

How Spin Stereochemistry Severely Complicates the Formation of a Carbon–Carbon Bond between Two Reactive Radicals in a Supercage

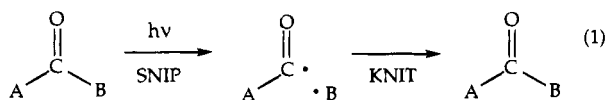
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Introduction to a Complication in Making Bonds between Reactive Carbon-Centered Radicals. Conservation of Angular Momentum Rears Its Ubiquitous Constraints

Equation 1 shows an example of two very simple chemical reactions: the photodissociation of a carbon–carbon bond (a snip process) to produce a reactive geminate radical pair and the re-formation of the same carbon–carbon bond (a knit process) from the geminate radical pair. For many photochemical reactions which appear to proceed through such an apparently snip and knit sequence, the mechanism of bond formation is actually remarkably complex. This Account shows how the structure and hyperdynamic kinetics of *supramolecular systems* provide an intellectually and experimentally exciting tableau for the investigation of the mechanism of formation of a carbon–carbon bond between two reactive carbon-centered free radicals which are contained by a supercage. We shall show that it is the involvement of *electron spin* in the bond-making process that causes the complications in carbon–carbon bond formation. These complications arise from the need to conserve *spin angular momentum* in any elementary chemical combination step involving the formation of a carbon–carbon bond from two reactive radicals.



This spin requirement allows the sorting of “reactive” radical pairs into two categories: (1) *extremely reactive singlet radical pairs*, for which there are no

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complications due to spin angular momentum in bond formation, and (2) *extremely “inert” triplet radical pairs*, for which the complications in bond formation are severe, especially in a supercage whose dimensions are of the order of tens of angstroms. This remarkable difference in reactivity between two otherwise chemically identical radical pairs results simply from the *stereochemistry or orientation* of the electron spins. We shall show that orbital overlap and electron exchange, an interaction that stabilizes carbon–carbon bonds, actually interfere with bond formation between two reactive carbon-centered radicals that are in the triplet state. We shall also show circumstances for which *collisions, which are essential in all bimolecular reactions, can actually decrease the probability of combination of two reactive carbon-centered radicals that are in the triplet state*. Because of these features, the “cage effect” between two radicals created in a triplet state in a nonviscous molecular liquid is essentially zero. However, a finite cage effect can be achieved if the triplet radical pair is embedded in a supercage (such as a micelle) that is capable of encouraging multiple reencounters of the pair. We shall present experimental support for a qualitative and a quantitative theoretical model for the mechanism of bond formation between two reactive radicals that are born together in a triplet state in a micellar supercage. The model correctly reproduces the observed dependence of the cage effect on the size of the micelle supercage and allows insight to the peculiar and nonintuitive complications of making carbon–carbon bonds from triplet pairs.

Paradigms for Understanding the Complications Imposed by Requirements To Conserve Angular Momentum. Photochemical Methods for Production of Triplet Geminate Radical Pairs

The paradigms of modern molecular photochemistry¹ teach us (Figure 1) that triplet radical pairs in liquids may be conveniently produced from photochemical excitation of ketones whose structure is appropriate for fast α -cleavage of the carbonyl α -carbon

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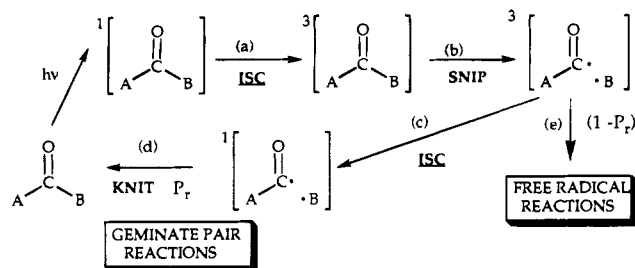


Figure 1. Paradigm for the α -cleavage reaction of ketones. See text for discussion.

bond. Photochemical excitation of the selected ketone (10^{-15} s) produces a singlet molecular state that rapidly (typically <1 ns) undergoes intersystem crossing (ISC) to produce a molecular triplet (step a), which then undergoes rapid α -cleavage (typically <1 ns), a "snip" process, to produce a *triplet, geminate* (i.e., "born together") *radical pair* (step b). This triplet, geminate radical pair generally has two options that eventuate in radical pair reactions. One option is step c (followed by d), a "knit" process. In the knit process, ISC is followed by *geminate radical pair recombinations* or *disproportionation* that lead to re-formation of the carbon-carbon bond that was originally cleaved (the latter process is the one of interest in this Account). Another option available to the geminate pair is step e, separation of the radical fragments into the bulk solvent, followed by free radical reactions that include *random radical pair recombinations*. The random radical combinations can also happen to form a carbon-carbon bond identical to the one that was cleaved. Clearly, although both geminate and free radical pathways formally may lead to re-formation of the same carbon-carbon bond, they do so by completely different mechanisms. Additionally, scavenging of the free radicals may occur.

In the gas phase at low pressure, the fraction of recombinations following a bond dissociation is usually found to be zero. The classical cage effect^{5a} of Franck and Rabinowitch is defined as the increase in the probability of recombinations in the liquid compared to the gas phase. In this Account we are concerned with the experimental measurement and the theoretical computation of the "cage effect"^{2,4,5} in liquids. We define the probability of recombination, P_r , as the fraction of reacting triplet geminate pairs that, generated by α -cleavage, undergo recombination reactions. The associated probability of free radical formation is simply $(1 - P_r)$. In particular, we shall be concerned with how hyperdynamic kinetics of a triplet geminate pair in a supramolecular structure determines the value of P_r . We now need to develop a paradigm for the cage effect² in homogeneous liquids and the supercage effect in microheterogeneous liquids. We also need to clarify the meaning of terms such as supercage and hyperdynamics.

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Cage Effect for Nonviscous Homogeneous Liquids. Collisions between Caged Reactive Radicals Occur in Sets

Rabinowitch and Wood^{5b} pointed out over 50 years ago that when a pair of potentially reactive carbon-centered radicals encounter and become nearest neighbors as a result of random diffusional motion in a homogeneous inert liquid, the solvent molecules serve as a "cage" whose "walls" cause collisions between the neighboring radicals to occur in "sets". The radical pair and the wall of solvent molecules constitute a primitive supramolecular structure for which noncovalent interactions produce phenomena (sets of collisions) which are absent compared to a simpler, molecular model, the isolated encounter and collision of a pair of radicals in the gas phase at low pressure. The restricted space created by the solvent walls is analogous to the supramolecular concept of a host system that has been such a powerful idea for understanding the behavior of enzymes. In general, any supramolecular structure,³ just as any molecular system, may be defined by the characteristics of composition, constitution, configuration, and conformation. A radical pair as guest and a solvent cage as host constitute a supramolecular structure commonly termed a "collision complex".^{5c} The lifetime of such a supramolecular structure for a nonviscous homogeneous liquid is so short (ca. 10^{-11} s) that most chemists prefer not to consider a species trapped in a solvent cage as a supramolecular system. However, for a physical chemist who investigates cage effects on the femtosecond and picosecond time scale,^{4c-e} the idea of a radical pair in a solvent cage can be as valid a supramolecular structural concept as that of a substrate in an enzyme is to an organic chemist.

