(119) The Triple Fluoresence of Benzanilide and the Dielectric Medium Modulation of its Competitive Excitation, J. Heldt, D. Gormin, and M. Kasha, *Chem. Phys. Lett.*, **150**, 433-436 (1988).

(120) The Role of the Anionic Potential in Excited-State Proton Transfer in Lumichrome Picosecond Spectroscopy, J. M. Maclnnis and M. Kasha, *Chem. Phys. Lett.*, **151**, 375-378 (1988).

(121) Intramolecular Charge-Transfer Transition in Benzanilides and Its Dielectric Medium Modulation. J. Heldt, D. Gormin, and M. Kasha, *J. Am. Chem. Soc.*, **110**, 8255-8256 (1988).

(122) Fast Optically-Induced Molecular Changes. The Proton-Transfer Laser. M. Kasha, *Proceedings of the 3rd International Symposium on Molecular Electronic Devices* F. L. Carter, R. E. Siatkowski, and H. Wohltjen, Eds.; Elsevier Science Publishers, Amsterdam, 107-121 (1988).

(123) Triple Fluorescence in Aminosalicylates. Modulation of Normal-, Proton-, Transfer-, and Twisted Intramolecular Charge-Transfer (TICT) Fluorescence by Physical and Chemical Perturbations. D. Gormin and M. Kasha, *Chem. Phys. Lett.*, **153**, 574-576 (1988).

(124) Science, Art, and a Box with the Sound You Dream About. M. Kasha, *Proceedings of the 1984 Biology of Music Making Conference* F. L. Roehamann and F. R. Wilson, Eds.; MMB Music Inc., St. Louis, MO, pp 205-207 (1989).

(125) A Comparative Picosecond Spectroscopic Study of the Competitive Triple Fluorescence of Aminosalicylates and Benzanilides. J. Heldt, D. Gormin, and M. Kasha, *Chem. Phys.*, **136**, 321-334 (1989).

(126) Dielectric Medium Interactions in Proton-Transfer and Charge-Transfer Molecular Electronic Excitation. J. Heldt and M. Kasha, *J. Mol. Liq.*, **41**, 305-313 (1989).

(127) A Life in Molecular Orbital Theory (Review of Robert Mulliken's Autobiography). M. Kasha, *Chem. Eng. News*, **68**, 29-30 (1990).

(128) Molecular Electronic Criteria for Selection of Radiation-Hard Scintillators. M. Kasha, A Kubicki, and H. R. Rawls, *Workshop on Radiation-Hardness of Plastic Scintillators* (USDOE, Kurtis F. Johnso, Ed.), Department of Physics, Florida State University, Tallahassee, FL, March 19-21, pp 49-60 (1990).

(129) Molecular Phosphorescence Enhancement via Tunneling through Proton-Transfer Potentials, D. Gormin, J. Heldt, and M. Kasha, *J. Phys. Chem.* **94**, 1185-1189 (1990).

(130) Four Great Personalities of Science, G. N. Lewis, J. Franck, R. S. Mulliken and A. Szent-Györgi (Porter Medal Address). M. Kasha, Symposium on Photochemistry, International Union of Pure and Applied Chemistry, *Pure Appl. Chem.*, **62**, 1615 (1990).

(131) Ground State Anion Formation and Picosecond Excitation Dynamics of 3-Hydroxyflavone in Formamide. D. A. Parthenopoulos and M. Kasha, *Chem. Phys. Lett.*, **173**, 303 (1990).

(132) Comparative Study of Stimulated Proton-Transfer Luminescence of Three Chromones, D. Parthenopoulos, D. McMorrow, and M. Kasha, *J. Phys. Chem.*, **95**, 2668-2674 (1991).

(133) Energy Transfer, Charge Transfer, and Proton Transfer in Molecular Composite Systems. M. Kasha, in *Physical and Chemical Mechanisms in Molecular Radiation Biology*, W. Glass and M. Varma, Eds.; Plenum Press, New York, 1991, 21 pp.

Photostereoisomerization and the Magnetic Isotope Effect

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The photodiastereomerization of *meso*- and *d,l*-2,4-diphenylpentan-3-one (*meso*-DPP and *d,l*-DPP, labeled and unlabeled with ^{13}C at the carbonyl carbon) was investigated in micellar solution to determine the probabilities of recombination of the micellized primary geminate radical pair toward formation of different combination products. A mathematical analysis is developed and employed to investigate the probabilities of formation of the combination products from the primary geminate radical pair produced by photochemical α-cleavage. The extent of chemical conversion, the chemical yields of combination products, and the dependence of these two observables on the application of external magnetic fields are employed to arrive at conclusions concerning the probabilities of formation of combination products from the primary radical pair. An experimental parameter, S, which is determined by the extent of diastereoisomerization as a function of conversion, was shown to be constant and obtainable with high experimental accuracy. The values of S were found to depend on the initial stereochemistry of the starting DPP. The constancy of S and the observation of different values of S for different initial substrates place strong constraints on the relationships which are possible between the probabilities of combination of the geminate radical pair. Within these constraints, several limiting cases are analyzed concerning the relationships between probabilities for combination. Further information was obtained experimentally from the measurement of ^{13}C isotope separation efficiencies due to the magnetic isotope effect and due to a classical (mass) isotope effect in the reaction of photodissociation at different magnetic fields. The results allow, within the confidence provided by highly accurate experimental data, the conclusion that primary geminate radical pairs of *sec*-phenethylacyl/*sec*-phenethyl radicals recombine, in micelle solutions, to regenerate the precursor substrate structure and diastereomer structure with equal probability.

Introduction

One of the simplest and most significant "elementary" reactions in solution organic chemistry is the formation of a bond between two colliding carbon-centered radicals. It is therefore important from the standpoint of basic research to understand the details of how a carbon–carbon bond is formed when a radial pair undergoes collisions within a solvent cage.[1,2] One approach to analyzing this issue is to employ a "snip and knit" method in which a carbon–carbon bond in a precursor molecule (such as a ketone[3]) is "snipped", or cleaved, as the result of the absorption of a photon and then some observation is monitored which tracks the "knitting", or combination, process of re-forming the *same* carbon–carbon bond. At the very instant of carbon–carbon bond cleavage, there exists an initial relative orientational structure of the geminate radical pairs (GRPs) and a specific configurational structure at the carbon centers. After this instant, the relative

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[†] Academy of Sciences USSR.

[‡] Columbia University.

(1) Benson, S. W. *Foundations of Chemical Kinetics*; McGraw-Hill: New York, 1960.

(2) (a) Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867. (b) Kopecky, K. R.; Gillan, T. *Can. J. Chem.* **1969**, *47*, 2371. (c) Baretz, B. H.; Turro, N. J. *J. Am. Chem. Soc.* **1983**, *105*, 1310.

(3) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin-Cummings: Menlo Park, CA, 1978; Chapter 13.

0022-3654/91/2095-10220$02.50/0

orientations and configurations of the structure begin to "relax" as the result of random diffusional trajectories of the fragments of the pair. However, if the GRP reacts before this "relaxation" is complete, information concerning the effect of trajectories on the precursor configurational stereochemistry may be locked into the structure of the combination products generated from reforming the carbon–carbon bond that was originally cleaved.

In general, geminate radical pairs, under unconstrained environmental conditions (nonviscous, homogeneous solutions or the gas phase), may undergo self-reactions by different chemical routes such as different bond-forming recombinations or as a specific recombination and disproportionation. A rather subtle, but intriguing question, concerning the dynamic behavior of geminate radical pairs, is whether different relative diffusional trajectories of the radical pair might lead to different products, i.e., are the trajectories leading to products of different recombination reactions or of recombination and disproportionation reactions different? Conceptually, it is clear that geminate recombination may occur with no change of the initial orientation of the radical pair generated by the elementary step of dissociation of the molecular precursor. However, differing sets of reactions such as geminate diastereomerization[2a,c] and racemization[2b,4,5] (or geminate combination and disproportionation) are not possible without some change in the geminate radical pair's initial relative orientation.

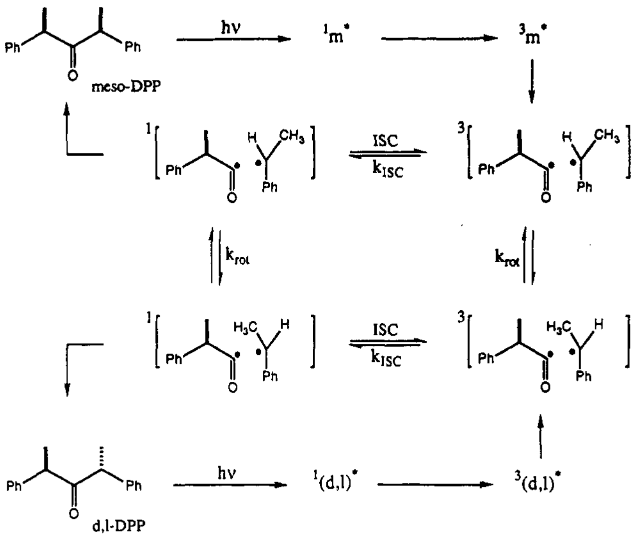
Acyl/benzyl *biradicals*,[6] generated by the photolysis of α-phenylcycloalkanones, provide another example where considerations of the diffusional trajectories of geminate radical fragments are valid and germane: some fraction of the biradicals recombine to regenerate the identical initial cyclic ketone structure or an epimeric structure (*through minimal relative orientational changes*) while another fraction recombines by the "head-to-tail" route eventually leading to the formation of the cyclophane products (*through a substantial relative orientational change*). In these cases the different products imply different trajectories of the radical moieties under the constraints of a flexible methylene chain.

The question which immediately arises after such considerations concerning the possibility of trajectory effects on product structure is what possible physical mechanisms could cause different trajectories to lead to different products and what are the experimental means to probe such mechanisms?

