Magnetic isotope effect in the reaction of disproportionation of radical pairs

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The photolysis of methyldeoxybenzoin was carried out in aqueous SDS solution in the earth's field and in a field of 1500 G. Benzaldehyde and styrene are produced by disproportionation of benzoyl–sec-phenethyl geminate radical pair. Both benzaldehyde and the recovered methyldeoxybenzoin are enriched in ^{13}C. These results represent the first direct evidence that both disproportionation and recombination of a radical pair are identically selective to the magnetic isotope effect, a result consistent with the conclusion that the reaction pathways which involve a triplet geminate radical pair are selected after the completion of intersystem crossing.

1. Introduction

The magnetic isotope effect (MIE) is a consequence of the dependence of the rate of the chemical reactions of radical pairs (RP) [1,2] on the spin and magnetic moments of the nuclei of the pairs. In particular, the rate of intersystem crossing (ISC) in RP is dependent upon several magnetic parameters operating on the "odd" electrons of the pair and, under certain conditions [1,2], ISC may be significantly controlled by the spin selective processes such as the hyperfine coupling interaction (HFI) of the "odd" electrons of the pair with magnetic nuclei embedded in the radical fragments. If the behavior of the RP is also influenced by processes that do not depend on spin and that compete with ISC (e.g. spin relaxation, irreversible diffusional separation or chemical reactions), magnetic and non-magnetic isotopes may be separated among the products [1,2].

The efficiency of the MIE can be quantified by an experimental parameter, α, which is characteristic of the specific hyperfine interactions of the pair and the details of the diffusional excursions executed by the pair during the ISC process. Another parameter, which may be derived from the experimental parameter α or computed from theory, is the probability of geminate reactions, P_i. Thus, the measurement of

α is a critical feature of both the experimental characterization of the MIE for a given system and is a critical link between experimental measurements and theory. The measurement of α involves well established analyses of the redistribution of isotopes in the starting material or the products of reactions involving geminate pairs. In general, when a ketone is photolyzed a triplet geminate pair is produced in close to quantitative yield. In particular, the triplet geminate pairs possessing ^{13}C undergo more rapid ISC and faster subsequent recombination reactions than triplet geminate pairs containing ^{12}C. If an "escape" process for the ^{12}C pairs exists, the starting ketone, a product of recombination, becomes enriched in ^{13}C as the reaction proceeds. The same arguments hold for disproportionation, the second important and widely observed reaction of geminate pairs.

Although the MIE concept has been widely studied and directly demonstrated [1,2] in many reactions involving recombination of RPs, MIE has not been unequivocally demonstrated in the commonly encountered disproportionation reaction of RP. For example, photolysis of dimethyldeoxybenzoin, $(C_6H_5COC(CH_3)_2C_6H_5)$ results [3] in the formation of the benzoyl and cumyl RP, which undergo recombination to regenerate the starting ketone and disproportionation to yield benzaldehyde and α-

methyl styrene. The chemical yield [3] (χ) of formation of benzaldehyde from the photolysis of $C_6H_5{}^{13}COC(CH_3)_2C_6H_5$ in HDTCl micelles was 41%, compared to only 30% for dimethyldeoxybenzoin from photolysis of $C_6H_5{}^{12}COC(CH_3)_2C_6H_5$. That disproportionation only occurs from the reaction of geminate RP was convincingly demonstrated by the observation that the photolysis of dimethyldeoxybenzoin in HDTCl aqueous solution in the presence and absence of Cu^{2+}, an efficient radical scavenger which resides only in the aqueous phase, gave the same yield of benzaldehyde and α-methylstyrene [3].

This interesting result may seem to provide direct and unambiguous evidence for the occurrence of a ^{13}C MIE in the disproportionation reaction of the geminate pair produced by photolysis of $C_6H_5COC(CH_3)_2C_6H_5$. However, a more detailed analysis shows that this is not quite correct. For the geminate RP produced in the photolysis of $C_6H_5COC(CH_3)_2C_6H_5$, let P_r to be probability of recombination, P_d be the probability of disproportionation and P_o to be the probability of all other reactions from the primary geminate pair produced by α-cleavage of a ketone. Since $1 = P_o + P_r + P_d$, then the chemical yield of disproportionation from the primary geminate RP produced from photolysis of dimethyldeoxybenzoin is given by $\chi_d = P_d / (1 - P_r)$. From this simple analysis, the ^{13}C isotope effect on the yield of disproportionation products is at least partially determined by variation of P_r with isotope substitution; as a result, no unambiguous conclusions concerning MIE on the disproportionation step follows from this result, because of the possible effects of magnetic isotopic substitution on P_o and P_r.