Hyperdynamic Kinetics of Radical Pairs

The cage effect is readily investigated experimentally by producing a geminate pair of radicals through a photochemically induced bond dissociation (Figure 1) and then measuring the fraction of radical recombinations relative to the irreversible escape of the fragments from the collision complex.^{2,4a,b} One would expect an increase in the cage effect upon going from a gas to a liquid to be general, because, in a liquid,^{5b,c} collisions occur in sets so that, after being produced by a bond dissociation, a reactive radical pair would exist for a brief period of time as a collision complex. However, this expectation is generally not observed, and we shall see that cage effects from the photolysis of ketones are experimentally found to be close to zero. To understand why this is the case, we need to understand the unusual hyperdynamics that control the reactivity of a triplet geminate radical pair toward combination reactions. Effectively, we seek to understand how ISC from the triplet to the singlet geminate radical pair occurs, since ISC is the "reactivity switch" which converts an inert triplet geminate pair, incapable of undergoing combination reactions after multiple collisions, into a reactive singlet geminate pair, which is capable of undergoing combination reactions upon a single collision!

To understand the concept of hyperdynamics, we view the geminate radical pair as a dynamic supramolecular system in which the primary radical partners

can diffuse, separate, and make random excursions in space and time and then return and reencounter. We call such an excursion from an initial solvent cage and return to the solvent cage a "random walk". It is during these random walks that ISC occurs as the result of magnetic interactions that the pair experiences. For the kinetics of ISC to be efficient during a random walk there must be an "overlap" or coincidence of four dynamic events, hence the concept of "hyperdynamic" kinetics.⁶

First, the radical pair leaves the initial collision complex at $t = 0$ and the radicals reencounter at a later time, t . The contribution to the kinetics of ISC due to the process of re-formation of collision complexes is determined by *molecular or diffusion dynamics of the pair*. The parameters controlling the molecular dynamics are the size and shape characteristics of the restricted space serving as host to the pair and the diffusion coefficient of the pair in the restricted space.

Second, at the instant t , the pair must be in the singlet state if a carbon-carbon bond is to be formed and combination reaction is to occur. The contribution to the kinetics of ISC due to the process of spin stereochemical reorientation is determined by *spin dynamics*. The parameters controlling the spin dynamics are the magnetic interactions (hyperfine coupling, spin-orbit coupling, Zeeman interactions, etc.) that the pair experiences during a random walk and the exchange interaction. The distance-dependent exchange interaction, although not magnetic, influences the spin dynamics indirectly by determining the energy of the singlet triplet splitting and the coupling of the spin motion of the electrons. Since the molecular dynamics randomly vary the distance of separation of the radical partners, the random walk modulates the exchange interaction and therefore influences the spin dynamics by creating *electron exchange dynamics*.

Third, during a random walk, the radical must survive chemical transformations such as fragmentations, rearrangements, and scavenging processes in order to return, at time t , to form a collision complex capable of re-forming the originally snapped carbon-carbon bond. The probability of chemistry occurring between $t = 0$ and t is determined by the *chemical dynamics* of the pair. The parameters controlling the chemical dynamics are the rate constants (unimolecular and bimolecular) of the chemical reactions available to the pair. Chemical reactions of the pair will destroy the original pair and create a new pair with its own set of hyperdynamics.

Fourth and finally, if after a random walk a geminate pair has survived chemical transformation, has achieved ISC, is in the singlet state, and forms a collision complex, all that is needed now to form a carbon-carbon bond is the achievement of favorable orientation for recombination. The probability of achieving this orientation is determined by the *rotational dynamics* of the pair in the collision complex.

Thus, the deceptively simple picture of a pair of carbon radicals coming together and forming a bond

must be replaced for a triplet pair, with a complicated, coincidental, and coordinated choreography or hyperdynamics which integrates the spin, chemical, molecular, and rotational motions of the pair within the overall restricted space available to it.

Let us now consider these dynamics *seriatim* and start with the *mechanical* motion of the radical pair which results from random diffusional motions of the dynamic geminate radical pair and the solvent molecules that form the cage walls.⁶

Paradigm of the Dynamic Radical Pair and the Cage Effect. Reencounters Also Occur in Sets

From Figure 1 we learn that when a ketone is dissociated into two reactive radicals in the liquid phase (for simplicity, in the absence of radical scavengers), the initial pair will eventually undergo "recombination" reactions (combination and disproportionation reactions are included in the term recombination, but we only consider recombination to form the original bond that was dissociated in this Account) in competition with random diffusive displacements resulting in either geminate reencounters or the formation of free radicals.⁷ The final products (all assumed to be derived from radical-radical reactions) may be conveniently classified as those occurring between geminate partners (geminate recombination) or between radicals produced from different dissociation events (random combination).

From Figure 2, the experimentally measured *overall* probability, P_r , for re-formation of a carbon-carbon bond could be derived from radical-radical reactions which occur in three separate stages and for three different types of cages: $P_r(1)$ is the probability that geminate recombination will occur in the *primary cage* or collision complex in which the pair is created; $P_r(2)$ is the probability that geminate recombination will occur in a *secondary cage* after the primary pair has been separated by at least one solvent molecule (we lump together into this probability all geminate recombinations except for the primary recombination, which may involve the reversible formation of a number of secondary cages); and $P_r(3)$ is the probability that combination reaction will occur through random radical combination of two nongeminate or "free" radicals in *random cages*. Experimentally, we seek to measure $P_r^{\text{gem}} = P_r(1) + P_r(2)$, the total probability of all *geminate recombinations* (which we shall term from this point on as the "cage effect"),^{7c} and we also seek to compute the value of P_r^{gem} from a theoretical model.

The magnitude of the probability of secondary geminate recombination, $P_r(2)$, is related to the probability of reencounters of the geminate pair after it has escaped from the primary solvent cage (step b in Figure 2). Experimentally, for nonviscous, homogeneous liquids, the probability of *triplet* geminate recombination is found to be quite small, so that the ability of an ordinary solvent such as benzene to "cage" a radical pair and encourage recombination is negligible.⁶ The ineffectiveness of the "cage" formed by a nonviscous homogeneous liquid will now be contrasted with the effectiveness of a "supercage" formed by a

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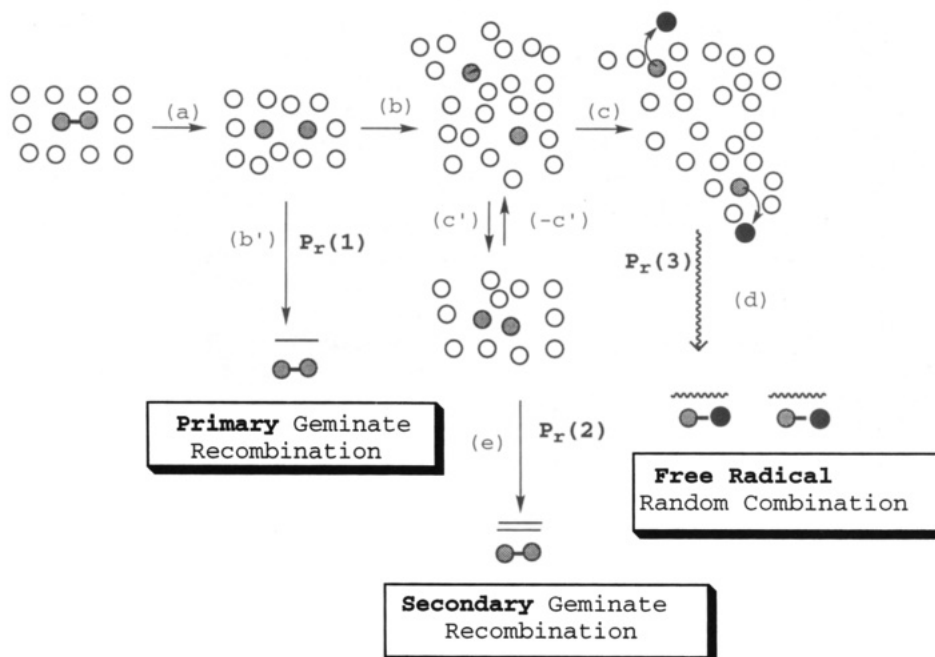


Figure 2. Paradigm for the cage effect in a homogeneous molecular liquid. See text for discussion.

nonviscous, heterogeneous liquid such as a colloidal micellar liquid.⁸

Paradigm for the Supramolecular System of a Geminate Radical Pair Guest in a Supercage Host. Micelles as Supercage Hosts

Micelles are colloidal aggregates formed by the association of surfactant molecules in appropriate cohesive solvents such as water.⁸ The surfactant possesses a schizophrenic molecular structure which is at once both hydrophobic and hydrophilic. In the micellar aggregate a cooperative association occurs, creating a supramolecular structure for which the hydrophobic moiety (usually a linear hydrocarbon chain) is packed into a roughly (average) spherical core and the hydrophilic moiety (usually a charged or highly polar group) forms the interface of the hydrophobic core with the aqueous phase. For the purposes of this Account, the micelle will be considered as a "nanoscopic oil drop" dispersed in the aqueous phase.