The paradigm of radical pair theory[7] provides a well-established basis for postulating that different trajectories might provide a mechanism for different product formation. For example, if a GRP is born in the triplet state, then geminate recombination can occur only after completion of an intersystem crossing (ISC) step. The rate of this ISC may depend significantly on the details of the diffusional and rotational trajectories available to the pair. This dependence on trajectories originates from the fact that ISC rates are determined by the intensity of magnetic interactions in the diffusing GRP as it executes diffusional trajectories in space.[7] Electron spin exchange, dipole–dipole electron–electron interactions, and spin–orbit coupling depend upon the mutual orientation of radicals and the distance between them. Therefore, it can be expected that different trajectories of the same pair may lead to different products, i.e., *an averaging of the interactions during diffusion may lead to different values and different magnetic field and magnetic isotope effects for different reaction routes and diffusional trajectories.*

The radical pair paradigm also provides a means of interpreting the variation of the isotope separation efficiency for different products in the recombination of acyl/benzyl biradicals.[6] For the recombination to regenerate the structure of the precursor ketone, the contribution of spin–orbit coupling (which is spin nonselective and more important for small trajectories of the radical centers) to the ISC will be greater than for recombination to form cycloplanes (which occurs through coupling or the acyl radical with the para position of the benzyl fragment and is nuclear spin selective and more important for large trajectories).

SCHEME I: Photodiastereomerization Pathways of *d,l*- and *meso*-DPP



We are probing for extremely subtle effects in the behavior of radical pairs, such as differences in the probabilities of recombination for two different diffusional routes, which lead to different recombination products when the initial mutual orientation of the radical pair (produced by photochemical cleavage of DPP) is fixed and not random. This paper experimentally investigates this possibility by examining both the magnetic isotope effect and the photodiastereomerization of 2,4-diphenylpentan-3-one (DPP, Scheme I) in sodium dodecyl sulfate (SDS) aqueous micellar solution. A major goal is to devise methods to determine whether the paradigm stated above for biradicals is also applicable to the relative diffusion of radical centers which are restricted not by an alkyl chain which serves as a tether (i.e. biradicals) but by association with the restricted space of a micellar core and its surface. The investigation of such subtle effects is difficult because of limiting experimental accuracies and by the absence of obvious mathematical relationships, possessing a compelling physical sense, connected to the conventionally measured mechanistic photochemical parameters such as quantum yields and chemical yields of products. We therefore have developed a reaction probability approach which allows the relation of quantities which can be measured with great experimental accuracy (e.g., reaction conversion and diastereomeric excesses) to probabilities of the various recombination pathways. This approach also possesses a clear physical meaning in terms of the standard paradigm for photolysis of ketones and therefore has the potential of providing mechanistic insight on the subtle distinctions we seek to discern. Although a kinetic analysis in terms of absolute rate constants determined by time-resolved methods allows, in principle, for a deep penetration into the problem, a much simpler steady state analysis is also very effective in examining the pertinent reaction probabilities. This is because such analyses allow organization of the rate constants into a matrix which possess a very well-defined mechanistic and physical meaning and which are therefore very powerful in allowing a clear interpretation of the results under given limiting conditions.

Experimental Section

Gas chromatographic analyses were carried out, using Hewlett Packard 5890 gas chromatographs with flame ionization detectors, on 25-m Carbowax 20M capillary columns and Hewlett Packard 3390 and 3392 electronic integrators. Mass spectra were acquired

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(4) Lewis, F. D.; Magayar, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 5973.

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

(6) Hwang, K.-C. Ph.D. Thesis, Columbia University, 1990. Turro, N. J.; Doubleday, C. E., Jr.; Hwang, K.-C.; Chung, C.-C.; Fehlner, J. R. *Tetrahedron Lett.* **1987**, *28*, 2929. Doubleday, C. E., Jr.; Turro, N. J.; Wang, J. F. *Acc. Chem. Res.* **1989**, *22*, 199.

(7) Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z.; Buchachenko, A. L. *Spin Polarization and Magnetic Effects in Radical Reactions*; Elsevier: Amsterdam, 1984; p 420. Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.

with a Hewlett Packard 5890 GC coupled to a mass selective detector and a HP-9136 computer and software system.

Electrophoresis-grade sodium dodecyl sulfate (SDS, Bio-Rad) was used as received.

2,4-Diphenylpentan-3-one (DPP in Scheme I) was synthesized by methylating dibenzyl ketone (DBK; Aldrich Chemical Co.) using 1 equiv of potassium hydride, followed by treatment with 1 equiv of butyllithium and then 2 equiv of methyl iodide.[2c] The *meso* and *d,l* forms were separated using reverse phase HPLC on a C-18 column (85/15 MeOH/H_2O) and collected with greater than 99% isomeric purity as determined by GC. Isotope enrichment experiments were conducted on ~25% enriched material which was prepared by diluting unlabeled isomerically pure DPP with isomerically pure DPP obtained from ^{13}C-labeled DBK; the labeled DBK itself was synthesized from ^{13}C-labeled (at carbonyl position) phenylacetic acid (Cambridge Isotopes Limited) as reported earlier.[8] Photolysis experiments, on the isomerically pure forms of DPP ([DPP] = 2.2 mM), were performed in aqueous solutions of SDS micelles ([SDS] = 0.1 M). These solutions were thoroughly purged with argon prior to and during photolysis. After photolysis, the reached solutions were extracted with a mixture of methylene chloride/ethyl acetate (1:9) and a known amount of a GC standard was added. Analysis was carried out, after drying over $MgSO_4$, by capillary GC to measure isomer purity and conversion and GC/MS for determination of isotopic content.

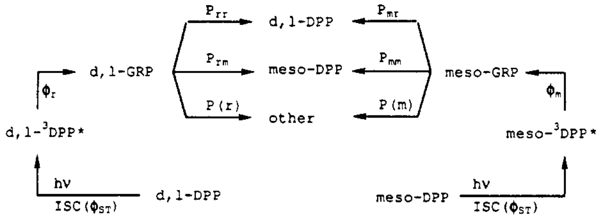
Results and Discussion

Paradigm for Photolysis of DPP in SDS Micelles. Photolysis of *d,l*-DPP in micelle solution results[2c] in the generation of *meso*-DPP (and vice versa for photolysis of *meso*-DPP). Following the conventional paradigm of ketone photochemistry,[3] α-cleavage of DPP occurs and the triplet GRP of *sec*-phenethyl and *sec*-phenethylacyl radicals is generated (Scheme I).

It is known, from simple product analysis, that the primary triplet GRP can then follow three different pathways: (1) decarbonylation of the *sec*-phenethylacyl fragment; (2) escape of one or both of the fragments of the GRP from the micelle to the bulk aqueous medium to form free radicals, generating a secondary geminate pair of *sec*-phenethyl radicals; and (3) geminate combination reactions. Of these, only (3) requires an ISC step. We now consider the quantitative aspects of the rates of these three processes for the pertinent pair in a SDS micelle.

The rate constant of CO (k_{-CO}) elimination in the *sec*-phenethylacyl radical is ca. 5×10^7 s^{-1}.[9] The rates of exit from SDS micelles for radicals[10] with structures related to those in the pair derived from DPP have been measured to be of the order of 10^6 s^{-1}. The rate of decay of structurally related geminate radical pair of benzoyl and cumyl radicals obtained from the photolysis of dimethyldeoxybenzoin, in SDS micellar solution, is[10] ca. 1.2×10^7 s^{-1}. Since the benzoyl radical does not decarbonylate, *all of the intramicellar reactions of the phenethylacyl/phenethyl pair are expected to occur with a rate of the order of* 10^7 s^{-1} *or faster.* Thus, decarbonylation of the *sec*-phenethylacyl radical (ca. 5×10^7 s^{-1}) is expected to be a much faster process than either radical escape (ca. 10^6 s^{-1}) or radical pair recombination (ca. 10^7 s^{-1}) from the triplet GRP produced from photolysis of DPP in SDS micelles. Elimination of carbon monoxide, therefore, restricts the lifetime of the GRP to ca. 22 ns and demands that *all combination processes involving the primary geminate pair occur within the restricted space of the micelle.* The short lifetime of the primary pair prevents the use of conventional nanosecond laser flash photolysis techniques available to us in studying the radical conversion and decay. We are thus compelled to employ steady state photolysis methods which rely on simple measurements of (1) quantum yields (Φ) of disappearance of the starting material and formation of products, (2) conversion of starting material to products (*f*), (3) chemical yields of products (χ) produced from the primary geminate pair, and (4) variation of these observables as a function of the extent of photolysis to probe the issues concerning diffusional trajectory control of reaction probabilities.

SCHEME II: Products and Their Corresponding Probabilities of Formation from the Photolysis of *meso*- and *d,l*-DPP



Photoisomerization and Probability of Radical Pair Recombination. DPP, by the virtue of its two asymmetric carbon atoms, can in principle exist in four unique stereoisomeric forms. However, the presence of a plane of symmetry renders two of these forms (termed collectively, the *meso* form) experimentally indistinguishable. In contrast to the difficulty in separating the two enantiomeric forms of DPP, the two *diastereomeric* forms of DPP [*d,l*-DPP (racemic structure) and *meso*-DPP (optically inactive form)] are readily separable by GC and reverse phase HPLC, allowing for an analytical method of high accuracy.

The photodiastereomerization[2a,c] which interconverts *meso*-DPP and *d,l*-DPP can be viewed as the result of mutual rotation between the radicals comprising the geminate pair (Scheme I). Although the isomerization could result from other mechanisms such as a unimolecular photoenolization which does not involve any carbon–carbon bond cleavage, the absence of any significant photodiastereomerization during photolysis in homogeneous nonviscous solution and the lack of precedence of photoenolization for related structures allows us to rule out such mechanisms.