Recently, it has been shown that in the photolysis of methyldeoxybenzoin in SDS micelles (scheme 1) yields benzaldehyde and styrene, disproportionation products of the RP produced by α-cleavage. The response of the yield of benzaldehyde to an applied external magnetic field is identical to that for the regeneration of the starting ketone [4,5]. Again the question arises as to whether these very elegant experiments provide direct and unambiguous evidence for MIE in the disproportionation reactions of the geminate pair. In order to probe this question let us define, as above, the probabilities of recombination, disproportionation and irreversible formation of free

radicals from the geminate RP formed in the photolysis of methyldeoxybenzoin as P_r, P_d and P_{fr}, respectively.

Evaluation of P_r requires the use of optically active methyldeoxybenzoin (*MeDOB) from which a racemization efficiency parameter, β, which is analogous to the isotopic enrichment efficiency parameter, α (vide infra). As in the case of isotopic enrichment measurements, where α could be related to P_r, in the case of racemization measurement, β can also be related to P_r. P_d is measurable directly from the chemical yield (χ_d) of benzaldehyde and knowledge of P_r from the relationship: $P_d = \chi_d / (1 - P_r)$. The experimental value P_d / P_r was found to be constant [4] for applied fields within the range 0–1700 G. It has also been found that a correlation exists between the decrease of the efficiency of $^{13}C / {}^{12}C$ isotope separation and the increase of chemical yield of benzaldehyde in the photolysis of different deoxybenzoins [5]. However, the experimental technique employed [5], did not allow the measurement of the ^{13}C enrichment of benzaldehyde.

Thus, at the commencement of this research, although strong indirect evidence was reported, there appeared to be no direct experimental evidence of the effect of the magnetic nuclei on the product yield or isotope selection due to MIE in a disproportionation reaction of a RP. We report here such direct evidence for $^{13}C / {}^{12}C$ MIE and isotope selection in the disproportionation reaction of RP formed in the photolysis of methyldeoxybenzoin (1) in SDS micelles. We found that benzaldehyde (BA), the product of this reaction, is enriched in ^{13}C isotope, and that the ratios of the disproportionation probabilities of "magnetic" and "non-magnetic" pairs are the same as the ratios of the corresponding probabilities in zero field and in a field of 1500 G.

2. Experimental

Methyldeoxybenzoin (1) was prepared by methylation of deoxybenzoin with methyl iodide [7]. ^{13}C-labeled 1 was synthesized by Dr. Naresh Ghatlia. Approximately 25% ^{13}C-enriched 1 was employed in the photolysis experiments. Sodium dodecylsulphate (SDS, Bio-Rad) was used without purification. Photolysis of 1 (1.7 mM) in Ar purged aqueous SDS so-

lution (0.1 M) was carried out with a 1 kW Hanovia Xe–Hg high pressure lamp through the glass filter LP-345 ($\lambda > 345$ nm) between the poles of electromagnet (Alpha Scientific) with power supply model 3002-1. The magnetic field was measured with a Bell-620 gaussmeter. After photolysis the reaction solutions were extracted with a mixture of ethyl acetate/methylene chloride to which a known amount of an internal standard (dibenzylketone) was added and then analyzed by GC to measure the conversion of **1** and by GC-MS to measure the isotope composition of **1** and benzaldehyde. Capillary GC analyses were carried out using Hewlett Packard 5890 gas chromatograph with flame ionization detector on 25 m HP-1 capillary column with Hewlett Packard 3392 electronic integrator. Mass spectra were acquired with Hewlett Packard 5988 GC-MS equiped with HP-9138 computer.

3. Results and discussion

Scheme 1 serves as a paradigm for the photolysis of **1** and for analysis of the MIE in the geminate RP produced by photolysis of **1**. Since we are only concerned with the recombination and disproportionation reactions of the geminate RP, we ignore the free radical products in our analysis. This assumption is justified theoretically because of the nature of the analysis but also experimentally by the observation of only very low yields of free radical coupling products (benzyl and 2,3-dimethyl-2,3-diphenyl butane) under micellar photolysis conditions. According to the MIE paradigm, the competition of hyperfine-induced ISC RP and escape from the micellar cage to form free radicals results in magnetic isotope selection between geminate products (recombination and

Scheme 1. Paradigm for the photolysis of methyldeoxybenzoin.

disproportionation) and escape products. The prediction of MIE is that the ^{13}C nucleus of the benzoyl radical of the geminate RP, since it possesses the largest HFI constant of the pair, will cause selective accumulation of ^{13}C in the geminate products of RP, i.e. the regenerated starting ketone and benzaldehyde are predicted to be enriched with ^{13}C mainly in carbonyl position. The issue we seek to resolve directly is whether the efficiency of enrichment in these two geminate products is identical or not.

In our analysis of the disproportionation products, we consider only benzaldehyde (BA), for the theoretical reason that benzaldehyde contains the ^{13}C nucleus that exerts the maximum hyperfine interaction in RP and for the experimental reason that the yield of styrene, the companion disproportionation product, is unreliable due to instability of styrene under the reaction conditions.