A micelle may serve as a host or supercage for a geminate radical pair produced by photochemically induced α -cleavage of ketones⁹ (Figure 1). A radical pair associated with a micelle constitutes a supramolecular system whose composition consists of one geminate radical pair (guest) per micelle (host). When one of the partners of the pair leaves the micelle (escape is assumed to be irreversible), the supramolecular structure is destroyed because the geminate correlation between the pair is lost. While the geminate pair is associated with the micellar volume, however, reencounters of the pair are frequent because the partners of the pair are hydrophobic and therefore experience a potential barrier when they approach the micellar boundary with the aqueous phase. We may say that the radical fragments are "forced into sets of reencounters" by the "walls" of the micellar supercage

in a manner that is analogous to the way the radical fragments are "forced into sets of collisions" by the "walls" of the solvent cage.

We now have a conceptual basis for differentiating a classical molecular solvent cage from a supramolecular supercage: a classical molecular solvent cage forces sets of collisions between the caged species but does not force reencounters; a supramolecular micellar supercage forces sets of collisions in local molecular solvent cages but also forces sets of reencounters throughout the supramolecular micellar supercage. If we take the elements of Figure 2 which refer to a homogeneous liquid and consider them to be embedded in a space corresponding to the volume of the supercage, we have the essence of the paradigm we shall employ for understanding the mechanical diffusional behavior of a radical pair in a micellar supercage.

Paradigm for Spin Dynamics. An Analogy between Stereoisomerization and Intersystem Crossing

Having developed paradigms for the photochemical production of dynamic triplet geminate radical pairs in a supercage of a certain size or volume, we now must consider the hyperdynamics which determine the kinetics of conversion of the inert geminate triplet into a reactive geminate singlet pair within the supercage. As a concrete paradigm for the spin dynamics required for ISC, we appeal to a simple analogy between the mechanism for the loss of molecular stereochemistry when α -cleavage occurs (Figure 3, left) and the loss of electron spin stereochemistry which must occur during the crucial triplet to singlet ISC (Figure 3, right). When the bond is snapped, a radical pair is formed; if the pair separates to a sufficient extent, the partners may undergo mutual rotational motions; if these motions occur, when the bond is knitted back together, the molecular stereochemistry is "mixed" or racemized, i.e., stereoisomerization has occurred. If the pair does not separate to

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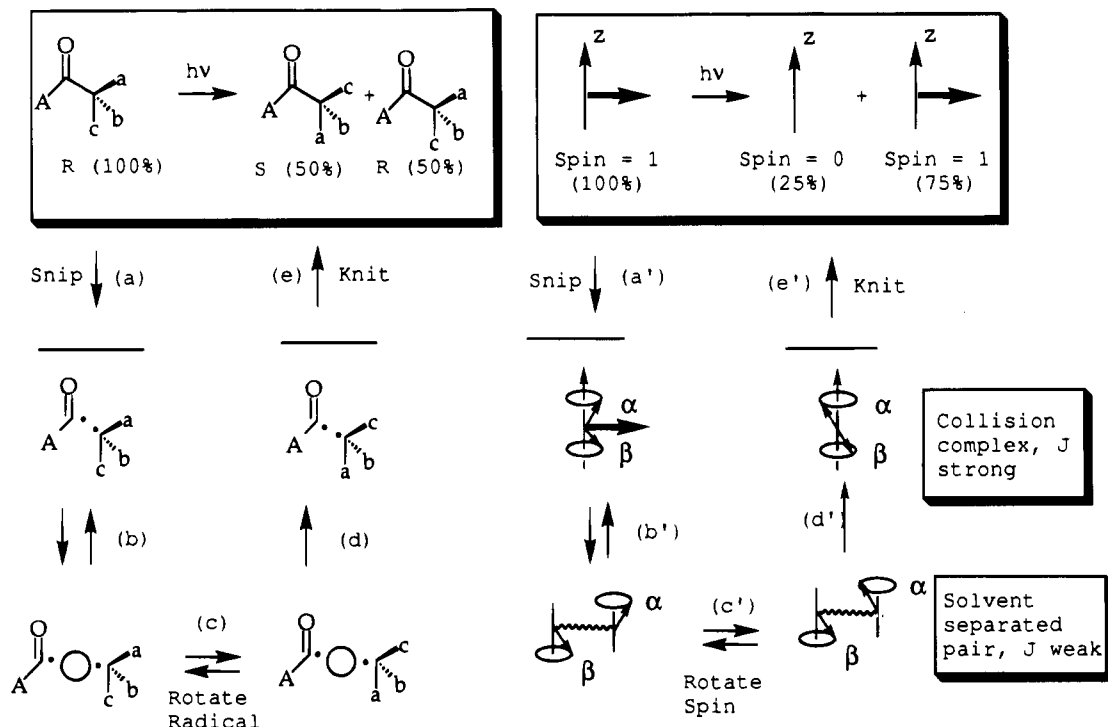


Figure 3. Paradigm for the spin dynamics of triplet to singlet intersystem crossing. An analogy is made between the mixing of molecular stereochemistry of an initially enantiomerically pure chiral ketone and the mixing of spin stereochemistry of the initial triplet radical pair. The top structures represent the overall molecular photostereoisomerization (enantiomeric or diastereomeric) of a ketone into a racemic mixture (left) and the spin stereoisomerization from a triplet to a singlet (right). The middle structures represent the loosely geminate radical pair (left) and the loosely coupled spins (right) in a collision complex. The bottom structures represent the solvent-separated, rotationally randomized geminate pair (left) and the weakly coupled, mixed spins. The loosely coupled geminate radical pair undergoes recombination to yield a "statistical" stereochemical mixture (50% R and 50% S), whereas the loosely coupled spin system yields a "statistical" stereochemical mixture of spin states (75% triplet and 25% singlet).

a sufficient extent, molecular stereochemistry is preserved upon recombination and the knit process will occur with retention instead of mixing of stereochemistry.

Now let us develop an analogous paradigm for "racemization" of the magnetic stereochemistry of the electron spins and how it relates to the role of the electron exchange interaction in modulating the spin dynamics. There is a strong analogy between the spectroscopic term "multiplicity" of spin state and the molecular structural term stereochemistry. Both terms refer to systems that are "stereoisomeric" (possess the same number and kinds of components and connections but differ in their configurations in space). In the case of molecular stereochemistry the meaning of the term is clear and refers to the difference in the structure of isomers resulting only from the orientation of atoms in space. For isomeric spin states to possess stereoisomeric relations, they must differ only by the orientation of the spin in space.

