

Diastereoselective induction in radical coupling reactions: photolysis of 2,4-diphenylpentan-3-ones adsorbed on faujasite zeolites

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Abstract

The photochemistry of *d*, *l* and *meso* isomers of 2,4-diphenylpentan-3-one (DPP), adsorbed onto various cation-exchanged X and Y faujasites, was investigated. LiY and NaY show greater diastereoselectivity for the formation of the *d,l* isomer of diphenylbutane over the *meso* isomer than LiX and NaX. KY displays a significantly attenuated selectivity relative to LiY and NaY. The magnitude of the diastereoselectivity is a function of the substrate configuration and the difference between the magnitude of diastereoselection exhibited by LiY and NaY over LiX and NaX is greater when the substrate is *d,l*-DPP rather than *meso*-DPP. All the zeolites studied show substantially more diastereomerization relative to decarbonylation, as measured by the *s* parameter (*vide infra*), when compared with other supercage media such as micelles and porous glass. However, substrate configuration is irrelevant when comparing the *s* parameters. The different cation-exchanged Y zeolites all show similar *s* parameters, whereas the X zeolites display a non-monotonic behavior with respect to the *s* parameter and cation size. The stereoselectivities for NaX and NaY are independent of loading and these media display cage effects of 100% for *d,l*-DPP.

1. Introduction

The modification of photochemical reactivity by conduction of reactions in constrained spaces (or microscopic reactors) is a rapidly burgeoning field [1-3]. The various cation-exchanged faujasite zeolites MX and MY (where M = Li, Na, K) have served as ideal substrates for these studies. The internal void structure of these zeolites consists of spherical cavities (approximately 13 Å in diameter), also known as supercages, which are connected by cylindrical channels (approximately 8 Å in diameter) in a diamond-type lattice [4] (Figs. 1(a) and 1(b)). The Y zeolites, with an Si/Al ratio of 2.4, have only type I and type II cations, whereas the X zeolites with an Si/Al ratio of 1.2, have all three types of cations (Fig. 1(b)). Organic photochemical substrates which are small enough to be adsorbed through the zeolite pore openings (approximately 8 Å in diameter) reside within the supercages. The nature and size of the cations, which occupy specific sites in the supercages, then determine the free space which may be experienced by the substrate molecule and can be influential in controlling the course of photoreactions of adsorbed guest molecules [5].

The photochemistry of dibenzyl ketone (DBK) adsorbed onto different X and Y zeolites (eqn. (1)) has been the subject of an extensive investigation [6, 7]

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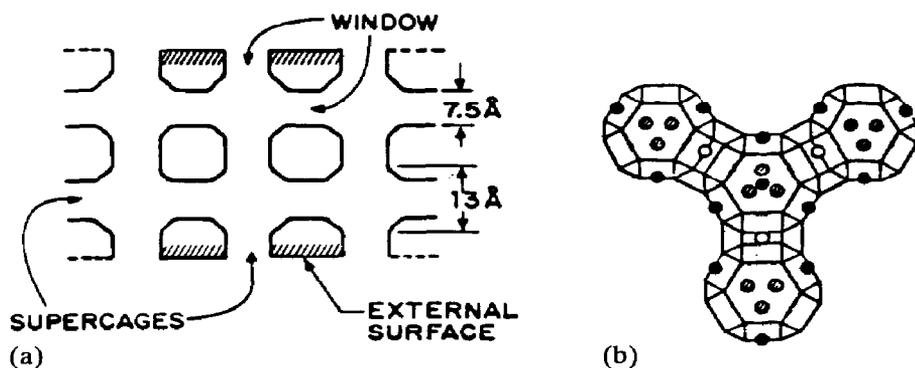
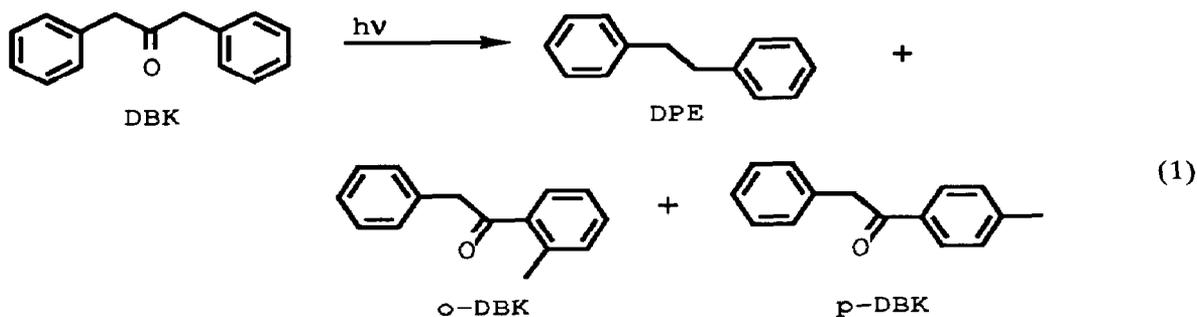


Fig. 1. (a) Simple topological representation of the structure of faujasite zeolites. (b) Location of cations within the zeolite framework: the X series contains all three types of cations, whereas the Y series contains only the type I and type II cations. (⊙, type I cations; ●, type II cations; ○, type III cations.)



