject of a kinetic study in aqueous solution, 25 °C, ionic strength 0.2 M (KCl). With the amine in excess, pseudo-first-order rate constants (k_{obsd}) are observed. The order in amine varies from 1 to 2 depending on the basicity of the amine and the reaction conditions. A reaction scheme is deduced on the basis of the existence of zwitterionic ($T^{\pm}$) and anionic (T^-) tetrahedral intermediates. Proton transfer from $T^{\pm}$ to an amine or base (to yield T^-) seems to compete with 4-nitrothiophenoxide (NPS^-) expulsion from $T^{\pm}$. The pK_a of $T^{\pm}$ and all the rate microconstants of the scheme are estimated. The rates of expulsion of NPS^- and amine from $T^{\pm}$ are smaller than those from analogous $T^{\pm}$ formed in the aminolyses of *O*-ethyl *S*-(4-nitrophenyl) dithiocarbonate and 4-nitrophenyl thiolacetate. It is claimed that substitution of Me by RO (R = alkyl) or S^- by O^- in $T^{\pm}$ destablizes this intermediate.

Introduction

The mechanism of the aminolysis of reactive oxyesters is well established.[1] In the reactions of secondary and primary amines with substrates with good leaving groups the rate of expulsion of the nucleofuge (k_2 of eq 1) from the zwitterionic tetrahedral intermediate ($T^{\pm}$) found in most of these reactions is fast, precluding therefore the occurrence of acid–base catalysis involving $T^{\pm}$.[1,2]



(1)

A similar situation seems to prevail during the aminolysis of aryl thiolacetates (MeCOSAr): no base catalysis was found in the reactions of secondary alicyclic amines with phenyl,[3] 4-nitrophenyl,[3] 2,4-dinitrophenyl,[4] and 2,4,6-trinitrophenyl thiolacetates.[4] This was attributed to instability of $T^{\pm}$ due to the fast nucleofugality rate from this intermediate of the arenethiolate anion which prevents deprotonation of $T^{\pm}$ by a base to give an anionic intermediate.[3,4]

In contrast to the above findings, base catalysis by amine was observed in the reactions of secondary alicyclic amines with phenyl dithioacetate (eq 2).[5] This was explained by the relatively slow leaving of thiophenoxide anion from $T^{\pm}$ (small k_2) due to the weaker "push" exerted by S^- in $T^{\pm}$ (relative to O^- in the similar $T^{\pm}$ formed with phenyl thiolacetate), which increases the lifetime of the dithio intermediate and allows time for proton removal from $T^{\pm}$ by the amine to yield T^- (eq 2).[5]

As a continuation of our studies on the aminolysis of thioesters we now examine the reactions of secondary alicyclic amines with 4-nitrophenyl dithioacetate. It was of particular interest to compare the results from this study with those of phenyl dithioacetate[5] in order to investigate whether there is still base catalysis involving the presumably more unstable $T^{\pm}$ formed in the present reactions (due to an expected larger k_2).

It was also of interest to compare the present reactions with the aminolyses of 4-nitrophenyl thiolacetate[3] and

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