As long as the partners of the pair are sufficiently close to one another (i.e., as long as they are in a collision complex), the exchange interaction between the two odd electrons is strong, and it is impossible to individualize the stereochemical characteristics of the two electrons (Pauli principle). Thus, in the collision complex the radical pair must possess a wave function with a spin part that is either symmetrical (triplet state) or antisymmetrical (singlet state) with respect to the interchange of the electrons. If we take the time scale of an "elementary chemical step" such as formation of a bond to be of the order of picoseconds, an analogy of the Franck-Condon principle (sometimes

called the Wigner spin selection rule) can be formulated.^{6c} spin multiplicity cannot change during an elementary chemical step of bond formation or bond cleavage because the rate of spin motion is too slow relative to the time scale for an elementary step. Hence, a singlet precursor molecule must lead to a singlet geminate radical pair in a snip process and a triplet precursor molecule must lead to a triplet geminate radical pair in a snip process. Because of these spin restrictions on an elementary step, the *triplet geminate radical pair collision complex is inert toward recombination reactions and the singlet geminate radical pair collision complex is reactive toward recombination reactions*. In terms of Figure 3, we conclude that the spin stereochemistry of a pair cannot change during the bond formation or the bond cleavage step in a collision complex. Thus, spin stereochemistry (triplet or singlet) holds the key to radical pair reactivity when a collision complex is formed!

In Figure 3 we represent the stereochemistry of the electron spin in terms of a conventional vector notation. In this notation the two spin vectors are strongly coupled (strong exchange interaction) when the radical pair is in a collision complex (top structures) and are weakly coupled when the radical pair is separated by one or more solvent molecules (bottom structures). Because of the Pauli principle, the stereochemistry (spin configuration) of the electron spin is only stable for symmetrical (triplet) or antisymmetrical (singlet) spin combinations. In the vector notation this means that the stereochemistry of the spin vectors must be pointing either in the same direction (symmetrical configuration, triplet) or in

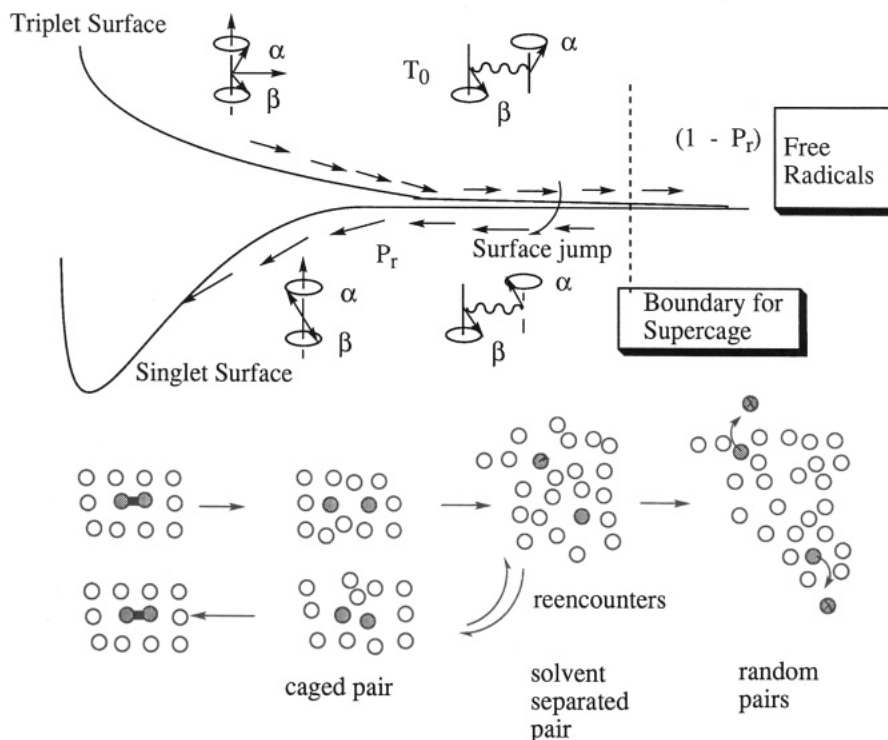


Figure 4. Representation of the hyperdynamics involved in the recombination reaction of a triplet geminate radical pair. The arrows moving along the singlet and triplet energy surfaces indicate the motion of the representative point of the nuclei of the radical pair. The spin dynamics is represented by the vector notation as in Figure 3. The diffusional dynamics is represented below the surfaces as in Figure 2. The boundary for a hypothetical supercage is shown. The shaded circles represent geminate radicals. The shaded circles with internal \times 's represent radicals from noncorrelated dissociations.

opposite directions (antisymmetrical configuration, singlet). These two possibilities correspond to the two stable stereochemistries of the electron spin of the radical pair and are analogous to the stable *R* or *S* configuration of two enantiomers whether the enantiomers possess a bond or the bond has been broken and rotation has not yet occurred. In the molecular racemization, the breaking of a carbon-carbon bond and the separation of the radical fragments in space kinetically enhance the racemization because loss of configuration can occur through rotations induced by thermal interactions available from the environment. In the spin racemization, the separation of the radical fragments in space enhances the intersystem crossing by causing the exchange interaction to decrease to values close to zero, so that loss of spin stereochemistry can occur through rotation of the spins induced by magnetic interactions available from the environment.

As mentioned above, when the geminate pair is in a collision complex, the exchange interaction, J , is so strong that the configuration of the spins is retained during collisions, i.e., ISC is unlikely to occur in a collision complex because the exchange force for maintaining spin stereochemistry is much more powerful than any available magnetic force available for reorienting spin stereochemistry.^{6,10} However, when the pair has separated in space and the exchange interaction, J , has decreased to a value that is small compared to the weak but available magnetic interac-

tions (the spins are "snipped" in the sense that their stereochemical correlation vanishes), the stereochemistry of the spins can be "mixed" or "racemized". This process is described quantum mechanically as "mixing" singlet character into an initially pure triplet radical pair and is analogous to racemization. After separation, when the pair reencounters and a collision complex is re-formed, the spins are "knitted" back together in the sense that their stereochemical correlation resulting from the exchange interaction, J , returns. *If the collision complex possesses singlet character, the knit process can occur without violating the law of conservation of angular momentum.* Thus, the process of separation of the inert triplet geminate pair from a collision complex, introduction of singlet character while the pair is separated, and reencounter to form a reactive collision complex with singlet character is a required process for a recombination reaction to occur starting from a primary triplet geminate pair.

Paradigm of Hyperdynamic Kinetics. The Cage Effect for Triplet Geminate Pairs in Homogeneous Molecular Solvents Is Expected To Be Zero

We now attempt to visualize the hyperdynamics required for ISC of the geminate pair by overlaying the chemical dynamics of Figure 1 with the molecular dynamics of Figure 2 and the spin dynamics of Figure 3. In Figure 4, the chemical dynamics of making a bond from an initial triplet state can be readily expressed by following the motion of a point representing the separation of the two carbon atoms involved in bond cleavage and bond formation along a triplet and a singlet energy surface. The representative point *simultaneously* represents the following

(10) The theoretical basis for understanding spin effects on radical pair chemistry is embedded in the theory of CIDNP proposed by Closs, Oosterhoff, and Kaptein: (a) Closs, G. L. *J. Am. Chem. Soc.* **1969**, *91*, 4552. (b) Kaptein, R.; Oosterhoff, L. *J. Chem. Phys. Lett.* **1969**, *4*, 195, 214. For a modern review, see: Buchachenko, A. L.; Frankevich, E. L. *Chemical Generation and Reception of Radio and Microwaves*; VCH: New York, 1994.

interacting dynamics, the overlap of which comprises the system's hyperdynamics: (1) the mechanical diffusional motion produced by the random walk involving the radical fragments (molecular dynamics, lower part of Figure 4); (2) the spin motion associated with the separation of the unpaired electrons and the reduction of the exchange interaction (spin dynamics, vector notation in Figure 4, above triplet surface); (3) the spin motion involving the reorientation of the spin stereochemistry when the pair is in the solvent-separated state (spin dynamics, vector notation in Figure 4, below singlet surface); and (4) the molecular motion representing the reorientation of the stereochemistry at carbon when the pair undergoes relative rotational motion (chemical dynamics, see Figure 3, left). In the solvent-separated state the representative point has a certain probability, P_r , of undergoing ISC and re-forming the bond (jump from the triplet surface to the singlet surface and then motion *back* into a solvent cage) and a probability $(1 - P_r)$ of separating further to form free radicals (movement along the triplet surface to the right or jump to the singlet surface followed by movement along the singlet surface to the right).