The major product obtained on photolysis of DBK in solution is 1,2-diphenylethane (DPE) resulting from the coupling of random free radical pairs after decarbonylation. However, when the photolysis of DBK is conducted in zeolitic cavities, significant amounts of the DBK isomers *o*-DBK and *p*-DBK (eqn. (1)) are observed, formed by the recombination of the primary geminate radical pair. The percentage of isomers of DBK relative to decarbonylated products increases with increasing steric congestion within the supercages, an effect which has been rationalized using the *lebensraum* paradigm for zeolitic reactions [6]. These results suggest that a systematic correlation of product ratios with changing environmental conditions may provide telling mechanistic insight into the interaction of the fragments of the radical pair with the surroundings and each other.

Other related studies have investigated the partitioning between type I and type II reactions of monoalkyl-substituted DBKs [8] and the modification of the stereochemistry of the dimerization of acenaphthalene in various cation-exchanged faujasites [9].

However, modification of stereoselectivities in product formation for radical coupling reactions has, to our knowledge, been unexplored in the field of zeolitic photochemistry. In this paper, we report the first example of diastereoselective induction observed during the photolysis of isomerically pure *d,l* and *meso* isomers of 2,4-diphenylpentan-3-one (*d,l*-DPP and *meso*-DPP) adsorbed on faujasite MX and MY zeolites.

2. Experimental details

2.1. General

Gas chromatographic analyses were carried out on a Hewlett Packard (HP) 5890 gas chromatograph (fitted with a 25 m Carbowax 20M capillary column) whose flame ionization detectors were interfaced to an HP 3396A electronic integrator. Mass spectra (gas chromatography/mass spectrometry (GC/MS)) were acquired with an HP 5890 gas chromatograph connected to an HP 5988 mass selective detector and an HP 9216 work station.

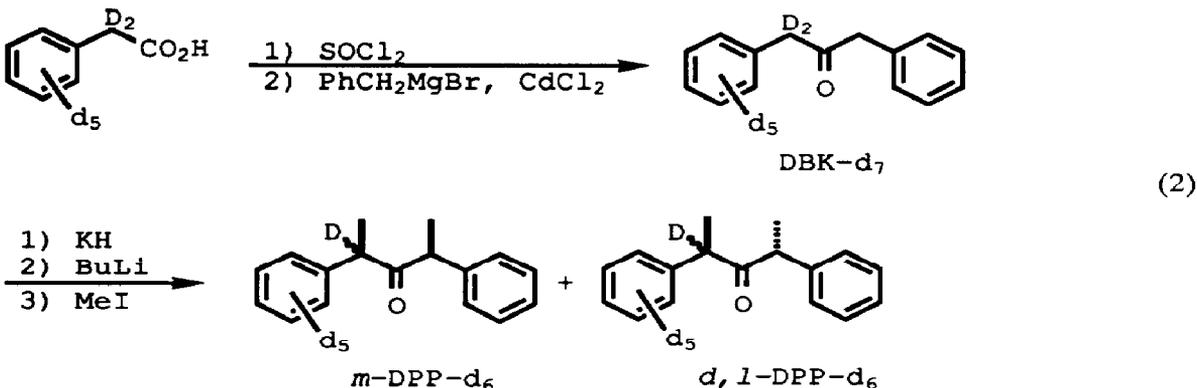
2.2. Materials

2.2.1. Preparation of *d,l* and *meso* isomers of 2,4-diphenylpentan-3-one (*d,l*-DPP and *meso*-DPP)

d,l-DPP and *meso*-DPP were synthesized by methylating the dianion of DBK. Separation and purification of the individual isomers (better than 99% isomer purity as judged by GC) was achieved by reverse-phase high performance liquid chromatography (HPLC) as outlined previously [10].

2.2.2. Preparation of *d,l* and *meso* isomers of 2,4-diphenylpentan-3-one- d_6 (*d,l*-DPP- d_6 and *meso*-DPP- d_6)

DBK- d_7 (more than 98% isotope content), synthesized from phenylacetic acid- d_7 (MSD Isotopes) according to a published report [5], was converted to DPP as a mixture of d_5 , d_6 and d_7 deuterated isotopic variants in a ratio of approximately 0.3:1:0.6, as described above (eqn. (2)).