An interesting stereochemical peculiarity of the system under investigation is the fact that *photoracemization* of DPP cannot result directly from simple α-cleavage occurring in either *d*-DPP or *l*-DPP, followed by a single-step re-formation of the cleaved carbon–carbon bond. This is because α-cleavage from either optically active form can result directly only in regeneration of a combination product with the initial configuration (net retention) or with conversion to *meso*-DPP (diastereomerization). *Photochemical transformation amongst the enantiomeric d and l forms of DPP is only possible via the intermediacy of the meso form.* This fact is critical since it allows us to use eq 1a to describe the change in the concentrations of isomeric DPPs which exist during the course of the photolysis. We now use eq 1a (vide infra) and an approach which employs the probability of primary geminate radical pair return to "knit" back the originally cleaved carbon–carbon bond to obtain information on diffusional trajectories that occur between the instant at which the bond is broken and the moment it is reconstituted. We shall then resort to accurate experimental information obtained from steady state analysis of the extent of starting material conversion and photodiastereomerization during the course of the photolysis, together with experimental information on ^{13}C enrichment of the starting material during the course of the photolysis to probe the question of whether different trajectories of the primary GRP result in different probabilities for product formation.

A Reaction Probability Approach to Photodiastereoisomerization. We now establish a mathematical framework which will relate accurately measurable quantities to the probabilities of return of an initial geminate radical pair produced from a given precursor structure to one of the possible diastereomeric combination products. In terms of this reaction probability approach, we can describe the variation of isomeric concentrations during the course of photolysis according to eq 1a, where the concentrations of *meso*- and *d,l*-DPP are denoted by *m* (*meso*) and *r* (racemic), respectively, $W\phi_r$ and $W\phi_m$ are the specific rates of

$$\mathrm{d}m/\mathrm{d}t = -W\phi_m m(1 - P_{mm}) + W\phi_r r P_{rm}$$

$$\mathrm{d}r/\mathrm{d}t = -W\phi_r r(1 - P_{rr}) + W\phi_m m P_{mr} \qquad (1a)$$

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[8] Zhang, Z. Ph.D. Thesis, Columbia University, 1989.

[9] Gould, I. R.; Baretz, B. H.; Turro, N. J. *J. Phys. Chem.* **1987**, *91*, 925.

[10] Gould, I. R.; Zimmt, M. B.; Turro, N. J.; Baretz, B. H.; Lehr, G. F. *J. Am. Chem. Soc.* **1985**, *107*, 4607.

triplet RP formation (ϕ_r and ϕ_m are the quantum yields of photodissociation and *not* disappearance of the starting material), Φ_i is the absolute quantum yield for disappearance of starting material, i = r or m), and P_{ik} is the probability of geminate recombination in which the subscripts i and k imply a corresponding configuration (i.e., *d,l* or *meso*) of precursor and products, respectively. Scheme II shows the definitions of the probability terms employed in this report. It should be noted that the total probability of all processes from a GRP is unity, i.e., $P_{rr} + P_{rm} + P(r) = 1 = P_{mr} + P_{mm} + P(m)$ where $P(m)$ and $P(r)$ are the probabilities for formation of all products other than recombination to generate the initial substrate structure and its diastereomer, starting from *meso*-DPP and *d,l*-DPP, respectively (Scheme II).

Experimentally, the quantum yields (Φ) for disappearance of *meso*-DPP and *d,l*-DPP in aqueous SDS solutions, are, within experimental error, the same ($\Phi = 0.33$).[2c] During photolysis of *d,l*-DPP in SDS micelles (in the earth's magnetic field), the chemical yield, χ_r^m, of the *meso* isomer extrapolated to zero conversion of ketone is ca. 9.7%; the chemical yield, χ_m^r, of *d,l*-DPP obtained from photolysis of *meso*-DPP is also ca. 9.7%. The GRP produced from photolysis of DPP also undergo disproportionation to produce 2-phenylpropanal and styrene to a minor degree. The elimination of CO transforms the primary GRPs into the secondary GRP comprising two identical *sec*-phenethyl radicals. These pairs recombine to produce either *d,l* or *meso* 2,3-diphenylbutanes (the actual ratio observed by us was *meso*:*d,l* = 1.040 ± 0.005) or disproportionate to form styrene and ethyl benzene. The only reactions studied in this report involve the primary GRP, and hence no mention is made of other reactions in Scheme I. Most (ca. 80%) of the consumed DPP undergoes decarbonylation and results in products derived from the secondary *sec*-phenethyl radicals. We emphasize that we are investigating a small fraction of the net reaction but that the pathways of interest to this study contain unique and intriguing mechanistic information.

The chemical yield (χ_r^m) of *meso*-DPP isomer from photolysis of *d,l*-DPP, *under the limit of small conversions*, in terms of probabilities of recombinations is given by $\chi_r^m = P_{rm}/(P_{rm} + P(r)) = P_{rm}/(1 - P_{rr})$, since the sum of all reaction probabilities from a given substrate equals unity, i.e., $1 = (P_{rm} + P(r) + P_{rr})$. Similarly, the corresponding yield of *d,l*-DPP from *meso*-DPP is given by $\chi_m^r = P_{mr}/(1 - P_{mm})$. The most probable interpretation of the observed equivalence ($\chi_r^m \sim \chi_m^r \sim 9.7\%$) between these two chemical yields is that $P_{mr} \approx P_{rm}$ and $P_{mm} \approx P_{rr}$ and the implication of the observed equality of quantum yields of disappearance is $P_{mm} \approx P_{rr}$.

One would expect that determination of quantum yields and chemical yields should serve as useful mechanistic parameters to obtain information concerning the probabilities, of the GRP, P_{ik}. Unfortunately, however, we find experimentally that neither the quantum yields of disappearance (Φ), as reflected by the slope of a plot of conversion (f) as a function of time (Figure 1a) nor the chemical yield of *meso*-DPP (Figure 1b), as judged by the slope of the plot of concentration of *meso*-DPP as a function of total conversion, are constant during the duration of the entire photolysis. The lack of linearity in these plots prevents the extraction of the mechanistic insights that are expected to be obtained from simple correlations between experimental observables. Furthermore, the above observations which imply the approximate equivalences $P_{mr} \approx P_{rm}$ and $P_{mm} \approx P_{rr}$ do not, for example, reveal anything about the relationship between P_{mr} and P_{mm}, i.e., are these probabilities equal or not? To answer such questions, we search for a more stringent analysis of eq 1a.

A Novel Approach to the Determination of Recombination Probabilities from Steady State Observables. We now present an analysis which establishes relationships between simple and accurately measured experimental quantities (the extent of conversion and the diastereomeric excess) and the related probabilities of recombination, P_{ik}. Such considerations allow for conclusions to be drawn concerning the interrelationships between the various P_{ik}s from Schemes I and II and the mechanism of the combination reaction pathways available to the primary geminate pairs.

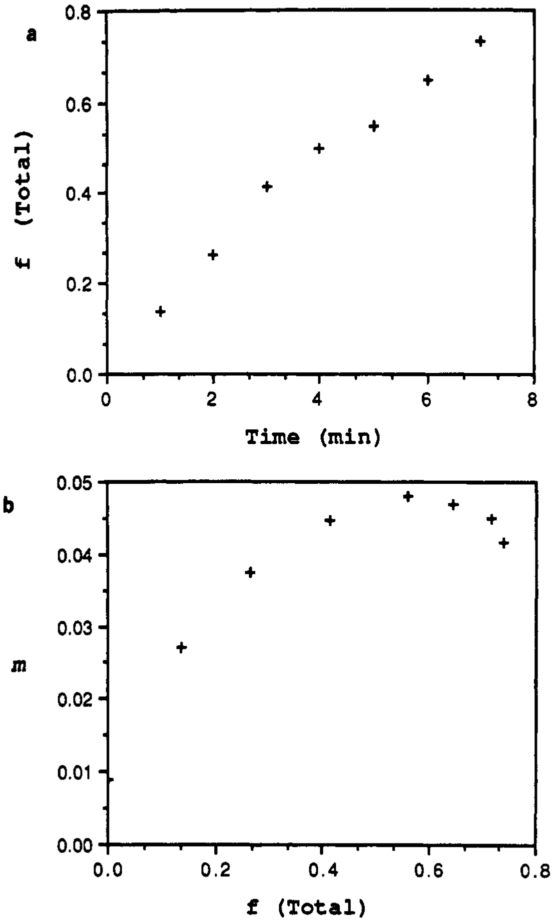

Figure 1. (a) Total conversion of DPP as a function of photolysis time at magnetic field of 30 G (high optical density). (b) Concentration of *meso*-DPP (in arbitrary units; *d,l*-DPP is substrate) as a function of total conversion.

We define $Z = (m - r)/(m + r)$ as the diastereomeric purity (Z_0 is the initial diastereomeric purity). Therefore starting with isomerically pure *meso*-DPP or *d,l*-DPP leads to Z_0 = 1 or −1, respectively. We also define parameter S in eq 2a, in analogy

$$S = \partial \ln (Z/Z_0)/\partial \ln (1 - f) \qquad (2a)$$

to the previously employed magnetic isotope separation efficiency parameter,[11,12] where $f = [(m + r)_0 - (m + r)]/[(m + r)_0]$ is the total conversion of the ketone. The value of S characterizes the efficiency of isomerization due to recombination of the GRP and can be considered as a one-stage isomerization efficiency. In the limit of zero conversion this value is given by eq 2b. The coordinates of eq 2b are obviously more convenient for experimental measurement.

$$S = \ln (Z/Z_0)/\ln (1 - f) \qquad (2b)$$

Measurements of $\ln (Z/Z_0)$ as a function of $\ln (1 - f)$ are shown in Figures 2a and 2b and these plots reveal an excellent linear dependence between $\ln (Z/Z_0)$ and $\ln (1 - f)$ so that the slopes may be measured with high precision. From the figures, it is found that the slope from the photolysis of *meso*-DPP, $S_m = 0.2314 \pm 0.0032$, does not equal the slope obtained from the photolysis of *d,l*-DPP, $S_r = 0.1984 \pm 0.0053$ (in both the cases the photolysis was performed between the poles of an electromagnet with a residual magnetic field, $\mathbf{B}_{res} \approx 31$ G; note that the value of S is in units of eq 2b).