There is a certain separation (indicated in Figure 4 by a vertical dotted line) for which the value of J is close to 0 and for which ISC can become efficient. In order for a recombination to occur, after reaching this point, the representative point must reverse its direction and move on the energy surface back toward smaller separations eventually leading to reencounters to form secondary collision complexes. However, in homogeneous, nonviscous solvents random collisions cause a random walk propelling the representative point along the energy surface in one direction or another. In a nonviscous homogeneous solvent, *the representative point generally proceeds from left to right at much faster speeds than the rate of intersystem crossing which switches the point to the singlet surface, so that the probability of ISC and recombination, $P_r(2)$, is small because the probability of formation of free radicals, $P_r(3)$, is much higher.* The situation for the representative point moving along the surface from left to right is analogous to that of a car moving along a highway. If the car cannot produce momentum to the left or right (no mechanism for angular momentum change) during the time that the car is in the region of the exit from the highway, the driver will keep going straight ahead. Similarly, the spin momentum of the representative point is difficult to change when it is in the region of the collision complex, and it is much easier to continue straight ahead along the energy surface than to make a sharp right or left turn.

These ideas may be clarified further by order of magnitude considerations of the representative point. During a random walk,¹⁰ the time of separation of a pair from the contact state to a solvent-separated state is of the order of 10^{-11} s. For a diffusion coefficient of ca. 10^{-5} cm²/s, a small molecule will travel ca. 10 Å, during a random walk, so that in tens of picoseconds the pair has separated to distances of tens of angstroms. At such separations, the exchange interaction has dropped to zero, but the pair is no longer geminate (each partner will have a higher probability of encountering a radical from an uncorrelated dissociation than making a geminate reencounter) and can be readily scavenged. Thus, the number of reencounters

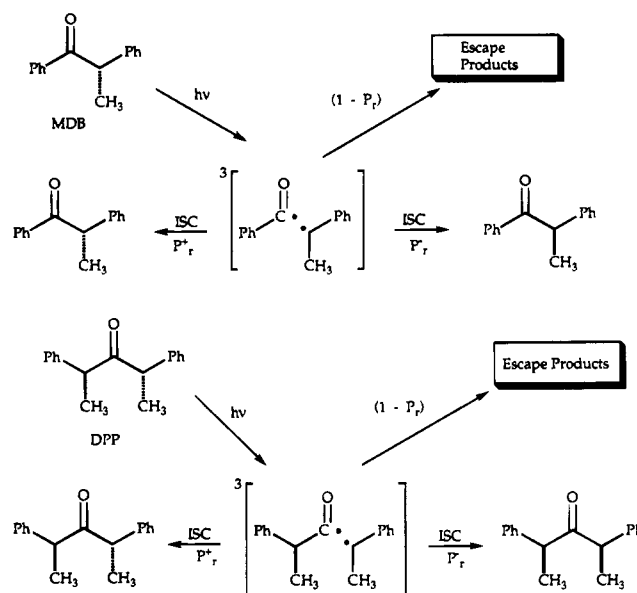


Figure 5. Top: Recombination of the geminate radical pair produced by the photolysis of methyldeoxybenzoin (MDB). Other combination and disproportionation products are formed in minor yields and are ignored. Bottom: Recombination of the geminate radical pair produced by the photolysis of 2,4-diphenyl-3-pentanone (DPP). Other combination and disproportionation products are formed in minor yields but are ignored.

of a geminate pair in a nonviscous homogeneous solution is expected (and found)¹¹ to be very small. Since cage recombination in the primary cage is not possible for a chemically inert geminate triplet pair, and since separation of the pair is required for ISC, and since reencounters of the geminate pair are essentially zero, *it is expected that essentially all of the triplet geminate pairs will become free radicals and undergo random combinations or be scavengable, i.e., the cage effect, P_r , in a homogeneous, molecular liquid is expected to be zero.*

Experimental Determination of P_r . The Experimental Value of the Cage Effect in Nonviscous Homogeneous Molecular Liquids Is Zero

The value of P_r may be determined experimentally¹¹ for any liquid system by measuring a recombination efficiency parameter, β , where $\beta = [P_r/(1 - P_r)]$. A simple way to measure β is by determining the loss of stereochemistry of a completely or partially resolved enantiomer of a chiral ketone (Figure 5, top: methyldeoxybenzoin, MDB) or a purified diastereomer of a ketone (Figure 5, bottom: 2,4-diphenyl-3-pentanone, DPP) according to eq 2, where Z is the experimentally measured enantiomeric (MDB) or diastereomeric (DPP) excess after the fraction conversion, f , to products and Z_0 is the initial enantiomeric or diastereomeric excess.

$$\ln\left(\frac{Z}{Z_0}\right) = \frac{P_r}{1 - P_r} \ln(1 - f) \quad (2)$$

The magnitude of β is experimentally derived¹¹ from the evaluation of the slope of an appropriate plot of the log of the loss of stereochemistry as a function of conversion of the starting material to the stereoisomer

(11) Tarasov, V. F.; Shkrob, I. A.; Step, E. N.; Buchachenko, A. L. *Chem. Phys.* **1989**, *135*, 391.

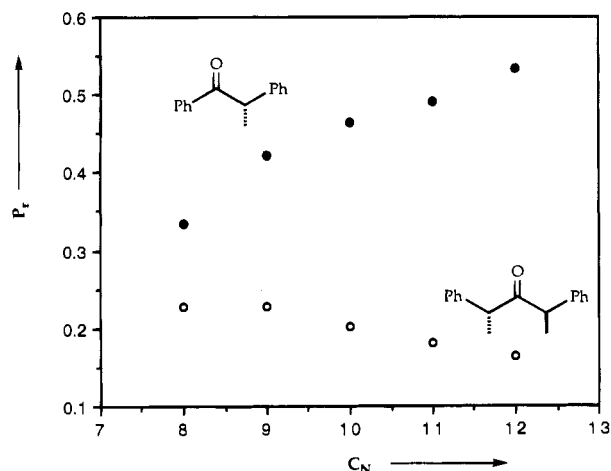


Figure 6. Experimental values of P_r for photolysis of MDB (solid circles) and DPP (open circles) in micelles of different sizes. C_N corresponds to the number of carbon atoms in the hydrocarbon chain of the detergent. The radius, L , of the surfactant employed in the model is the length of the fully extended surfactant in the all trans conformation: $L_{\max} = 1.5 + 1.265N$ according to Tanford: Tanford, C. J. *Phys. Chem.* **1972**, *76*, 3020.

and other products. From these slopes and a simple relationship of β to P_r , the experimental value of P_r is evaluated.