2.3. Photolysis of DPP adsorbed on zeolites

A typical experiment consisted of weighing 30 mg of a calcined zeolite and then recalcining it at 550–600 °C for 10–12 h. A known and measured amount of a solution of the ketone in pentane (1 mg ml⁻¹) was added to the zeolite after it had been cooled in a desiccator. The zeolite was soaked in the pentane solution for approximately 30 min and the solvent was removed by blowing a stream of warm nitrogen over the sample. The solid was transferred to a photocell, with care being taken to minimize its exposure time to the atmosphere, and degassed under high vacuum (approximately 1 mTorr) for 45 min. Photolyses were performed with light from a Hanovia medium pressure mercury lamp which had been filtered through a dichromate solution. The photocell was continuously tumbled during the photolysis to ensure uniform irradiation. The solid was then dissolved by stirring it with approximately 22 ml of 0.5 N HCl

(which causes dissolution of the zeolitic structure) for 5 min or less and extracting the acidic solution with ether (3×15 ml). The ethereal extracts were dried over MgSO_4 , filtered, concentrated and analyzed by GC. The *d,l*-/*meso*-diphenylbutane ratios deviate by less than 10% from the reported value. The *s* parameters (*vide infra*) deviate by less than 15% from the reported value.

3. Results

3.1. Diastereoselectivity in product formation

The primary product in solution from the photolysis of *d,l*- or *meso*-DPP is 2,3-diphenylbutane (DPB) which may also exist in the *d,l* or *meso* diastereomeric forms (Fig. 2). Following an earlier protocol [5], preliminary experiments involved soaking the zeolites overnight in CH_2Cl_2 after photolysis to extract the reaction products. The accuracies of the selectivities obtained from these experiments were dependent on the assumption that the observed results were not due to a preferential absorption of one of the DPB or DPP isomers over the other. Control experiments, which involved loading artificially generated mixtures containing known ratios of DPB and DPP isomers onto the zeolites followed by soaking in CH_2Cl_2 , without photolysis, were carried out

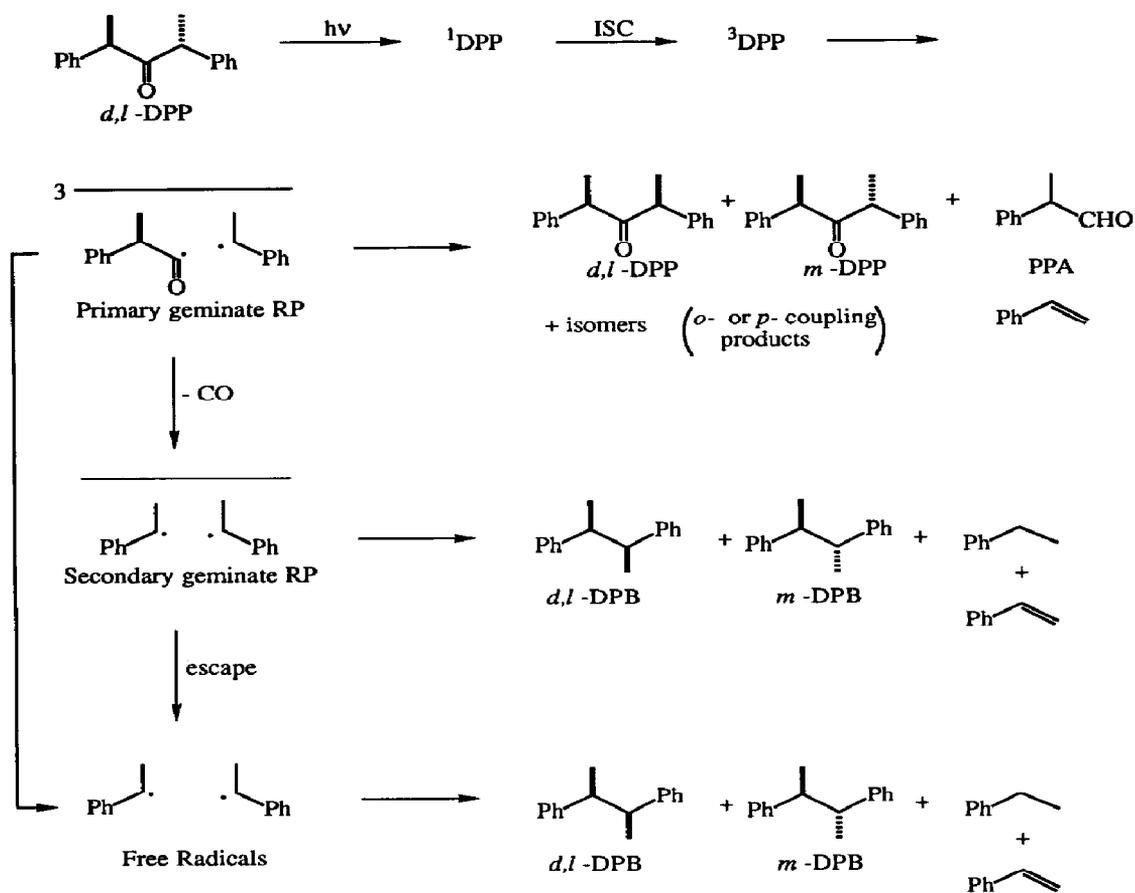


Fig. 2. Possible reaction pathways of photolysis of *d,l*-DPP.