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(11) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369. Turro, N. J.; Kraeutler, B. Magnetic Isotope Effects in *Isotope Effects*, Vol. 6; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1984; pp 107–160. Gould, I. R.; Turro, N. J.; Zimmt, M. B. Magnetic Field and Magnetic Isotope Effects on the Products of Organic Reactions. *Adv. Phys. Org. Chem.* **1984**, *20*, 1–53.

(12) Buchachenko, A. L. *Prog. React. Kinet.* **1984**, *13*, 163.

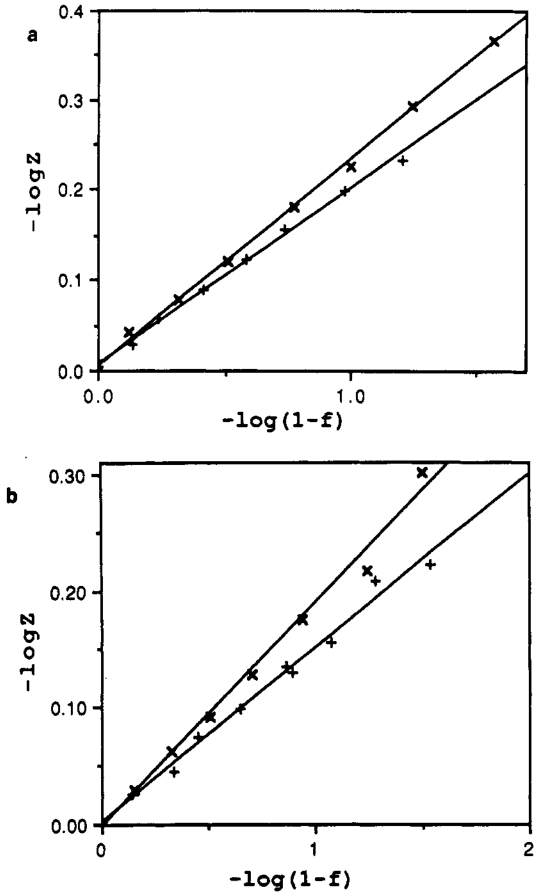

Figure 2. Applicability of eq 2a to the photodiastereomerization of DPP at (a) low (31 G) magnetic field and (b) at high (3000 G) field (*x*, *meso*-DPP; +, *d,l*-DPP).

From an analysis of eq 1a and from the definition of S (eq 2a), there is only one case where the value of S is exactly constant. This occurs when $\phi_r = \phi_m$ (the quantum yields for α-cleavage of each diastereomer are exactly equal) and $P_{rr} = P_{mm} = P_{ret}$ (probabilities of recombination with retention of configuration are exactly equal) and $P_{rm} = P_{mr} = P_{inv}$ (probabilities of recombination with inversion of configuration are exactly equal). Under these stringent conditions, there is no stereospecificity in the reactions of photodissociation and no stereoselectivity in the reactions of recombination. However, when these conditions are met we find $S_r = S_m = 2P_{inv}/(1 - P_{inv} - P_{ret})$, which is inconsistent with our experimental observations that $S_r \neq S_m$ (vide supra). This lets us conclude that at least one of the equalities ($\phi_r = \phi_m$, $P_{rr} = P_{mm}$, or $P_{rm} = P_{mr}$) considered above is not maintained, and it is appropriate to attempt to determine whether this equality can be determined with a small experimental error.

Since the measured difference between S_m and S_r is small, we consider some cases for which a linear dependence of ln (Z/Z_0) on ln $(1 - f)$ is not strictly observed but is experimentally observable only for large conversions (greater than 70%; see Figure 2). By "not strictly" we mean that the mathematical form of the relationship is not linear; however, the deviations from linearity are smaller than our experimental accuracy for small conversions and it is only for large conversions that these deviations (which increase with increasing conversions) can be experimentally measured.

Limiting Cases and Experimental Tests for These Cases. In the first instance, let us assume a limiting case for which the following equalities apply (note they are different from the example discussed in the previous section), $P_{rm} = P_{mm} = P_m$, $P_{mr} = P_{rr} = P_r$, and $\phi_r = \phi_m$. This limiting case means that stereochemical reorientation of the radicals is fast relative to the rate of ISC (i.e. $k_{rot} \gg k_{ISC}$; Scheme I), so that stereochemical information contained in the precursor structure is completely lost before the combination occurs. However, there still may be some energetic preference which causes the preferential formation of one isomer relative to another (i.e. there is *product control* in the combination step so that P_m is not equal to P_r). These conditions imply that the probability of recombination is completely determined by the stereochemical configuration of the product and is independent of the precursor stereochemistry. The lack of stereoselectivity in radical pair recombination in homogeneous solution is well known but the restriction of the diffusional motion of the radicals in restricted volumes may induce some selectivity in the recombination stage.[13]

Thus, we can seek to determine if P_m equals P_r or not. Any difference between P_m and P_r, however, must be consistent with the experimental observation that the values of S are experimentally constant and that S_m is not equal to S_r. From the definitions 2a and eq 1a, simple but extended algebraic manipulations show that S may be given by eq 3a and the experimentally constant value of S implies that $|P_m - P_r|/(P_m + P_r) \ll 1$. In this case, which we call the limit of fast reorientation, we find from eqs 1a and 2a that S is

$$S = \frac{P_m + P_r}{1 - P_m - P_r}\left[1 + \frac{P_r - P_m}{P_m + P_r}\frac{1}{Z'}\right] \tag{3a}$$

where Z' is the approximate middle point, $Z' \approx (Z_0 + Z)/2$.

Since the term in the parentheses of eq 3a possesses a different mathematical sign for the two diastereomeric substrates defined by Z' we have $(S_m + S_r)/2 = P/(1 - P)$, where $P = P_r + P_m$ is the total recombination of the GRP; subtraction of the two slopes, on the other hand, leads to the conclusion that $P_r > P_m$ and $P_r - P_m \approx 0.015$. We can conclude, therefore, that if this limiting condition is realized, it is possible to evaluate the total probability of recombination ($P_r + P_m$) from the products of photolysis starting with two pure substrates and to estimate the magnitude of the difference between P_r and P_m.

There is also a second limiting case to explain an experimental constant value of S. This case can be formulated as the condition where $P_{rm} = P_{mr} = P_{inv}$ and $P_{rr} = P_{mm} = P_{ret}$ but for which a difference in the quantum yield of dissociation $\delta\phi$ for the two isomeric substrates is allowed to exist. Again the requirement of the experimental constancy of S imposes the limitation that $\delta\phi Z' = (\phi_m - \phi_r)Z' \ll 1$. This second limiting case corresponds to the lack of stereoselectivity in the formation of combination products from the geminate pair. In this limit eq 3b instead of eq 3a applies

$$S = \frac{2P_{inv}}{1 - P_{inv} - P_{ret}}\left[1 + \frac{1 - P_{ret} + P_{inv}}{2P_{inv}}\delta\phi\frac{1 - Z'^2}{Z'}\right] \tag{3b}$$

The term in the bracket in eq 3b, as in the case of eq 3a, has different signs for the two diastereomeric substrates. Addition of the slopes in this instance gives $S = S_m + S_r = 2P_{inv}/(1 - P_{inv} - P_{ret})$ and subtraction leads to the value of $\delta\phi$ from which the conclusion is made *that if the limit of no stereoselectivity is achieved then the quantum yield of photodissociation of meso-DPP is larger than that of d,l-DPP* ($\phi_m > \phi_r$) *and that* $\phi_m - \phi_r \approx 0.06 \pm 0.02$.

The conclusion that ϕ_m is not exactly equal to ϕ_r is experimentally verifiable by an independent photolysis experiment with DPP in homogeneous nonviscous solutions where geminate recombination may be neglected due to the fast separation of the RPs (i.e. $P_{ik} = 0$). Under these conditions eq 3c follows from eq 1a. From photolysis on a known mixture of isomers, carried out

$$\ln (r/r_0) = \phi_m/\phi_r \ln (m/m_0) \tag{3c}$$

in methanol solution, we determine from the slope of a plot of eq 3c (see Figure 3) $\phi_m/\phi_r = 1.060 \pm 0.005$, which is in reasonable agreement with the value estimated above using eq 3b. This means that the estimated value of $(P_r - P_m) \approx 0.015$ (vide supra) is an upper bound and that the limit of lack of stereoselectivity in recombination is physically not unrealistic.

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[13] Ghatlia, N. D.; Turro, N. J. *J. Photochem. Photobio. Chem.: A* **1991**, *57*, 7. Brittain, W. J.; Porter, N. A.; Krebs, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7652.

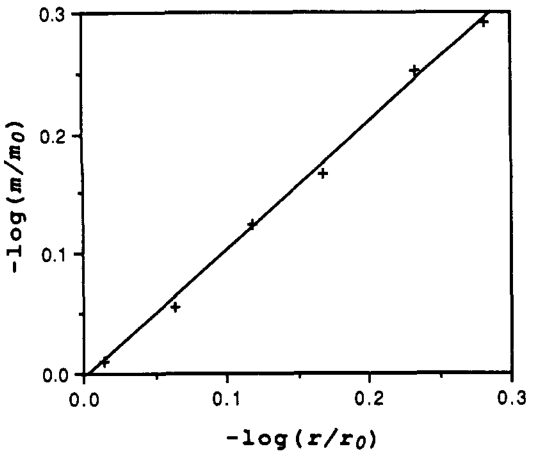

Figure 3. Change in isomer purity of DPP during photolysis in methanol solution (slope = 1.061; corr coeff = 0.999).