As expected, the value of P_r is experimentally close to 0 for the photolysis of either MDB or DPP in homogeneous, molecular liquids such as benzene or acetonitrile.^{12,13} This result confirms the weakness of the walls of the solvent cage as a confining supramolecular structure and the absence of a significant number of reencounters of geminate pairs that have escaped the primary solvent cage, i.e., in nonviscous, homogeneous liquids, as expected: $P_r(1) + P_r(2) = 0$.

Experimental Determination of P_r . The Experimental Value of the Cage Effect in a Micellar Supercage Is Greater Than 0 and Depends on the Size of the Supercage

In contrast to the results in homogeneous molecular liquids, the value of P_r is significant¹⁴ (ca. 0.1–0.6) for the photolysis of MDB or DPP in microheterogeneous, micellar solutions (Figure 6). This result confirms the supercage structure of the micelle with respect to geminate radical pairs. A striking feature of the results is the divergent relationship of P_r and micelle size for the two systems: P_r increases as the micelle size increases for MDB, but P_r decreases as the micelle size increases for DPP. Understanding this important and intriguing relationship between the cage effect and cage size requires a proper theoretical model.

Theoretical Computation of P_r from a Microreactor Model of a Micelle

The value of P_r may be determined theoretically by computing the recombination probability based on a specific model of a dynamic radical pair.^{14–16} Any realistic model must include explicit forms for handling the influence of the size of the restricted space

and the hyperdynamics involved in determining the kinetics of the recombination reaction: (1) the magnetic spin dynamics (triplet to singlet intersystem crossing); (2) the details of the random walk of the radical pair (modulation of the exchange interaction as a function of separation); (3) the chemical dynamics (only collisions of singlet pairs lead to recombination); and (4) the role of the size and viscosity (relative pair diffusion coefficient) of the supercage. The key magnetic parameters incorporated into the spin dynamics of the model are the magnitude of an applied external magnetic field (if any), the hyperfine couplings of the magnetic nuclei embedded in the pair, the g factors of the individual radicals of the pair, and other magnetic interactions (e.g., spin–orbit coupling) that might induce intersystem crossing of the triplet pair. From a number of investigations,¹⁷ it has been concluded that hyperfine coupling is one of the most important mechanisms for carbon-centered radical pairs of the type described in this report.

According to the model, the rate of intersystem crossing is strongly influenced by the size and “viscosity” of the supercage in which the pair is embedded (for reasons to be discussed, *vide infra*). In the case of a micelle, a specific model must include these factors and others, such as the probability of one of the radicals leaving the micelle when it approaches the micellar boundary. The model must also consider that the intersystem crossing probability is also influenced by other factors such as the rates of reencounters and the modulating, distance-dependent exchange interaction, J , which tends to “quench” intersystem crossing when the pair is in the state of collision (because the exchange interaction causes singlet triplet splitting that is much larger than the magnetic interactions available for triplet singlet mixing).

Theoretical Model of a Geminate Radical Pair in a Micelle. Supramolecular Structures and Hyperdynamic Kinetics

A schematic description of the specific supramolecular model of a radical pair in a micelle we have developed is given in Figure 7. The micelle is modeled as a liquid sphere of radius L (the maximum length of an extended surfactant chain) and with a viscosity (diffusion coefficient for the geminate pair) that depends on micelle size.¹⁴ The diffusional dynamics of the radical pair are simulated by maintaining one of the partners of the pair in the center of the micelle and allowing the other to execute a freely diffusive random walk in the micellar space. When the random-walking partner approaches the micellar boundary, there is a certain probability that it will leave the micelle and pop into the aqueous phase. For computational simplicity, it is assumed that the escape is irreversible. The size of the supercage is extracted from knowledge of the length of the surfactant molecule making up the micelle and from experimentally determined aggregation numbers, and the diffusion

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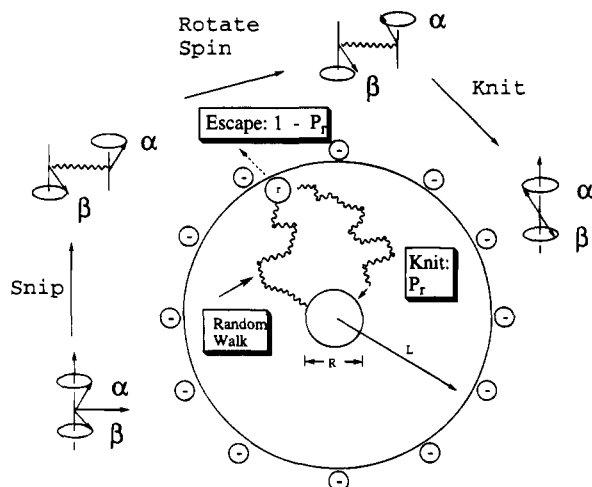


Figure 7. Schematic representation of the model employed to compute the value of P_r for the recombination (snip-knit) reaction of a geminate radical pair in a micelle. See text for discussion.

coefficient for the pair adsorbed in the micelle was obtained from experimental measurements involving diffusional probes of micelles.¹⁴

The concept of snip and knit is correlated with the diffusional trajectory of the walker radical as it moves around the spherical micelle as shown in Figure 7. As one of the partners of the pair leaves the collision complex and begins its random walk excursion about the supercage, the diffusional dynamics of the pair interact with the spin dynamics and electron exchange modulation dynamics, i.e., *hyperdynamics are in full operation*. Thus, the micellar size, micellar viscosity, time scale of intersystem crossing, and duration of the walk are critical in determining the value of P_r , as outlined in Figure 7 (see the original papers¹⁴⁻¹⁶ for details). When the time for a "round trip" for a random walk (starting from and returning to the origin so that re-formation of a collision complex occurs) is of the same order as the time scale of the reorientation of the stereochemistry of the spin vectors, an effective "resonance" occurs, the pair picks up singlet character, and the collision complex becomes reactive.

Comparison of the Experimental and Theoretical Values of P_r as a Function of Micelle Size

The experimental values of P_r were determined¹⁴ as described above, for the methyldeoxybenzoin (MDB) and 2,5-diphenylpropanone (DPP) systems as a function of micelle size for micelles consisting of anionic surfactants containing 8, 9, 10, 11, and 12 carbon atoms in the surfactant chain (variation of micellar diameter between 20 and 32 Å). The results, shown in Figure 6, are disparate in that for MDB the value of P_r increases as the size of the micelle increases, whereas for DPP the value of P_r decreases as the size of the micelle increases. Such a qualitatively different behavior for two radical pairs of seemingly similar chemical structure provides a real challenge to the theory.

A reasonable agreement¹⁶ has been achieved for each of the systems (Figure 8). Thus, it is concluded