The literature possesses the well documented paradigm of the ^{13}C MIE in the photolysis of dibenzyl ketone for the evaluation of α_r for the regenerated **1**. The evaluation of an analogous and comparable α_d for the analysis of the experimental data on the yield of BA, is available from the same set of equations that were employed [8] for the treatment of experimental data of enrichment of p-tolylbenzylketone (TBK) in the photolysis of dibenzylketone in micelles

$$\ln S_r = (1 - \alpha_r) \ln(1 - F^*) , \tag{1}$$

$$S_d = (\alpha_r / \alpha_d)(F^*/F) , \tag{2}$$

$$\alpha_r = (1 - P_r)/(1 - P_r^*) , \tag{3}$$

$$\alpha_d = P_d / P_d^* . \tag{4}$$

In these equations, subscripts r and d refer to measurements and parameters associated with the recombination and disproportionation reactions, respectively. The MIE efficiency parameters are given by α_r and α_d, and the extent of measured enrichment is given by $S = \delta/\delta_0$, $\delta = [^{13}C/^{12}C]$, $\delta_0 = [^{13}C/^{12}C]_0$, assuming that all of the enrichment occurs in the carbonyl group. The quantity F is the experimental conversion of starting ketone, F^* conversion of "magnetic" ketone (asterisk in all cases refers to "magnetic" molecules, containing a ^{13}C nucleus at the carbonyl group) where the relationship of S, F, F^* and δ are given by
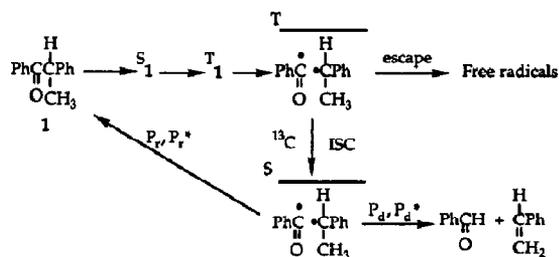
$$1-F^* = S(1-F)(1+\delta)/(1+S\delta),\qquad (5)$$

α-efficiency of isotope selection in the reaction.

Measuring the isotopic content, δ, of starting ketone yields S_r and plotting the values of S_r as a function of conversion according to eqs. (1) and (5) gives α_r. Measuring isotopic content of benzaldehyde yields S_d and plotting of $S_d F = (\alpha_r/\alpha_d)F^*$ allows computation of α_r/α_d. Since α_r is available from an independent measurement, α_d is obtained from the experimentally determined ratio α_r/α_d.

Fig. 1 shows a plot of experimental data of ^{13}C enrichment of MeDOB plotted in accordance with eq. (1). These plots yield a slope of $\alpha_r = 1.196 \pm 0.002$ for zero field and $\alpha_r = 1.177 \pm 0.005$ for 1500 G. The ^{13}C enrichment of benzaldehyde derived from experimental data and eq. (2) is given in fig. 2 for both $H=0$ ($\alpha_r/\alpha_d = 1.237 \pm 0.012$) and $H=1500$ G ($\alpha_r/\alpha_d = 1.217 \pm 0.031$). Finally from eq. (4) one obtains $P_d^*/P_d = 1/\alpha_d$, which is characteristic of isotope selectivity of reaction of disproportionation: $P_d^*/P_d = 1.034 \pm 0.010$ for $H=0$ and $P_d^*/P_d = 1.034 \pm 0.026$ for $H=1500$ G. The experimental value of α_r obtained in this work is slightly smaller than that previously reported [6] for 1, employing natural abundance of ^{13}C. In the earlier report, the enrichment of 1 was calculated under the assumption that the latter only occurred for the carbonyl group, but HFI constants in other positions are not insignificant (for example for the α-carbon in a benzoyl group $a_{C-13} = 50$ G) and definitely contribute to α_r, increas-
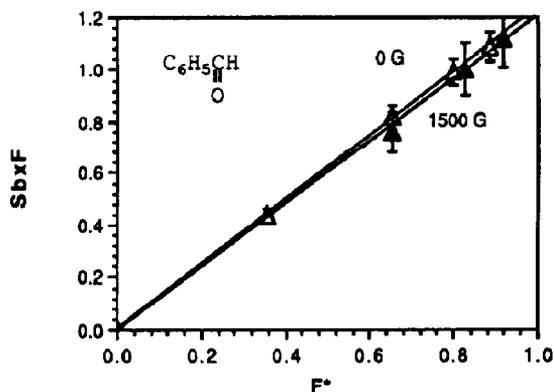
Fig. 2. ^{13}C enrichment of benzaldehyde (BA) in the variables of eq. (2) in the magnetic field of 0 and 1500 G. (The error barr in the plot of BA enrichment is 6 times larger than in the case of 1 for two reasons. First, the experimental error in the measurement of the ^{13}C content of BA is larger since the latter has very intensive $(M-1)^+$ peaks in mass spectra, which complicates the measurement, and second, the slope on fig. 2 as one can see from eq. (2) contains two experimental errors – one from BA measurements and another from measurement of 1.)

ing it. Therefore, the actual α_r value for $^{13}C/^{12}C$ enrichment in the carbonyl group of 1, which was obtained employing synthetically enriched 1 as the starting material, is expected to be smaller than the value reported previously [6].