on NaX and NaY zeolites. These experiments revealed that the zeolites preferentially retained the *d,l* isomer of both DPB and DPP. Other solvents, such as ether and benzene, together with mechanical agitation in the form of stirring or sonication, were tried in order to achieve acceptable recovery of material. None of these methods proved satisfactory for the purposes at hand. Traditional Soxhlet extractions were unsuccessful since the impurities that were extracted from the thimble had GC retention times which interfered with the detection of the compounds of interest. Pre-extraction of the thimble for 24 h prior to placing the zeolite sample in it did not solve this problem. All of these unsuccessful attempts led us to dissolve the zeolites in acid, followed by extraction of the organic materials from the aqueous acid layer, in order to ensure complete recovery.

In argon-purged pentane solutions photolysis of *meso*-DPP leads to the formation of *d,l*- and *meso*-DPB in a 93% yield with less than 0.5% diastereomerization of the substrate. Figures 3(a) and 3(b) graphically display the *d,l*-/*meso*-DPB ratios isolated after the photolysis of isomerically pure *d,l*- and *meso*-DPP respectively, at a 2 wt.% loading, on lithium-, sodium- and potassium-exchanged X and Y zeolites. Several salient features can be observed from these graphs: (1) all zeolites exhibiting a selectivity for DPB formation favor the *d,l* isomer over the *meso* isomer independent of the stereochemistry of the substrate ketone; (2) the magnitude of the selectivity is greater for the LiY and NaY zeolites relative to the LiX and NaX zeolites; (3) the magnitude of the selectivity is not independent of the substrate configuration and the selectivity

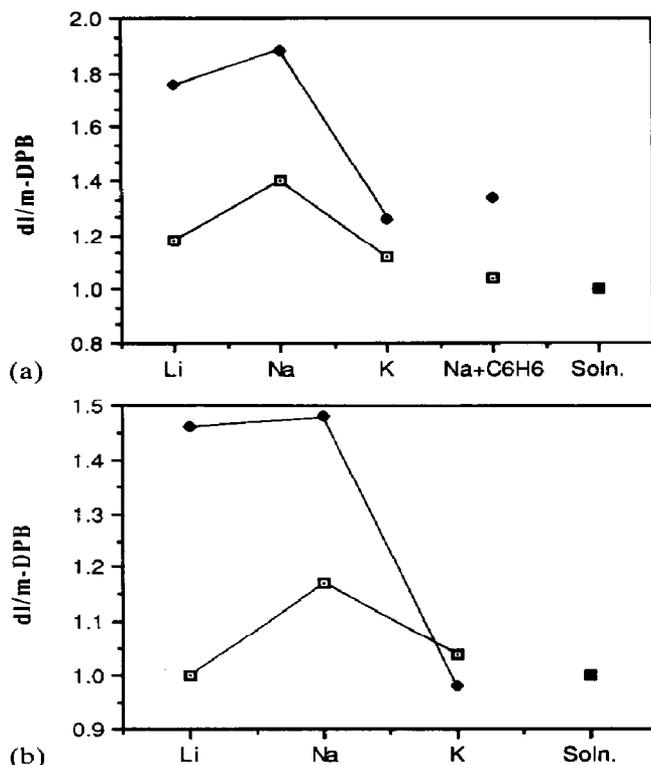


Fig. 3. (a) Ratio of *d,l*-/*meso*-DPB obtained from photolysis of *d,l*-DPP in different zeolites and in solution. (b) Ratio of *d,l*-/*meso*-DPB obtained from photolysis of *meso*-DPP in different zeolites and in solution. (□, X series; ◆, Y series.)

differential between the lithium- and sodium-exchanged X and Y zeolites is greater when *d,l*-DPP is the substrate; (4) the selectivity is similar for the LiY and NaY zeolites but decreases sharply with the potassium-exchanged zeolite.

It is important to note that all the photolyses were performed to conversions of 25% or less, since the ratios observed are not independent of substrate configuration, and the isomeric purity of the substrate suffers a continuous diminution during the course of the photolysis due to recombination reactions in the primary geminate radical pair which cause diastereomerization.