Estimation of the Relative Time Constants for Competing Processes of the Primary Geminate Radical Pair. The limit of lack of stereoselectivity ($P_{rm} = P_{mr} = P_{inv}$ and $P_{rr} = P_{mm} = P_{ret}$) does not impose any limitation on the relative values of τ_{rot} (k_{rot}) and τ_{ISC} (k_{ISC}). We now seek to estimate the range of the values of τ_{rot} and τ_{ISC} from experimental measurements. The rotational correlation time (τ_c) of 2,2,6,6-tetramethylpiperidin-1-oxyl–4-benzoyl radical solubilized in SDS micelles is about 0.6 ns[12] and for smaller nitroxyl radicals, e.g., di-*tert*-butylnitroxyl and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy, the time τ_c is ca. 60 ps and 0.2 ns, respectively.[14] The fragments of the RP generated from DPP are intermediate in size between these two radicals and are therefore expected to have a corresponding intermediate value (between 0.06 and 0.6 ns) for τ_c.

If $\tau_c \ll \tau_{ISC}$, then the relative orientations of the RP in the singlet state at the moment of contact (assumed to be the moment of bond formation) will have achieved an equilibrium statistical distribution that is independent of the precursor stereochemistry; however, if τ_c and τ_{ISC} are comparable, then the relative orientation of radical fragments in the singlet contact state will be a function of stereochemistry of their precursor and the initial orientation. If the ISC rate for RP obtained from DPP would be determined by hyperfine interaction, its charcteristic time τ_{ISC}, according to quasiclassical theory[15] of magnetic effects, would be ca. 1 ns for RP possessing a ^{12}C nucleus at the carbonyl group ($\tau_{ISC^*} \approx 0.3$ ns for DPP with ^{13}C in the carbonyl group).

Therefore, from experimental estimates of τ_c and estimates of the range of the characteristic times of hyperfine induced ISC, we find that for ^{12}C RP and for ^{13}C RP the ranges for the ratios of characteristic lifetimes of $\tau_c/\tau_{ISC} \approx 0.5$–$0.05$ and $\tau_c/\tau_{ISC^*} \approx 2$–$0.2$, respectively. This analysis clearly shows that there is no obvious reason to neglect possible differences between P_{mr} and P_{rr} and between P_{rm} and P_{mm}, especially for those RPs with a ^{13}C at the carbonyl position, for which ISC and rotational correlational times are predicted to be competitive for the entire range of estimated typical values.

Interactions due to electron exchange for RPs that remain in close proximity throughout all trajectories can lead to a suppression of the rate of ISC resulting from hyperfine-induced ISC, yet close proximity should also lead to an enhancement of the rate of ISC resulting from spin–orbit coupling. These issues are raised here only to emphasize the fact that it is not possible to make a clear prediction concerning the effect of trajectories because of compensating distance-dependent factors.

Thus, the analysis of experimental data shows that if the recombination of *sec*-phenethylacyl/*sec*-phenethyl triplet GRP in micelles takes place in the limit of fast reorientation with a small thermodynamic preference to form the *d,l* isomer, then the total recombination probability (P) of the triplet GRP can be measured. If, however, recombination occurs with a lack of stereoselectivity for any of the diastereomers and with different quantum yields of dissociation for the two isomeric forms, then no conclusions can be drawn regarding the relationship between P_{inv} and P_{ret}.

The recombination of the secondary GRP (RP resulting from decarbonylation) occurs with a slight stereoselectivity since the relative yields of the *meso*- and *d,l*-diphenylbutanes are slightly different (vide supra). But in this instance the initial distance between the secondary radicals, which is proportional to the square root of the lifetime of the *sec*-phenethylacyl radical, is likely to be ~8–10 Å. Under these conditions there is no physical meaning to the question of whether $P_{inv} = P_{ret}$ for the phenethyl radicals because during the time that these radical fragments take to achieve the reactive contact state the orientation of the radicals will have randomized. Nevertheless, the presence of a small stereoselectivity in the diphenylbutane formation may be used to argue that some stereoselectivity may exist for the formation of DPP isomers too.

The major question that we wanted to answer concerned the relationship between the probabilities of inversion and retention, P_{inv} and P_{ret}, i.e., are they equal or not? Fast reorientation ($\tau_c/\tau_{ISC} \ll 1$) leads to a randomization of the RP stereochemistry and effectively settles the issue, i.e., P_{inv} equals P_{ret} exactly. However, if the hypothesis regarding the lack of stereoselectivity is not correct and that regarding $\delta\phi$ is valid, then the slopes of Figures 2 and 3 contain information concerning P_{inv} and P_{ret} and the question concerning their possible equality remains both relevant and unanswered experimentally.

To address this issue we consider the behavior of RPs possessing a ^{13}C label at the carbonyl position. For these molecules the condition of fast reorientation is far from settled (vide supra: $\tau_c/\tau_{ISC} \sim 1$) and hence such labeled pairs provide an ideal system for our study. Although experiments could be conducted measuring quantum yields with 100% labeled material, we opted instead to study the isotope separation due to magnetic isotope effects since the GRPs of different isotopes in such an experiment are reacted and analyzed under identical conditions (temperature, light intensity, wavelength, instrumental analysis, etc.), thereby insuring the highest degree of experimental accuracy and precision.

Magnetic Isotope Effect and the Separation of Isotopes ^{13}C/^{12}C during the Photolysis of *d,l*-DPP. The theoretical framework and experimental results concerning magnetic isotope effects (MIE) and isotope separation under photolysis of different ketones are well defined and the subject of several papers and reviews.[7,11,12] Because of the analogous mechanistic basis for the trajectories of RPs involved in ^{13}C separation by the MIE and the RPs involved in the diastereoisomerizations under investigation in this report, we have attempted to use the MIE as a probe for spin and molecular dynamics rather than making it the primary focus of our study.

The changes of concentration of labeled ketone and the corresponding diastereomer, similar to eq 1a, are described by eqs 1b, where the parameters are defined with the same sense as for eq 1a, except that the * denotes material with a ^{13}C label at the carbonyl group, and where W is the specific rate of photogeneration of GRP and GRP*.

$$\mathrm{d}m^*/\mathrm{d}t = -W\phi_m{}^*m^*(1 - P_{mm^*}) + W\phi_r{}^*r^*P_{rm^*}$$
$$\mathrm{d}r^*/\mathrm{d}t = -W\phi_r{}^*r^*(1 - P_{rr^*}) + W\phi_m{}^*m^*P_{mr^*} \qquad (1b)$$

Since we are dealing with small effects, we must consider the possibility of a classical mass isotope effect on the quantum yield of photodissociation. For simplicity we assume that $\phi_m/\phi_{m^*} = \phi_r/\phi_{r^*} = (\phi_m + \phi_r)/(\phi_{m^*} + \phi_{r^*})$ or Q, the classical mass isotope effect in the reaction of photodissociation. This isotope effect may be manifest in different stages such as the act of absorption of light, during the ISC from the excited singlet state and during the act of the dissociation of the carbon–carbon bond itself (see for example, a discussion on the photodissociation of acetone[16]).

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(14) (a) Ottaviani, M. F.; Baglioni, F.; Martini, G. *J. Phys. Chem.* **1983**, *87*, 3146. (b) Atherton, N. M.; Strach, S. J. *J. Chem. Soc., Faraday Trans. II* **1972**, 374.

(15) Schulten, K.; Wolynes, P. G. *J. Phys. Chem.* **1978**, *68*, 3292. Schulten, K.; Epstein, I. R. *J. Chem. Phys.* **1979**, *71*, 309.

(16) Gehrz, M.; Brauchle, C.; Voitlander, J. *Mol. Phys.* **1984**, *53*, 769.

