

Radical pair recombination stereoselectivity as a probe of magnetic isotope and magnetic field effects

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Photolysis of *meso*- or *dl*-2,4-diphenylpentan-3-one within NaY zeolites, coadsorbed with a chiral inductor, lead to enantioselective radical pair recombinations which are sensitive to ^{13}C isotope effects, but insensitive towards external magnetic field effects.

We report here rationally designed systems, based on well-established radical pair chemistry, which investigate the stereoselectivity of recombination of prochiral radical pairs for which significant magnetic field effects and magnetic isotope effects have been observed in micelles.^{1,2} The concept of the systems is the following. A prochiral triplet radical pair that can be produced reversibly is generated in a chiral, supramolecular³ environment that (i) allows the separation of the pair to distances allowing for the exchange interaction between the partners of the pair to decrease to values of the order smaller than those available from external or internal magnetic fields,¹ and (ii) encourages reencounters of the pair. Each recombination of the pair can produce either the (+) or (–)-enantiomer, but in the presence of a chiral inductor within the supramolecular environment, a certain enantiomeric selectivity can result.⁴ For any given system in which some ee is observed, the efficiency of ee resulting from radical pair recombination is expected to depend on the radical pair lifetime, which has consequences in terms of the effective interactions between the pair and the chiral inductor. In this scenario, magnetic field and magnetic isotope effects on the enantioselectivity may result if the lifetime of the pair is extended or diminished. From a survey of published results, we selected the supercage of NaY faujasite zeolites⁵ as the host supramolecular environment,⁶ the photolyses of *meso*- and *dl*-2,4-diphenylpentan-3-one (*meso*-**1** and *dl*-**1**, respectively) to generate triplet radical pairs and a coadsorbed chiral inductor such as diethyl L-tartrate and (+)- or (–)-ephedrine as chiral inductors.

As depicted in Scheme 1, photolysis of *meso*-**1** results in the formation of *dl*-**1** and *vice versa* (for simplicity only the photoprocesses of *meso*-**1** are shown).⁷ According to the conventional paradigm of ketone photochemistry,⁸ α -cleavage of triplet excited **1** leads to the formation of *sec*-phenethyl and *sec*-phenethylacyl triplet geminate radical pairs (GRP). If the space available in the supercage allows rapid diffusional separation of the primary geminate pair, then decarbonylation of the *sec*-phenethylacyl radical and subsequent formation of diastereomeric 2,3-diphenylbutanes **2** occurs.⁷ If diffusion is restricted, but rotation of the triplet radical pairs relative to one another is permitted, intersystem crossing (ISC) of the radical pairs occurs to yield *meso*-**1** or *dl*-**1**. Additionally, if the environment is chiral, *dl*-**1** with some degree of enantiomeric

enrichment can be produced. Of these processes, only the rate of ISC is sensitive towards magnetic effects.^{1a,b} Thus, the ratios between decarbonylation products and recombination products,^{2c} as well as the ee of photoproducted *dl*-**1** can serve as probes for magnetic effects on the radical pair recombination stereochemistry. While we expect the ratio of recombination products/decarbonylation products to increase as the rate of ISC increases, predictions on the direction of change of the ee of photoproducted *dl*-**1** cannot be made *a priori*.