3.2. Isomerization of the substrate relative to the formation of decarbonylated products

Recombination of the primary geminate radical pair, produced from the photolysis of DPP (Fig. 2), may occur with the preservation or loss of its original stereochemical integrity. This recombination leads to the formation of material that is diastereomerically related to the substrate.

To gain a quantitative feel for the competition between diastereomerization of the substrate and the formation of decarbonylated products, we define a parameter *s* (when *d,l*-DPP is the substrate photolysed)

$$s = \frac{[\textit{meso}\text{-DPP}]/([\textit{meso}\text{-DPP}] + [d,l\text{-DPP}])}{([\textit{meso}\text{-DPB}] + [d,l\text{-DPB}])/([\textit{meso}\text{-DPB}] + [d,l\text{-DPB}] + [d,l\text{-DPP}])} \quad (3)$$

This parameter is very similar to that defined in an earlier study which involved the photochemistry of DPP in micelles and porous glass [10]. A large value for *s* implies that there is substantial primary pair recombination occurring in competition with decarbonylation. For comparison purposes, the value for *s* in pentane solution was found to be 0.01.

Figures 4(a) and 4(b) depict graphically the *s* values that are obtained on photolysis of isomerically pure *d,l*- and *meso*-DPP respectively on the various faujasites at a constant loading of 2 wt.%. The striking features of these data are that, unlike the *d,l*-/*meso*-DPB ratios, the *s* values are not sensitive to the substrate configuration; for the Y zeolites the values of *s* obtained fall within a narrow range and appear to be independent of the cation; in the X series the *s* values are non-monotonic, with NaX consistently exhibiting a substantially smaller *s* value than LiX or KX. From our extraction control experiments, we also determined that very little acid-catalyzed isomerization of the substrate occurred during the acid dissolution procedure. After loading an artificial mixture of *d,l*-/*meso*-DPP = 6.2 onto NaY we were able to recover the diastereomers in a ratio of 6.0. The strength of the acid chosen was determined by the solubility of the Y zeolites (the X zeolites are more easily soluble) and an effort to achieve the minimum amount of isomerization in our control samples.

3.3. Effect of benzene as an added spectator

Samples of NaX and NaY adsorbed with *d,l*-DPP were prepared in the standard fashion (see Section 2.3). These samples were then affixed to a vacuum line and benzene, from the gas phase, was deposited onto them (46 wt.% on NaX and 40 wt.% on NaY). Photolysis and work-up were then performed as usual. Figure 3(a) shows that selectivity in DPB formation decreases on both NaX and NaY relative to those experiments with no spectator molecules. Figure 4(a) shows that the *s* parameter increases in both the zeolites, as a result of the added benzene, but the effect is more dramatic for NaX.

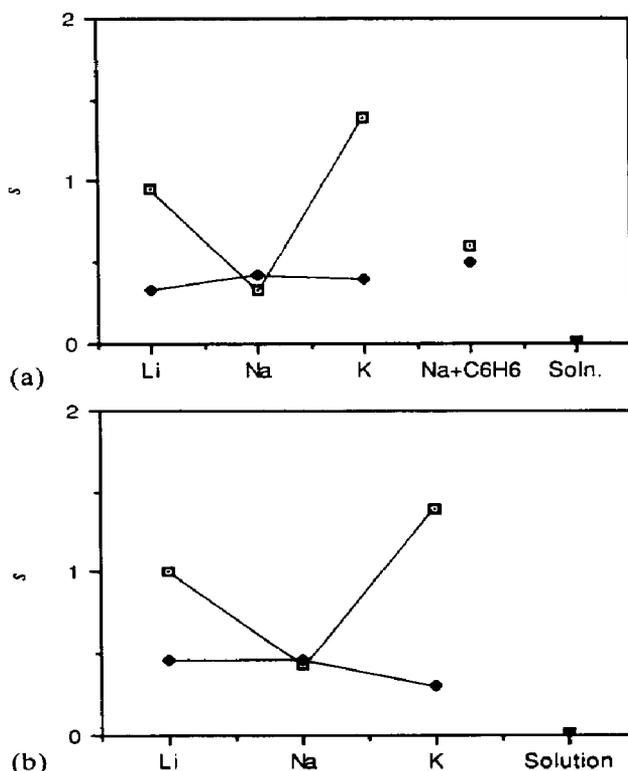


Fig. 4. (a) s parameter obtained from photolysis of d,l -DPP in different zeolites and in solution. (b) s parameter obtained from photolysis of $meso$ -DPP in different zeolites and in solution. (\square , X series; \blacklozenge , Y series.)