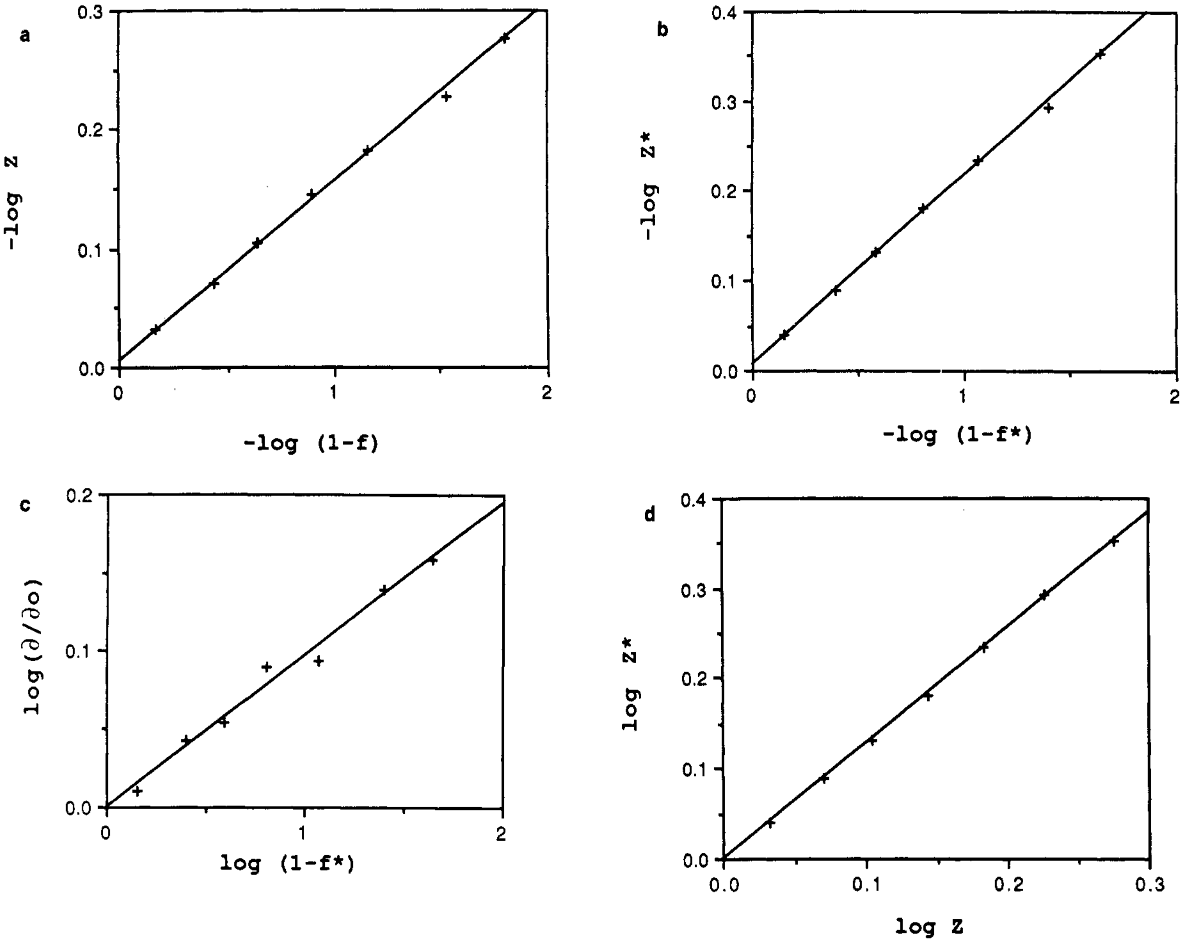

Figure 4. Plots at 900 G for (a) efficiency of photoisomerization of unlabeled *d,l*-DPP (eq 2a), (b) efficiency of photoisomerization of ^{13}C-labeled *d,l*-DPP, (c) efficiency of isotope separation for DPP as judged by conversion (α parameter), and (d) efficiency of isotope separation in DPP as judged by isomerization (β parameter, eq 5).

TABLE I: Experimentally Determined α and β Parameters at Different Magnetic Fields[a]

H (G)	α	β	S_r	S_r^*
0	1.1111 ± 0.0042	1.2363 ± 0.0072	0.1990 ± 0.0038	0.2731 ± 0.055
30	1.1164 ± 0.0051	1.2651 ± 0.0094	0.2002 ± 0.0041	0.2827 ± 0.0050
60	1.1213 ± 0.0070	1.338 ± 0.011	0.1862 ± 0.0039	0.2797 ± 0.0050
260	1.1245 ± 0.0034	1.383 ± 0.012	0.1589 ± 0.0033	0.2481 ± 0.0038
900	1.0976 ± 0.0045	1.2811 ± 0.0071	0.1522 ± 0.0018	0.2143 ± 0.0021
3000	1.0901 ± 0.0030	1.2434 ± 0.0092	0.1524 ± 0.0045	0.2067 ± 0.0052

[a] All values are the result of averaging 8 measurements at different conversions.

We define α as the efficiency of isotope separation due to magnetic isotope effects (MIE) according to the total isotope content irrespective of content in the individual isomers, in the usual way[17] as given in eq 4, where f is the total conversion of unlabeled ketone and f^* is the total conversion of the labeled ketone, respectively (see Appendix).

$$\alpha = \partial \ln (1 - f)/\partial \ln (1 - f^*) \qquad (4)$$

A comparison of the equations for the efficiency of diastereomerization and the efficiency of isotopic separation suggests a relationship between the isomerization of the labeled and unlabeled DPP given in eq 5. β, in eq 5, is a new isotope separation efficiency parameter since, in contrast to α, it is not directly dependent upon conversion.

$$\beta = \partial \ln (Z^*/Z_0^*)/\partial \ln (Z/Z_0) \qquad (5)$$

α can be measured in a conventional way,[11,12,18] as seen in Figure 4c, using the relationship $\ln (\delta/\delta_0) = (\alpha - 1) \ln (1 - f^*)$, where δ is the ^{13}C isotope content in the carbonyl group (see Appendix). Figure 4a shows that the proportionality between $\ln (Z^*/Z_0^*)$ and $\ln (Z/Z_0)$ is maintained with excellent accuracy. Therefore, α and β are measured directly from these plots and not as the derivatives. In contrast to the S values, which are different depending on the stereochemistry of the substrate, both α and β are, within experimental error, the same whether they are evaluated from the photolysis of the *d,l*-DPP or the *meso*-DPP (α and β from the photolysis of *d,l*-DPP are 1.1111 ± 0.0042 and 1.2363 ± 0.0072, whereas the corresponding values from the photolysis of *meso*-DPP are 1.1153 ± 0.0084 and 1.2300 ± 0.0011). This allows us to evaluate α and β starting with pure *d,l*-DPP as our substrate.

Experimentally, four parameters may be determined: S, S^*, α, and β. These parameters are presented in Table I. However, only three of the four parameters are independent since $\alpha\beta = S^*/S$ is obvious from eqs 2, 4, and 5.

In the first part, we showed that the experimental data could be considered under two limiting cases: (1) the lack of stereoselectivity for combination processes of the GRPs ($P_{\mathrm{rm}} = P_{\mathrm{mr}}$ and P_{inv} and $P_{\mathrm{rr}} = P_{\mathrm{mm}} = P_{\mathrm{ret}}$) with a difference in quantum yield of photodissociation ($\phi_{\mathrm{m}} - \phi_{\mathrm{r}} \neq 0$) for the two different isomers and (2) the presence of stereoselectivity for the formation of one isomer,

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[17] Bernstein, R. B. *J. Phys. Chem.* **1952**, *56*, 893. Bernstein, R. B. *Science* **1957**, *126*, 119.

[18] Tarasov, V. F.; Buchachenko, A. L. *Bull. Acad. Sci. USSR., Ser. Chem.* **1983**, 82. Tarasov, V. F.; Buchachenko, A. L. *Bull. Acad. Sci. USSR., Ser. Chem.* **1983**, 86.

TABLE II: Calculated (from S_r and S_r^*) α_c and β_c Parameters and Their Comparison with Experimentally Determined Values (Table I) for α and β; Probabilities of Recombination at Different Magnetic Fields[a]

H (G)	α_c	β_c	α/α_c	β_c/β	P	P^*
0.	1.0618	1.2925	1.0464	1.0455	0.166	0.215
30	1.0687	1.3213	1.0446	1.0444	0.167	0.220
60	1.0788	1.3924	1.0394	1.0407	0.157	0.219
260	1.0770	1.4498	1.0441	1.0483	0.137	0.199
900	1.0539	1.3360	1.0415	1.0429	0.132	0.177
3000	1.0471	1.2953	1.0411	1.0417	0.132	0.171

[a] $Q = 1.0434 \pm 0.0029$.

in the limit of fast reorientation, in the recombination step with no difference in the quantum yields of photodissociation ($\phi_m - \phi_r = 0$). The second limiting case already contains the assumption that we wish to test, i.e., whether $P_{inv} = P_{ret}$ ($P_{inv}^* = P_{ret}^*$) for each pair of chemical routes (i.e., $P_{mr} = P_{rr}$, $P_{rm} = P_{rr}$, and corresponding equations for labeled material). This case is not of interest to us, since it is precisely the equality or the lack thereof between P_{inv} and P_{ret} that we wish to determine experimentally. On the other hand, the first limiting case does indeed allow for the possibility that the inequalities $P_{inv} \neq P_{ret}$ ($P_{inv}^* \neq P_{ret}^*$) occur.

In the latter limiting case, we must determine the contribution of the classical mass isotope effect, Q. In this regard we note the relationships between the observables α and β (obtained from eqs 4 and 5) given in eqs 6 and 7, where $P = (P_{inv} + P_{ret})$ and $P^* = (P_{inv}^* + P_{ret}^*)$ are the total recombination probabilities.

$$\alpha = Q(1 - P)/(1 - P^*) = Q\alpha_c \tag{6}$$

$$\beta = P_{inv}^*/(QP_{inv}) = \beta_c/Q \tag{7}$$

We have only three independent equations for determining five (P_{inv}, P_{ret}, P_{inv}^*, P_{ret}^*, and Q) unknowns and hence we can only attempt to verify certain simplifying suppositions. First, let us assume that $P_{inv} = P_{ret}$ and P_{inv}^* and P_{ret}^*. Under this simplification, we have, using eqs 3b, 4, 5, 6, and 7, the additional identities given by eqs 8a and 8b that may be employed.

$$\beta = 1/Q[(1 + S^*)/(1 + S)](S^*/S) \tag{8a}$$

$$\alpha = Q(1 + S^*)/(1 + S) \tag{8b}$$

The experimental checks of the identities in eqs 8a and 8b are the tests for our starting supposition. We have used the experimentally determined values of S and S^* to calculate P and P^*. The applicability of our assumption (i.e., $P_{inv} = P_{ret}$) should be independent of the strength of an applied external magnetic field but the absolute magnitude of the probabilities, and therefore the S values, *should* be a function of the external field. This circumstance allows for the test of our supposition under conditions where we can manipulate the absolute value of the experimentally measured parameters (i.e., the probabilities of recombination) while in no way modifying the validity of our assumption. The calculated values of P and P^* are used to determine α_c and β_c according to eqs 6 and 7. These values are presented in the second and third columns of Table II. Comparison of α with α_c and β with β_c leads us to the calculated value of Q. Corresponding values are placed in the third and fourth columns of Table II; it is seen that α/α_c and β_c/β are approximately equal to each other for all magnetic fields investigated. This constant and equal ratio of α/α_c and β/β_c at all the fields lets us conclude that this is not a fortuitous circumstance and that the ratio is a mechanistic parameter that is probably independent of the magnetic nature of the isotope. However, the force of this last conclusion is not very strong because of the expectation that the deviations due to magnetic field effects on Q are of the order of the experimental error. In any case, the observed experimental finding that $Q = 1.043 \pm 0.0029$ is a key point for our discussion.