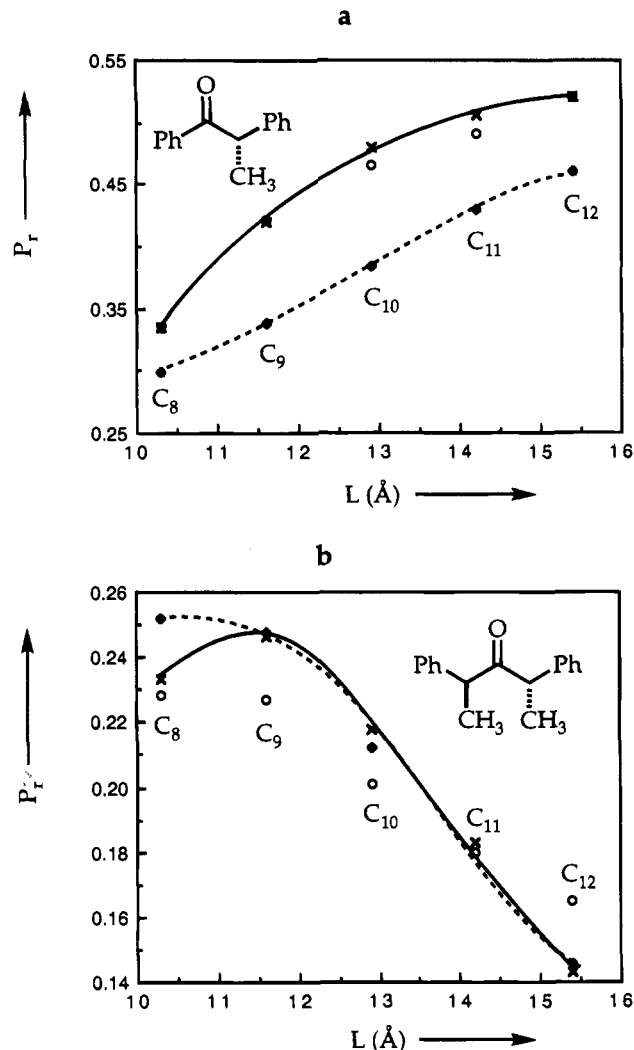


Figure 8. Comparison of the experimental (circles) and computational results for P_r (solid line for the distance-dependent electron spin exchange and dashed line for the effective value of the electron spin exchange). L corresponds to the radius of the micelle and is taken as the maximum extended length of the detergent chain.

that a realistic model of the supercage must explicitly include (1) a characteristic micelle size; (2) a distance-dependent electron spin exchange interaction; (3) a permeability-dependent boundary which allows distance-dependent exit from the supercage; (4) a coefficient of mutual diffusion that is a function of the micelle size. Finally, an important qualitative result is that there can be an increase in the effectiveness of the electron spin exchange in suppressing ISC as the micelle size decreases. For smaller micelles this effect results in ISC becoming the rate-determining step for the MDB system. In this system ISC is not determined purely by hyperfine interactions, but by hyperfine interactions modulated by a distance-dependent electron spin exchange.

The ability to obtain a reasonable fit to the considerable data^{14,16} of Figure 8 (10 independent experimental supramolecular systems) is considered as excellent evidence that all the major physical and chemical features of the supramolecular system of geminate radical pairs in micelles have been captured correctly by the model.

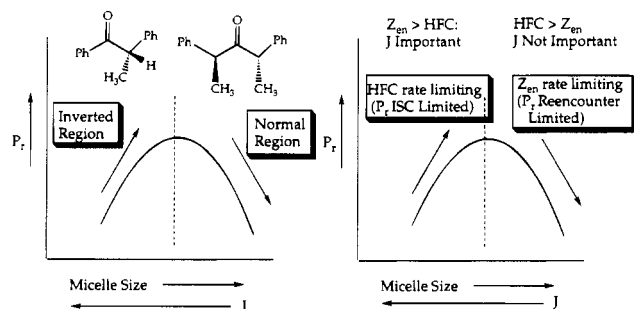


Figure 9. The normal and inverted regions of supramolecular restricted space for recombination of a carbon-carbon bond of a triplet geminate radical pair.

Frequency of Reencounters vs the Frequency of Intersystem Crossing

The probability of the cage effect, P_r , is determined by the competition of the rate of recombination of the geminate pair within the supercage and the rate of irreversible escape of one of the partners of the geminate pair from the supercage into the bulk solvent. The rate of escape has been shown to depend simply on the solubility of the radical fragments in the supercage and to decrease as the size of the micelle increases,¹⁸ i.e., a given carbon radical is more soluble in a larger micelle, as expected from the greater hydrophobic volume associated with the larger micellar volume. It is clear that if the rate of escape from the micelle were the sole feature determining the value of P_r , the latter would decrease, for both systems studied, as the radius of the micelle, L , decreased. Thus, we must look to the features of the rate of recombination to understand the experimental results of Figure 6.

The rate of recombination of a triplet geminate pair can be viewed in terms of two key frequencies: (1) the frequency of intersystem crossing, k_{isc} , and (2) the frequency of reencounters, Z , that increases as the micelle size decreases because the size of the supercage decreases as the micelle volume decreases; however, the frequency of intersystem crossing, k_{isc} , decreases as the micelle size decreases because of the quenching effect of electron exchange which is more important in smaller restricted spaces. Because a number of results support the hypothesis that hyperfine interactions in geminate radical pairs are critical in the determination of the rate of ISC for geminate pairs of the structure investigated here,¹⁷ we assume that the frequency of ISC is proportional to an "effective hyperfine constant", A , representing the total hyperfine interactions present in the radical pair. Although spin-orbit coupling is expected to contribute to the ISC process, the theory does not require its explicit inclusion. Computation shows that, under the assumption of hyperfine controlled ISC, the dependence of P_r on L shows a maximum (Figure 9, right). Furthermore, the value of L_{max} decreases as A increases, but the value of L_{max} increases as J increases.

Thus, a theoretical analysis reveals that ratio A (effective hyperfine frequency for the geminate pair) to Z (frequency of reencounters) is critical in deter-

mining whether P_r increases or decreases with a change in L . If $A/Z \gg 1$, then A is much larger than Z and the rate of reencounters is slow and is the rate determining feature of the recombination act. However, if $A/Z \ll 1$, then A is much smaller than Z . The rate of ISC is slow and is the rate-determining feature of the recombination act. In the latter case electron spin exchange must be explicitly considered in the computation. Thus, an important conclusion of the model is that *the significance of electron spin exchange on the rate of recombination of the geminate pair in a supercage is determined by the rate of ISC due to A relative to the rate of reencounters, Z . The smaller the value of A/Z , the greater the role played by the exchange interaction; the greater the value of A/Z , the smaller the role played by the exchange interaction.*

The results of Figure 6 may now be interpreted in terms of Figure 9. Qualitatively, we can assume that the nonmagnetic aspects of radical pair reactivity, such as the pair's irreversible exit from the micelle, will depend mainly on properties such as hydrophobicity. Thus, P_r is qualitatively related to the ratio of the rate constants for ISC and for escape from the micelle. We therefore can focus on the qualitative features of the rate of intersystem crossing as a function of micelle size.

For the case of MDB, *the larger the micelle, the larger P_r* . Thus, we conclude that $A/Z \ll 1$, i.e., since the value of P_r decreases with increasing micelle size, the system is in a region of collisional reactivity for which a larger volume results in rate-determining hyperfine interactions. This occurs because J is important *during the radical pair lifetime* and must be minimized by radical pair separation for ISC to occur. Even though the rate of reencounters decreases as the micelle size increases, this is not the rate-determining feature, and it is more important to have the larger size so that the value of J can readily drop to values near 0. This analysis is not quite correct, since a total simulation of the system, which includes the effect of the shorter lifetime of the geminate pair due to decarbonylation, is required to even qualitatively reproduce the results. However, for the sake of simplicity, we shall proceed by considering the results as if only the A/Z ratio were determining the value of P_r .

For DPP, *the larger the micelle, the smaller P_r* . Thus, we conclude that $A/Z > 1$ and that reencounters are rate-determining. This corresponds to a region for collisional reactivity. As the rate of reencounters increases, the value of P_r increases because the effect of hyperfine coupling and therefore J is not important in determining P_r . Thus, in terms of Figure 9, the influence of hyperfine interactions and the exchange interaction is less important for the geminate pair from MDB than for DPP.