3.4. Effect of loading of DPP on NaX and NaY zeolites

The study involving DBK revealed a significant effect of loading on the product ratios and cage effect in the NaX zeolite and the absence of such an effect in the NaY zeolite [5, 11]. In comparable studies, photolyses of d,l -DPP with loadings of 0.5, 1 and 2 wt.% on NaY and 0.5, 2 and 5 wt.% on NaX were carried out. No significant variation was observed in the diastereoselectivities of the DPBs formed or the s parameters in either case. Hence DPP on NaX appeared to be insensitive to loadings of up to at least 5 wt.% (which translates to an occupation number of approximately one molecule per three supercages).

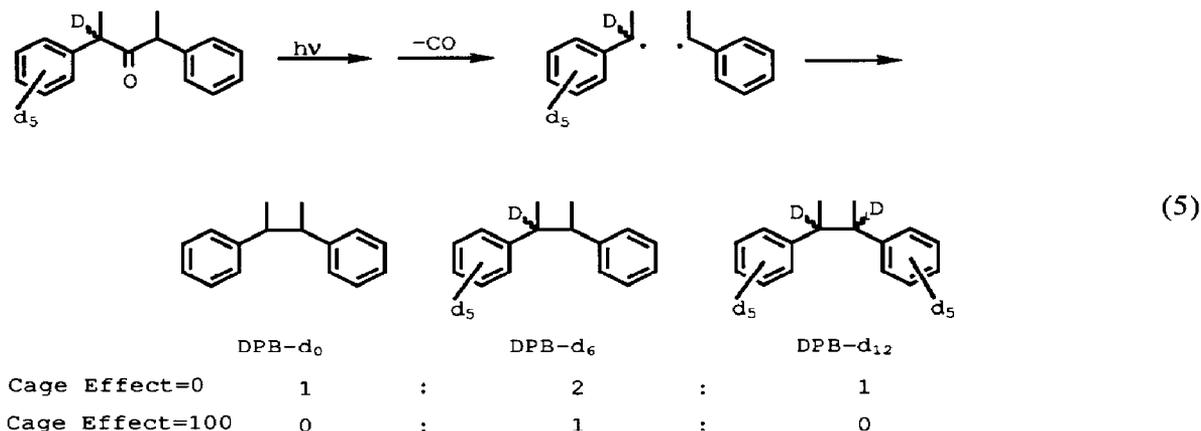
3.5. Cage effect studies on NaX and NaY zeolites

The photolysis of an unsymmetrical ketone, which may be represented as ACOB, can lead to the formation of three distinct products from radical recombination reactions after decarbonylation occurs; these three products may be represented as AA, AB and BB. The amount of recombination which occurs from the geminate pair is reflected in the parameter known as the cage effect

$$\text{Cage effect} = \frac{AB - (AA + BB)}{AA + AB + BB} \quad (4)$$

Thus a cage effect of 100% implies that there is no escape from the geminate cage, whereas a cage effect of 0%, as is usually observed in non-viscous solutions, implies that there is complete escape from the cage.

With DPP- d_6 , we expect to observe DPB- d_0 , DPB- d_6 and DPB- d_{12} in a ratio of 1:2:1 for a cage effect of 0% and in a ratio of 0:1:0 for a cage effect of 100% (eqn. (5)). For a loading of 2 wt.% of d,l -DPP- d_6 on both NaY and NaX we observed a cage effect of 100%. Again this is in contrast with the results observed for DBK where a cage effect of approximately 20% was obtained at a loading of 2 wt.% on both NaY and NaX. The cage effect for the related compound α -methyl DBK, from which the radical pair would have a slower rate of decarbonylation, was found to be 74% in sodium dodecylsulfate (SDS) micelles [10].



4. Discussion

Based on precedent [10], Fig. 2 depicts the expected pathways that are probably traversed by a molecule of DPP after the absorption of a photon. If intersystem crossing (ISC), in the initial triplet primary geminate radical pair, occurs prior to decarbonylation or escape from the cage, recombination may occur to regenerate starting ketone. If recombination occurs after an effective rotation of 180° of one radical fragment relative to another (Fig. 5), then material which is diastereomerically related to the starting substrate is generated. It is important to note that this process cannot lead to interconversion between the enantiomers: the photoisomerization of either the d or the l form of DPP can only lead to the meso isomer and not to interconversion between the d and the l forms. Recombination to give ortho or para coupling products as seen with DBK is also possible, but is not observed to be a significant pathway for DPP under the conditions studied. The presence of the additional methyl groups at the benzylic positions may also allow for the formation of disproportionation products, styrene and 2-phenylpropionaldehyde (PPA, Fig. 2). The presence of the additional methyl group could then, in principle, serve as an exquisitely sensitive probe for the motion of the radical fragments relative to one another because of the multiplicity of the potential products from the primary geminate pair.