Since other possibilities in addition to the classical isotope effect may be invoked to explain the discrepancy between α and α_c and β and β_c, we must consider these possibilities and eliminate them for our arguments concerning reaction probabilities to be valid. These possibilities are (1) unequal quantum yields of dissociation for the two isomers (i.e. $\phi_m \neq \phi_r$), (2) the presence of a small stereoselectivity for recombination to yield preferentially one diastereomer, and (3) isotope enrichment in positions other than the carbonyl position. The concerns raised by these possibilities are addressed below.

The neglect of any possible stereoselectivity in recombination leads to a correction of approximately 0.004 to $(Q - 1)$. This however is not significant since this correction to $(Q - 1)$ is an order of magnitude less than the actual value of $(Q - 1)$, i.e., 0.043 ± 0.0029.

Another source of experimental error that we have not yet considered is a change in the isotope content at carbon atoms other than the carbonyl atom. For $(\alpha - 1) \leq 0.2$, eq 9 is valid, where

$$N(1 - 1/\alpha') = \sum_k \delta_k{}^0(1 - 1/\alpha_k) \tag{9}$$

N is the number of carbon atoms in the molecule, α_k is the separation efficiency coefficient for the kth carbon, $\delta_k{}^0$ is the initial content of ^{13}C in the kth position, and α' is an average coefficient. The left side of eq 9 represents the experimentally obtained α. The correction to α_{CO} can be calculated after considering that $\delta_{CO}{}^0 = 0.35$, $\delta_k{}^0 = 0.011$ for all other carbon atoms, and the known dependence of α_k for DBK.[19] The resulting correction of ~0.2% cannot account for deviations on an observable scale with our experimental conditions.

The isotope separation efficiency parameter α for photolysis of DBK in benzene (MIE under these conditions is comparable with the classical isotope effect) is 1.027[20a] or 1.040 ± 0.020.[20b] Besides dissociation, kinetic effects could arise in the decarbonylation of the acyl radical (in this case α should be >1) and the recombination of the RP (these effects are contained in α_c and β_c). These last two contributions are negligible for photolysis in the gas phase at 550 K where $\alpha \approx 1.036$ for DBK.[20c] Since MIE can be neglected too for the reaction in the gas phase, the value of Q is in good agreement with the value for α in simple homogeneous solutions for DBK and is of the order of an expected value for a classical isotope effect.

However, there is still one more possibility which is useful to consider. Suppose $P_{inv} = P_{ret}$ but $P_{inv}^* \neq P_{ret}^*$ and the value of the one-stage isotope separation due to the classical isotope effect in photodissociation is smaller than 1.043. In the frame of this approximation we find that $P_{ret}^*/P_{ret} > P_{inv}^*/P_{inv}$ or in other words that the closer GRPs are more sensitive to hyperfine interactions than the more distant GRPs. This is possible for the case of low magnetic fields if exchange interaction in the GRP recombining without inversion is positive but is negative for GRP recombination with inversion. Although conceivable, there is no precedent or obvious physical basis for such a situation. Furthermore, $P_{ret}^*/P_{ret} > P_{inv}^*/P_{inv}$ also holds for high magnetic fields (Table I). Therefore, this approximation could be considered as unlikely since the ST$_-$ mechanism of ISC in RP is inoperative at high magnetic fields. To have a more physically possible situation of $P_{ret}^*/P_{ret} < P_{inv}^*/P_{inv}$, we are forced to assume that $Q > 1.043$, which is again unprecedented and appears to be extremely unlikely.

Note that even if one were to know the exact value of Q, one could not determine P_{ret} and P_{inv} individually without additional suppositions, nor could one evaluate a difference between them. *A steady state photoisomerization or photoracemization experiment does not, even in principle, allow us to measure the difference between P_{ret} and P_{inv} but can allow us to determine if such a difference does indeed exist.*

In summary, the experiments performed are completely consistent with the assumption that $P_{ret} = P_{inv}$ under conditions of very high experimental accuracy. It is most likely that the classical isotope effect is the basis for the differences in α and β obtained

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[19] Turro, N. J.; Chung, C.-J.; Lawler, R. G.; Smith, W. J., III *Tetrahedron Lett.* **1982**, *23*, 3223. Tarasov, V. F.; Askerov, D. B.; Buchachenko, A. L. *Bull. Acad. Sci. USSR., Ser. Chem.* **1982**, 2023.

[20] (a) Turro, N. J.; Kraeutler, B. *J. Am. Chem. Soc.* **1978**, *100*, 7432. (b) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Kraeutler, B. *J. Am. Chem. Soc.* **1981**, *105*, 3886. (c) Step, E. N.; Tarasov, V. F. Unpublished results.

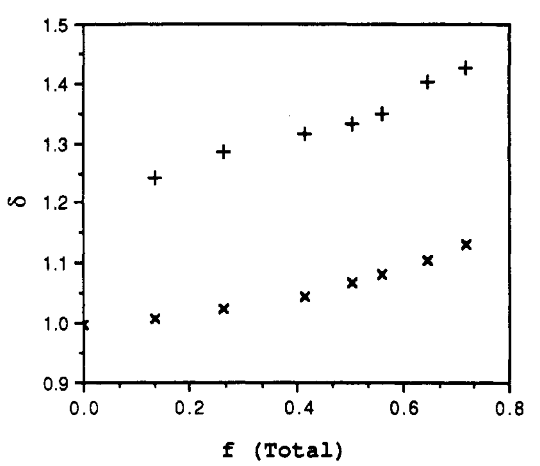

Figure 5. Dependence of isotope content of carbonyl group (δ) in *d,l*-DPP (×) and *meso*-DPP (+) (*d,l*-DPP is substrate) at 30 G.

directly and α_c and β_c calculated from probabilities found from the photoisomerization experiment. Equations 2, 6, and 7 and identities 8a,b may be considered as rules for the determination of P, P^*, and Q parameters.

Thus, the results and discussion in this paper show that the possibility that different trajectories of radical pairs from DPP result in different stereochemical consequence on the combination products is not valid within the experimental accuracy of our measurements.

Note that the ratio of recombination probabilities of magnetic and nonmagnetic RPs for the case of dibenzyl ketone 1.27[18] and DPP 1.32 (this work) are approximately the same. It implies that magnetic isotope effects originate in contact RPs, but the efficiency of isotope separation to a strong extent depends upon the cage effect, since α for the case of DBK is equal to 1.209 ± 0.008[21] in the same conditions.

In this respect, it is useful to observe that our analysis yields the conversion dependences of δ_m and δ_r (see Figure 5, obtained from photolysis of *d,l*-DPP), which are very similar to the dependences of isotope (^{13}C) content in the carbonyl group of the starting cycloalkanone and corresponding cyclophane[6] formed during the photolysis of α-phenylcycloalkanones. One should emphasize that the sharp increase in the ^{13}C content of the isomeric material is a result of the lack of dilution of the ^{13}C pool in the new isomer as opposed to the generation of starting material, i.e., the kinetics of isotope enrichment to a large extent and not the difference in MIE in ISC of closed and open biradicals is the reason for the sharp increase of the ^{13}C content for cyclophane in the photolysis of the cycloalkanones at small conversions since it follows from eqs 1a and 1b that for small conversions, starting from *d,l*-DPP, the ratio of the isotope content in the meso isomer to that in the starting ketone = $P_{inv}^*/P_{inv} = P^*/P$. Enrichment of tolyl benzyl ketone (the side product of dibenzyl ketone photolysis) demonstrates the same behavior.[22] Nevertheless, for the case of biradicals, the more restricted mutual rotation of radical centers can in principle provide for a difference in the sensitivity of open and closed biradicals to hyperfine interaction because of exchange interaction and spin–orbit coupling.

Conclusions

We have demonstrated that by a novel mathematical treatment and accurate experimental analysis, the phenomenon of photodiastereomerization can be used to determine directly the probability of recombination of geminate radical pairs in micellar aggregates. In SDS micelles the probability of recombination for the primary *sec*-phenethylacyl/*sec*-phenethyl GRP at 0 field is 0.166 and at high field is 0.132. For the same GRP with a ^{13}C label at the carbonyl position the corresponding probabilities at low and high field are 0.215 and 0.171.

The slopes of the lines (which are functions of the probability of recombination) obtained from the application of eq 2 to the *meso* and *d,l* isomers are slightly different. This difference is rationalized on the basis of either unequal efficiencies of α-bond cleavage ($\delta\phi$) or on the basis of different probabilities of recombination to form the *meso* and *d,l* isomers of DPP. Although it is not possible, with the experimental data at hand, to determine which of these factors is responsible for the unequal slopes, we can determine that if $S_m \neq S_r$ due to $\delta\phi = 0$, then $\phi_m > \phi_r$, or if $S_m \neq S_r$ due to differences in probabilities of recombination, then the GRP prefers to recombine to form *d,l*-DPP with a slight preference.

We have also demonstrated that the primary *sec*-phenethylacyl/*sec*-phenethyl GRP recombines with retention and with inversion of configuration with no detectable experimental difference.