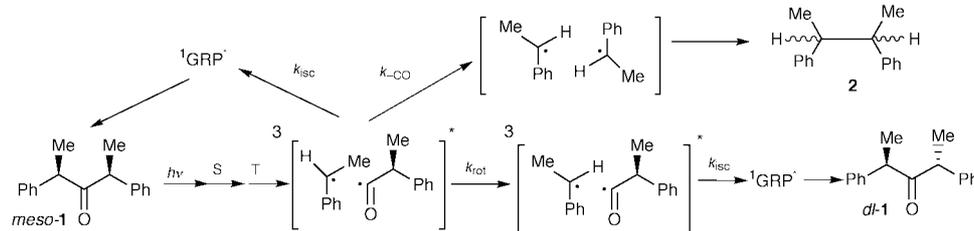
Table 1 summarizes the ee values of recovered *dl*-**1** upon photolysis of *dl*-**1** in NaY co-loaded with diethyl L-tartrate as a function of both external magnetic field strength and isotope. It can be seen that there are no differences, within experimental error, in the ee (measured by chiral GC) of the photolyzed *dl*-**1** when the photoreaction is carried out at either 0 or 2 kG. However, upon photolysis at 0 kG of *dl*-**1** enriched in ^{13}C (98% enriched) at the carbonyl carbon, a significant increase in the ee of the recovered *dl*-**1** is observed when the ^{13}C labeled isomer is photolyzed relative to the unlabeled isotopomer (3.0 vs. 1.6%, respectively). Additionally, a slight increase in the amount of recombination product vs. decarbonylation products was observed in the photolysis of *dl*-**1**- ^{13}C O relative to *dl*-**1**- ^{12}C O.⁹ However, no such trend has been seen in the photolysis of *dl*-**1**- ^{12}C O performed at 0 vs. 2 kG.

In order to assess the influence of initial stereochemistry of **1** on the enantioselectivity of *dl*-**1** as a function of external magnetic field and isotope effects, photolyses of *meso*-**1** were performed in NaY using ephedrine as the chiral inductor.¹⁰ From Table 2, it can be seen that photolyses of *meso*-**1** in NaY in the presence of ephedrine, significantly higher ees for *dl*-**1** are obtained compared to utilizing *dl*-**1** as the starting material and diethyl L-tartrate as the inductor. However, similar to the results obtained with diethyl L-tartrate, only a ^{13}C isotope effect is observed while external field effects are absent. Thus, an

Table 1 Photolysis of *dl*-**1** in NaY co-loaded with diethyl tartrate^a

Magnetic field/kG ^b	Ketone	Chiral inductor	Ee of <i>dl</i> - 1 (%) ^{c,d}
2	<i>dl</i> - 1 - ^{12}C O	diethyl L-tartrate	+2.0 \pm 0.2
0	<i>dl</i> - 1 - ^{12}C O	diethyl L-tartrate	+1.6 \pm 0.3
0	<i>dl</i> - 1 - ^{13}C O	diethyl L-tartrate	+3.0 \pm 0.1

^a The average occupancy of *dl*-**1** in NaY is \sim 0.05 molecules per cage and that of diethyl tartrate \sim 1 molecules per cage; *dl*-**1** was photolyzed to 35–45% conversion. ^b Ref. 12. ^c Errors correspond to standard deviations derived from three or more independent experiments. ^d After photolysis, *dl*-**1** is separated from *meso*-**1** via preparative TLC and analyzed by chiral GC.



Scheme 1

Table 2 Photolysis of *meso-1* in NaY co-loaded with ephedrine^a

Magnetic field/kG ^b	Ketone	Chiral inductor	Ee of <i>dl-1</i> (%) ^{cd}
2	<i>meso-1-12</i> CO	(-)-ephedrine	+4.9 ± 1.9
0	<i>meso-1-12</i> CO	(-)-ephedrine	+4.7 ± 1.9
0	<i>meso-1-13</i> CO	(-)-ephedrine	+9.9 ± 1.3
2	<i>meso-1-12</i> CO	(+)-ephedrine ^e	-4.3 ± 1.6
0	<i>meso-1-12</i> CO	(+)-ephedrine ^e	-3.6 ± 0.6
0	<i>meso-1-13</i> CO	(+)-ephedrine ^e	-7.1 ± 0.5

^a The average occupancy of *meso-1* in NaY is ~0.05 molecules per cage and that of ephedrine ~1 molecules per cage; *meso-1* was photolyzed to 26–50% conversion. ^b Ref. 12. ^c Errors correspond to standard deviations derived from three independent experiments. ^d After the photolysis, *dl-1* is separated from *meso-1* via preparative TLC and analyzed by chiral GC. ^e The hemihydrate form was used.

approximate two-fold increase in the ee of *dl-1* is observed upon photolysis of *meso-1-13*CO compared to that of *meso-1-12*CO [+10% vs. +5%, with (-)-ephedrine] (Table 2). Additionally, more recombination product was observed for the photolysis of *meso-1-13*CO compared to that of *meso-1-12*CO.¹¹