Decarbonylation leads to the formation of a secondary geminate radical pair. If ISC occurs prior to cage escape, then the various products that may arise are the recombination products d,l - and meso-DPB or disproportionation products styrene and

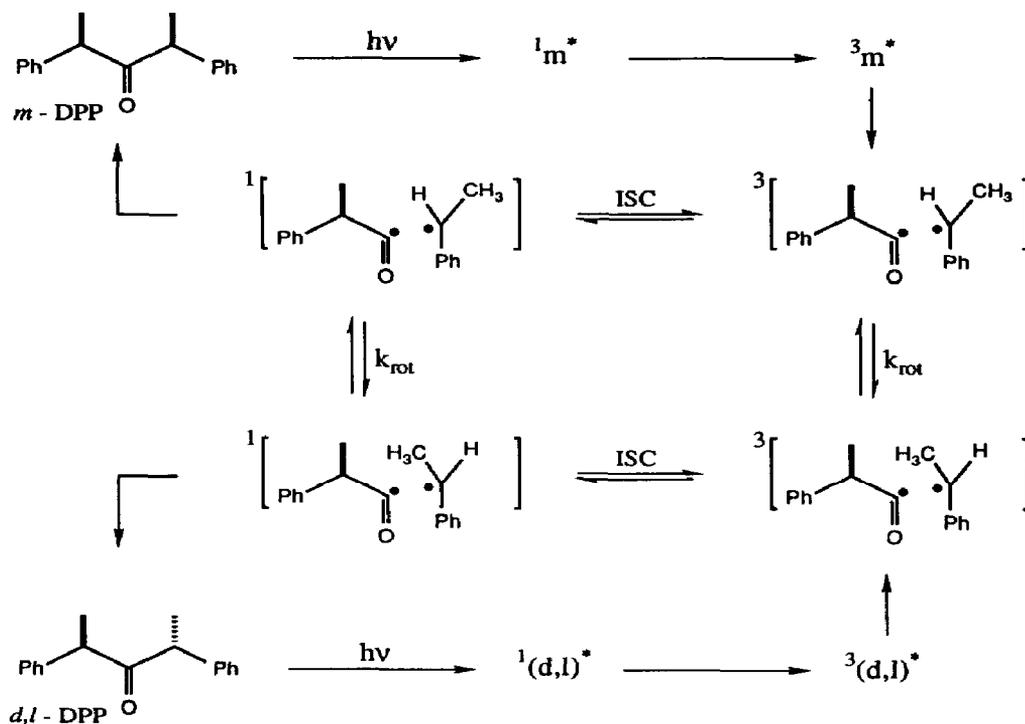


Fig. 5. Photodiastereomerization of *d,l*- and *meso*-DPP.

ethylbenzene (Fig. 2). Escape from the secondary cage leads to the formation of two free *sec*-phenethyl radicals which can react to give products that, in the absence of any isotopic label, are identical to those obtained from the secondary geminate radical pair.

An earlier study [10] focused on the photochemistry of *meso*-DPP in homogeneous solution, in micellar media and on porous glass. In pentane solution, 93% of the product mixture consisted of DPB with less than 0.5% of *d,l*-DPP isomer being formed. When photolysis was conducted in SDS micelles, the yield of DPB decreased to 72% and the yield of *d,l*-DPP increased to 8%. The micellar core acting as a microreactor increased the probability of recombination, relative to homogeneous solution, by diminishing the cage escape rate of the primary radical pair. Also relevant to the present study was the fact that no stereoselectivity was seen in DPB formation: *d,l*- and *meso*-DPB were formed in a ratio of 1:1. Similar results were obtained when the reaction was conducted on porous glass.

The specific cations present within the supercage cavity determine the nature of the steric and electronic interactions experienced by the adsorbed substrates. During the photolysis of DBK, the amount of isomeric coupling products (*o*-DBK and *p*-DBK) formed relative to DPE was taken to a measure of the relative rotational to diffusional mobility. In solution, where diffusion is very large, none of the coupling products of the primary radical pair are seen. Thus increasing the steric congestion within the zeolite cavities, by changing the cation from lithium to sodium to potassium, should result in a lowering of the diffusional mobility relative to rotational freedom, leading to the formation of more isomeric coupling products at the expense of DPE. Such an effect was indeed observed [5, 6].

The nature and contribution of the electronic effects of the cations are less obvious. IR studies with adsorbed CO [11] and CO₂ [12] and calculations of field strengths [11] suggest that the cations in Y zeolites have larger effective field strengths than the cations in the X zeolites. However, the number density of cations in the X zeolites is known to be larger than in the Y zeolites. Other more recent manifestations of the electronic effects of cations, are as follows: (1) the perturbation of the absorption spectra of aromatic molecules such as naphthalene and anthracene is a function of the cation present within the zeolitic cavity; (2) the desorption of alkyl aryl ketones adsorbed onto different X faujasites occurs at decreasing temperatures in the cationic series lithium, sodium, potassium, rubidium, cesium (determined by thermogravimetric analysis) [8].