From these considerations, it is clear that the dependence of P_r on micelle size will be either inverse (collisions rate determining, P_r decreases as the micelle size increases) or direct (intersystem crossing rate determining, P_r increases as the micelle size increases). This feature of either the mechanical diffusional motion (Z) or the magnetic spin motion (A) being rate determining is quite analogous to the situation found for large, flexible carbon-centered

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biradicals for which the rate-limiting step can be determined by either chain dynamics or spin dynamics.¹⁹

A final, more subtle point to be considered is the role of the lifetime of the geminate pair. In the case of DPP, the pair experiences a decarbonylation which chemically limits its lifetime to ca. 50 ns. In the case of MDB, decarbonylation does not occur and the lifetime of the pair is limited by exit from the micelle or recombination within the micelle, both of which are expected to take considerably longer than 50 ns. The shorter lifetime of the pair derived from DPP implies that this pair has less time to separate and explore the volume of the micelle. This may mean that only reencounters due to short trajectories are contributing to the intersystem crossing step because decarbonylation occurs during longer trajectories. The role of radical pair lifetimes in influencing the value of P_r as a function of micelle size is worthy of further study. The possibility of controlling the lifetime of the radical pair by applying a second pulse which destroys the pair at a predetermined time is a particularly appealing avenue for future research.

The role of hyperfine coupling in determining ISC was demonstrated by a comparison of the values of P_r for MDB and MDB labeled with ¹³C in the carbonyl position.^{16b} The carbonyl carbon in the benzoyl radical derived from the labeled MDB possesses a very strong hyperfine coupling of ca. 125 G, which exceeds considerably the total ¹H hyperfine interactions in the entire radical pair derived from unlabeled MDB. Since all other parameters of the unlabeled and labeled pair are identical, we expect an increase in the value of A/Z and movement further away from ISC control of the recombination reaction. For each of the micellar systems, the value of P_r was significantly greater for the labeled pair than that for the unlabeled pair and the results could be satisfactorily fitted by the model.

“Normal” and “Inverted” Regions of Recombination Probability

Our results (Figure 8, top and bottom) provide a certain analogy with the nonintuitive results of electron transfer reactions for which “normal” and “inverted” regions of reactivity are observed. In the “normal” region the rate constant for electron transfer increases with increasing exothermicity of the electron transfer step, as expected intuitively. However, in the “inverted” region the rate constant for electron transfer decreases with increasing exothermicity of the electron transfer step, a rather nonintuitive result.

We find analogous “normal” and “inverted” regions for recombination reactions of triplet geminate pairs in supercages. By normal, we mean that, from a simple mechanical analysis of a geminate pair in a micelle, the probability of recombination is expected to increase as the micelle size decreases because the probability of recombination is expected to depend on

the number of collisions and reencounters between reacting partners. More frequent encounters are expected in the smaller volume of smaller micelles; hence recombination should compete more favorably with micelle escape and other non-geminate pair reactions. Thus, in the “normal” region of reactivity, the probability of recombination increases as the size of the supercage decreases and as the frequency of reencounters increases, as expected intuitively.

In the “inverted” region the probability of recombination decreases as the size of the supercage decreases and the frequency of reencounters increases. The model of Figure 7 concurrently considers the hyperdynamics of spin and electron spin exchange and shows that along with concurrent molecular motion dynamics the dependence of P_r on micelle size will reach a maximum whose position depends on the critical parameter A/Z . When the hyperfine coupling is rate determining ($A/Z \ll 1$), electron spin exchange cannot be ignored in the analysis and the value of P_r gets smaller as the space for reaction gets smaller, in contrast to the expectations of the intuitive mechanical model. Thus, the model predicts that for appropriate situations *the rate of spin-selective reactions in micellized pairs will be decelerated if the encounter frequency properly couples with the electron spin exchange.*

Experimental examples of both the normal and inverted regions are provided by the two supramolecular systems: DPP in micelles and MDB in micelles, respectively. Since the probability of recombination increases with increasing micelle size for MDB and since the number of collisions between the precursor geminate pair is expected to decrease with increasing micelle size, this system is in the *inverted* region: fewer collisions, but higher probability of making a bond (Figure 9, left). On the other hand, for the DPP system, the probability of recombination decreases with increasing micelle size, so that this system is in the *normal* region: fewer collisions, higher probability of making a bond (Figure 9, left). The mechanistic interpretation of these results is given on the right side of Figure 9: the probability of reaction increases with the volume of the supercage when hyperfine coupling is rate determining, and the probability of reaction decreases with increasing micelle size when reencounters are rate determining.

Summary

Supramolecular photochemistry offers the photochemist an opportunity to both quantitatively and qualitatively modify the photochemistry of systems whose molecular photochemistry has been well established. The notion that true supramolecular systems require more than an understanding of the additive chemistry of the molecular systems is clearly evident in these investigations. In addition to the ideas of supramolecular structure, these systems require the application of the concept of hyperdynamic kinetics for which the probability of the process of interest is determined not by the dynamics of a single kinetic process but by the kinetics of several overlapping dynamic processes. In the case of radical pairs in supercages, the roles of interacting spin, molecular, and chemical dynamics and the size of the supercage are made clear by a quantitative model. Geminate

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radical reactions in supercages are excellent systems for the investigation of distance-dependent interactions (electron exchange and spin-orbit coupling) between radical fragments. These interactions can determine the reactivity of the radical pair in a supramolecular system. This occurs despite the fact that the strength of these interactions may be much smaller than kT for the separations under consideration. The physical basis for this nonintuitive result resides in the spin selectivity of bond formation from a geminate pair, the influence of the interactions on the rate of ISC, and the fact that kT refers to kinetic and electrostatic energy and that neither is effective in causing a change in spin stereochemistry; i.e., magnetic energy is required for ISC.

Through the use of a quantitative theoretical model and simulations of the experimentally measured probabilities for recombination of geminate pairs as a function of micelle size, the following conclusions were reached: In order to understand even qualitatively the variation of P_r with micelle size, electron spin exchange, J , modulated by the random walk of the pair in the micellar volume must be included. When ISC is slow and rate determining, the modulation of J can suppress ISC (by causing the S and T states to go "off resonance") and can overcome the expected advantage of faster rates of collisions in geminate pairs promoting recombination.

An analogy between the supramolecular geminate pair in a micelle and a biradical whose radical centers are connected by a flexible chain is apparent. However, for the radical pair the distance-dependent interactions are modulated by the random motions of a geminate pair in a supercage, whereas for the biradical, the distance-dependent interactions are modulated by the correlated motions of rotations about the bonds of a supermolecule. Another distinction is that the supramolecular system remains an isolated system only as long as the pair is geminate, i.e., individual radicals in a radical pair may exit the micelle into the bulk solvent, whereas the radical centers in a biradical are forced to remain geminate

throughout the full biradical lifetime. Thus, future investigations of a more detailed comparison of supramolecular systems of radical pairs in micelles and of supermolecular flexible biradicals are of interest.

Supramolecular Spin Chemistry of the Future

What sorts of experiments and theory should be pursued for exploring supramolecular spin chemistry in the future? Issues such as the influence of ambiguous or neglected magnetic interactions should be pursued from both a theoretical and an experimental level. A basic strategy is to measure by direct experiment as many of the currently unknown parameters as possible. One such parameter is the absolute rate of escape of radicals from micelles, which may be examined by standard flash photolysis techniques with EPR or optical analysis. Another parameter is the lifetime of the radical pair, which in principle can be controlled by two-photon photolysis.²² The first photon pulse is a "synthesis pulse", which produces the radical pair, and the second photon pulse is a "destruction" pulse which destroys one of the partners of the pair. An obvious extension of this research involves optically active cyclic ketones that, upon photolysis, produce flexible biradicals. The probability of recombination can be measured as a function of chain length (with a pseudo-first-order scavenger being present) in a manner analogous to the methods described here for the measurement of P_r as a function of micelle size.

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