We can interpret the data in Tables 1 and 2 based on the mechanism of triplet–singlet ISC for triplet biradicals.^{13,2c,f} It is recognized that if triplet radical pairs are separated by distances of several Å or more, the singlet–triplet energy gap is decreased and ISC is controlled by weak hyperfine couplings induced by nuclear-spin interactions which are magnetic field and isotope dependent. Thus, ¹³C is expected to induce a faster ISC in the radical pair relative to ¹²C, for which only protons provide a hyperfine mechanism for ISC. External magnetic fields can reduce the rate of ISC by increasing the S–T energy gap for two of the three triplet sublevels. Experimental results for such phenomena have been the subject of several reviews.^{1,2}

In hydrocarbon solutions, *sec*-phenethylacyl radicals decarbonylate with a rate constant of ~5 × 10⁷ s⁻¹.¹⁴ In polar solvents, the rate of CO loss can be reduced.¹⁵ Since the internal cages of zeolite supercages are considered highly polar,¹⁶ decarbonylation in the zeolite must be significantly slower than 5 × 10⁷ s⁻¹. Recombination of structurally related benzoyl and cumyl radical pairs obtained from the photolysis of dimethyldeoxybenzoin, in SDS micellar solutions, has been measured to occur with a rate constant on the order of ~1.2 × 10⁷ s⁻¹.¹⁷ This rate is expected to be increased by ¹³C isotope effects, via changes in the rate of ISC. An increased rate of ISC can be manifested in the different ee values for recovered *dl-1* obtained upon irradiation of either *meso-* or *dl-1* containing different isotopic labels at the carbonyl carbon. Since there is a lack of information in the rotational dynamics between the prochiral GRPs and the chiral inductor, the trend of the ee of the photoreaction cannot be predicted *a priori*.

The experimental results show an increase in the ee of *dl-1-13*CO relative to its ¹²C isotopomer. Furthermore, photolysis of *1-13*CO leads to a slight decrease in the amount of decarbonylated products relative to the ¹²C labeled isotopomer.^{9,11} Similar results have also been previously observed for the photolysis of dibenzylketone-¹³CO in faujasites.^{2c} Hence, an increase in the ee of the photoproduct *dl-1-13*CO may be a function of its faster rate of ISC, leading to a greater number of recombinational processes from the primary GRP as compared to *dl-1-12*CO which maintains a relatively lower rate of ISC from the triplet GRP and thus higher propensity to form decarbonylated products.^{2a,b,4a,18}

According to the product ratios and the ee values expressed in Tables 1 and 2, there are no observable external field effects in the photolysis of either *meso-* or *dl-1*. At this time we lack a theoretical kinetic model to explain these experimental results. Although it has been widely demonstrated that magnetic field and magnetic isotope effects can influence the rate of ISC for triplet biradicals in opposite manners, there is a lack of information on the *magnitudes* of those rates. It can be argued that external field effects, as they pertain to **1** in faujasites, are very small and subtle as compared to magnetic isotope effects. Indeed, in similar product studies done with dibenzyl ketone

(DBK) adsorbed in faujasites, external magnetic field effects were significantly smaller than those observed for ¹³C isotope effects.^{2c}

The results show that photochemical enantiomeric selectivity through geminate radical recombinations in zeolite cavities is feasible. The most important finding is that ee values are sensitive to magnetic isotope effects, and consequently can be used as a probe of radical pair dynamics in zeolites.

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- Ratio of *meso-1:2* = 0.12 for the photolysis of *dl-1-12*CO, ratio of *meso-1:2* = 0.19 for the photolysis of *dl-1-13*CO.
- No data is reported for the stereoselectivity of the photoreaction of *meso-1* in NaY–diethyl tartrate systems due to analytical difficulties in measuring the ee of *dl-1* recovered from such photolysis.
- Ratio of *dl-1:2* = 0.64 for the photolysis of *meso-1-12*CO, ratio of *dl-1:2* = 0.92 for the photolysis of *meso-1-13*CO.
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