The experimental identity of P_{mr} and P_{rm} has also been demonstrated for the RP which have a large HFI (^{13}C nucleus at the carbonyl position). Thus, the major conclusion of this paper is that *the average magnitudes of the magnetic interactions (exchange, electron–electron dipole–dipole, spin–orbit) along the trajectories for recombination with retention or with inversion of configuration are the same, or the partitioning of the RP along the trajectories of the different chemical reactions occurs after the completion of the spin state evolution of this system.*

The experimentally determined probability of recombination has allowed us to calculate the isotope separation parameter α (according to the general scheme) and compare it to the value determined from isotope enrichment experiments and its dependence upon an external magnetic field. Comparing the probabilities of recombination from labeled and unlabeled material allows us to evaluate the classical isotope effect in this reaction. This effect ($Q = 1.0434$) can be assigned to the photoexcitation or bond cleavage process and not for the decarbonylation or the recombination step. The magnetic isotope separation efficiency parameter is $\alpha = 1.0618$ (Table II) and its field dependence will be the subject of future discussion.

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Appendix

We describe here how the conversions and diastereomeric excesses for the labeled material may be calculated from the corresponding values determined experimentally for the total (sum of labeled and unlabeled) material.

The experimentally measured values are δ_m ($= m^*/m$) and δ_r ($= r^*/r$), and ^{13}C isotope content in *meso*-DPP and in *d,l*-DPP, respectively; Z_σ and f_σ are the combined (sum of ^{12}C and ^{13}C ketones) isomer purity and conversion, respectively ($Z_\sigma = |(r + r^* - m - m^*)/(r + r^* + m + m^*)|$, $(1 - f_\sigma) = (r + r^* + m + m^*)/(r_0 + r_0^* + m_0 + m_0^*)$). $\delta_{m,r}$ were measured by mass spectrometry and Z_σ and f_σ by standard VPC methods. Z, Z^* and f, f^* may be found from $\delta_{m,r}$, Z_σ, and f_σ, where $\delta_{\sigma 0} = (m_0^* + r_0^*)/(m_0 + r_0)$

$$Z = \frac{(1 + \delta_m)(1 + Z_\sigma) - (1 + \delta_r)(1 - Z_\sigma)}{(1 + \delta_m)(1 + Z_\sigma) + (1 + \delta_r)(1 - Z_\sigma)}$$

$$Z^* = \frac{\delta_r(1 + \delta_m)(1 + Z_\sigma) - \delta_m(1 + \delta_r)(1 - Z_\sigma)}{\delta_r(1 + \delta_m)(1 + Z_\sigma) + \delta_m(1 + \delta_r)(1 - Z_\sigma)}$$

$$1 - f = \tfrac{1}{2}(1 - f_\sigma)(1 + \delta_{\sigma 0})\left[\frac{(1 + \delta_m)(1 + Z_\sigma) + (1 + \delta_r)(1 - Z_\sigma)}{(1 + \delta_r)(1 + \delta_m)}\right]$$

$$1 - f^* = \tfrac{1}{2}(1 - f_\sigma)\left[\frac{1 + \delta_{\sigma 0}}{\delta_{\sigma 0}}\right] \times \left[\frac{\delta_r(1 + \delta_m)(1 + Z_\sigma) + \delta_m(1 + \delta_r)(1 - Z_\sigma)}{(1 + \delta_r)(1 + \delta_m)}\right]$$

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(21) Tarasov, V. F.; Bagraynskay, E. G. Unpublished results.
(22) Kraeutler, B.; Turro, N. J. *Chem. Phys. Lett.* **1980**, *70*, 269.

The experimental results, as seen in Figures 4c and 4d are in good agreement with eqs 4 and 5. The corresponding measured parameters are represented in Table I.

Glossary

P_{ik} = probability of recombination in GRP where the subscripts i and k refer to the configuration of the substrate and product, respectively (j, k = *meso*- and *d,l*-DPP)
P_{inv} = probability of recombination with inversion of configuration = P_{rm} = P_{mr}
P_{ret} = probability of recombination with retention of configuration = P_{rr} = P_{mm}
P_{rm} = probability of recombination of GRP from *d,l*-DPP reacting to yield *meso*-DPP
P_{mr} = probability of recombination of GRP from *meso*-DPP reacting to yield *d,l*-DPP
P_{rr} = probability of recombination of GRP from *d,l*-DPP reacting to yield *d,l*-DPP
P_{mm} = probability of recombination of GRP from *meso*-DPP reacting to yield *meso*-DPP
Q = classical ^{13}C mass isotope effect for the photodissociation reaction
ϕ_i = quantum yield of photodissociation for substrate with configuration i (i = *meso*- or *d,l*-DPP)
Φ = quantum yield of disappearance
f = total conversion of the ketone
Z = diastereomeric excess of ketone
S_m = slope of plot of ln (Z/Z_0) vs ln ($1 - f$) using *meso*-DPP as a substrate
S_r = slope of plot of ln (Z/Z_0) vs ln ($1 - f$) using *d,l*-DPP as substrate
α = one-stage isotope separation efficiency parameter
m = concentration of *meso*-DPP
r = concentration of *d,l*-DPP
χ_j^k = yield of isomer k using isomer j as the substrate

Investigation of Proton-Transferred Enol Tautomers in the Lowest Excited Triplet States of Methyl Salicylate and Related Molecules[†]

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Properties of the lowest excited triplet states of methyl salicylate and *o*-hydroxyacetophenone have been investigated by means of time-resolved electron paramagnetic resonance and molecular orbital calculations. From detailed analyses of the experimental results, zero-field splittings, spin distributions, and sublevel decay rate constants in the lowest excited triplet states of the proton-transferred enol tautomers of methyl salicylate and *o*-hydroxyacetophenone have been obtained. The calculated results of the spin distribution and the zero-field splitting of the enol tautomer are in good agreement with the experimental values.

Introduction

The photoinduced intramolecular proton transfer of hydrogen-bonded molecules is a topic of current interest.[1-5] It is a very simple chemical process and is of great interest in view of its use as polymer-protecting agent[6] and the possibilities of making a proton-transfer laser[7] and an information storage device at a molecular level.[8] *o*-Hydroxybenzaldehyde (OHBA) is the simplest aromatic molecule with intramolecular hydrogen bonding involving a carbonyl group and is readily accessible to both accurate measurements and quantitative theoretical analyses. Accordingly, Nagaoka et al. have investigated the dynamic processes of various excited states of OHBA in detail.[6,9-14] Some of the conclusions obtained are as follows.

The stable molecular structure in the ground state of OHBA is an intramolecularly hydrogen-bonded closed conformer. The potential surface of the ground state (S_0 state) of this conformer has only one minimum, and no S_0-state tautomer exists as a metastable state. In the first excited $^1(\pi,\pi^*)$ state ($S_1^{(\pi)}$ state) of OHBA, an intramolecular proton transfer takes place accompanied by an isomerization into the enol tautomer. The deformation of the benzene skeleton plays an important role in this isomerization process in the $S_1^{(\pi)}$ state. The process occurring in the $S_1^{(\pi)}$ state is more properly called hydrogen transfer, but in this paper, we will use the term proton transfer, according to custom. In the second excited $^1(\pi,\pi^*)$ state and the first ionic state of OHBA, the intramolecular proton transfer yielding the enol tautomer does not take place. These results are consistent with the explanation that the enol tautomer is stabilized only in the first excited (π,π^*) state due to the nodal plane of the wave function. From the nodal pattern of the wave function, it is also considered that the stable molecular structure in the lowest excited $^3(\pi,\pi^*)$ state (T_1 state) of OHBA is the enol tautomer. The observed behavior concerning proton transfer of various hydrogen-bonded molecules can be explained similarly.[12,13,15,16]

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(1) Klöpffer, W. *Adv. Photochem.* **1977**, *10*, 311.
(2) Rentzepis, P. M.; Barbara, P. F. *Adv. Chem. Phys.* **1981**, *47*, 627.
(3) Huppert, D.; Gutman, M.; Kaufmann, K. J. *Adv. Chem. Phys.* **1981**, *47*, 643.
(4) Barbara, P. F.; Walsh, P. K.; Brus, L. E. *J. Phys. Chem.* **1989**, *93*, 29.
(5) *Spectroscopy and Dynamics of Elementary Proton Transfers in Polyatomic Systems* (special issue of *Chem. Phys.*); Barbara, P. F., Trommsdorff, H. P., Eds.; North-Holland: Amsterdam, 1989; Vol. 136, pp 153-360.
(6) Nagaoka, S.; Hirota, N.; Sumitani, M.; Yoshihara, K. *J. Am. Chem. Soc.* **1983**, *105*, 4220.
(7) Chou, P.; McMorrow, D.; Aartsma, T. J.; Kasha, M. *J. Phys. Chem.* **1984**, *88*, 4596.
(8) Nishiya, T.; Yamauchi, S.; Hirota, N.; Baba M.; Hanazaki, I. *J. Phys. Chem.* **1986**, *90*, 5730.
(9) Nagaoka, S.; Hirota, N.; Sumitani, M.; Yoshihara, K.; Lipczynska-Kochany, E.; Iwamura, H. *J. Am. Chem. Soc.* **1984**, *106*, 6913.
(10) Nagaoka, S.; Fujita, M.; Takemura, T.; Baba, H. *Chem. Phys. Lett.* **1986**, *123*, 489.
(11) Nagaoka, S. *J. Photochem. Photobiol.* **1987**, *A40*, 185.
(12) Nagaoka, S.; Nagashima, U.; Ohta, N.; Fujita, M.; Takemura, T. *J. Phys. Chem.* **1988**, *92*, 166.
(13) Nagaoka, S.; Nagashima, U. *Chem. Phys.* **1989**, *136*, 153.
(14) Nagashima, U.; Nagaoka, S.; Katsumata, S. *J. Phys. Chem.* **1991**, *95*, 3532.

0022-3654/91/2095-10229$02.50/0