Eqs. (1)–(4) assume that there is no classical mass isotope effect in the dissociation step of the molecule which is the precursor of the RP. This effect has been found to exist and even measured, $\alpha_{cl} = 1.04$ [9,10]. Thus, in order to compare isotope selectivity of both reaction $(P^*/P)_d$ and $(P^*/P)_r$ one has to multiply the former with α_{cl}: $(P^*/P)_d \alpha_{cl} = 1.075 \pm 0.011$ for $H=0$ and 1.075 ± 0.032 for $H=1500$ G. These values are within reasonable agreement with values of $(P^*/P)_r$ measured in the photoracemization experiments [11] of *MeDOB and *MeDOB C-13. $(P^*/P)_r = 1.10$ for zero field and 1.09 for $H=1500$ G. (The reference values [11] P_r^* and P_r are experimental ones and are not corrected for the mass isotope effect.)

The values of $(P^*/P)_d$ obtained in the present experiment cannot be rationalized as classical $^{13}C/^{12}C$ secondary isotope effect in the elementary step of hydrogen abstraction which occurs in the disproportionation reaction, since this sort of isotope effect is known to have an opposite sign and should result in
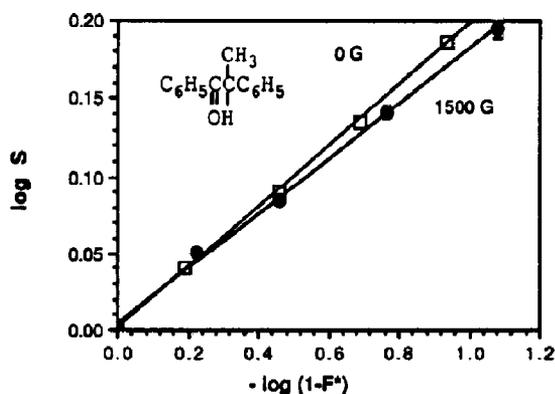
Fig. 1. ^{13}C enrichment of methyldeoxybenzoin (1) versus conversion in the variables of eq. (1) in the magnetic field of 0 and 1500 G.

Table 1
The efficiency of $^{13}C/^{12}C$ isotope enrichment of 1 and benzaldehyde and isotope selectivity of recombination and disproportionation reactions of geminate sec-phenethyl–benzoyl RP under photolysis of 1 in SDS aqueous solution

Value	0 G	1500 G
$\alpha_r - (1-P_r)/(1-P_r^*)$	1.196 ± 0.002	1.177 ± 0.005
α_r/α_d	1.237 ± 0.012	1.217 ± 0.031
$1/\alpha_d = P_d^*/P_d$	1.034 ± 0.010	1.034 ± 0.026
$(P_d^*/P_d)\alpha_{cl}$	1.075 ± 0.011	1.075 ± 0.032
(P_r^*/P_r) [a]	1.10	1.09

[a] From ref. [11].

depletion of BA with ^{13}C isotope with the efficiency $k_{12}/k_{13} = 1.015-1.020$ [12].

The data of the efficiency of isotope enrichment of both starting ketone (1) and benzaldehyde as well as isotope selectivity of recombination and disproportionation reactions in geminate RP formed in photolysis of 1 are summarized in table 1.

4. Conclusions

We have found the following experimental results concerning the disproportionation which occurs from the geminate radical pair produced in the photolysis of methyldeoxybenzoin (1): (1) benzaldehyde – the product of the reaction of disproportionation is enriched in ^{13}C, (2) the ratios of the disproportionation probabilities of "magnetic" and "non-magnetic" radical pairs $(P^*/P)_d$ corrected for the mass isotope effect are the same as the ratios of probabilities of recombination of the same RP in zero field (1.075 ± 0.011) and in a field of 1500 G (1.075 ± 0.032). From these results we conclude that reaction of geminate disproportionation of RP is selective to a ^{13}C magnetic isotope to the same extent as reaction of geminate recombination. An obvious extension of

this conclusion is the expectation that both MIE and isotope enrichment of the product of the reaction of disproportionation are affected by the same factors as MIE and enrichment in reaction of recombination. From the equal isotope selectivity of both reactions, we conclude that the final choice of the geminate reaction pathways of RP – disproportionation versus recombination – is made only after completion of ISC.

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