The lack of selectivity in DPB formation in homogeneous solutions and in micellar and porous glass media indicates that the transition state energies for the coupling of the two radical fragments to yield *d,l*- and *meso*-DPB must be very similar. The maximum selectivity of approximately 1.9:1 observed for the formation of *d,l*-DPB over *meso*-DPB translates into a value of $\Delta\Delta G^\ddagger = 380 \text{ cal mol}^{-1}$ at 25 °C. Thus the differences between the interactions experienced by the two transition states are very slight and are difficult to attribute to any particular gross characteristic of the zeolite environment.

The subtle combination of steric and electronic effects of the cations in the supercages is highlighted in the variation of the diastereoselectivity. The larger field strengths of the cations within the Y zeolites [11] will lead to a more effective stabilization of the radicals in the Y zeolites relative to the X zeolites, resulting in greater stereoselectivities in DPB formation. Such an effect is indeed observed for the LiY and NaY zeolites relative to the corresponding X zeolites. On going to the potassium-exchanged zeolite, steric factors seem to overwhelm any electronic bias towards the formation of the *d,l* isomer and the increased congestion manifests itself as a substantial loss of stereoselectivity in DPB formation. The non-monotonic behavior of NaX in the X series is probably due to a subtle interplay of the mutually opposing steric and electronic factors.

The observation that the magnitude of the DPB stereoselectivity is a function of the stereochemistry of the starting substrate is probably indicative of the fact that complete rotational randomization of the radicals does not occur prior to recombination. If rotation of the radical fragments relative to one another (Fig. 5) could be prevented, then *d,l*-DPP would yield *d,l*-DPB and *meso*-DPP would yield *meso*-DPB. Since *d,l*-DPB is the favored isomer, the above hypothesis rationalizes the observation that lower selectivities in product formation are found when *meso*-DPP is the substrate photolyzed.

The magnitudes of the *s* values of approximately 0.4–1.4 measured in this study (Figs. 4(a) and 4(b)) are put in better perspective when considered with the observation that the value for *s* in pentane solution is only 0.01 and the values for *s* obtained on SDS and porous glass are 0.15 and 0.17 respectively. The values obtained from photolysis in zeolites are significantly larger. These results are in complete accordance with the intuitive expectation that a more closed, tighter cage environment will favor more return to starting material in the primary geminate radical pair. Increased steric congestion within the zeolitic environment will therefore lead to a larger value for *s*. The larger environment provided by the Y faujasite cavities, due to the presence of a smaller (relative to the X zeolites) number of cations, is apparently spacious enough to preclude steric effects from becoming dominant on changing the cation from lithium to potassium and is thus responsible for the relatively constant value for *s* in this

series; alternatively it may be that a compensating electronic interaction attenuates the increasing steric effect on going from lithium to potassium and keeps the value of s relatively constant. This result is in accordance with the observation that the ratio of (*o*-DBK + *p*-DBK)/DPE for DBK photolysis on Y zeolites is relatively constant [5]. The larger value for s in LiX and KX (relative to the Y zeolites) is to be expected, again in agreement with the results for DBK (more rearrangement products at the expense of DPE when steric congestion increases). The decrease in s on going to NaX from either LiX or KX is again due to the subtle interplay between steric and electronic factors which conspire to produce this non-monotonic behavior.

Benzene, as an added spectator molecule, undoubtedly increases the steric congestion experienced by the substrate molecules. Its presence also results in the attenuation of some of the electronic effects associated with the cations. The decrease in the stereoselectivities of DPB formation, in the presence of benzene, may be attributable to a combination of both these effects. The corresponding modest increase in the s values is probably a result of the increasing congestion, since diffusional separation followed by decarbonylation is relatively hampered. This is analogous to the effect of benzene on the photolysis of DBK on NaY and NaX: more rearrangement products are observed at the expense of DPE in the presence of added benzene [5].

The effect of loading of DBK on NaX reveals some spectacular results [5]. The ratio of (*o*-DBK + *p*-DBK)/DPE changes from approximately 1:4 to about 4:1 on going from a loading of 0.4% to 5% (which translates to a change in mean occupation number from one molecule per 32 supercages to one molecule per 2.5 supercages). In contrast, NaY displays only a very small sensitivity to loading: (*o*-DBK + *p*-DBK)/DPE changes from approximately 13:87 to 33:59 on going from 0.4% to 5%. These results can be rationalized by applying the principles of percolation theory and topological analysis to zeolite morphology, assuming that the benzylic radicals are relatively free to diffuse within the zeolite framework [13]. The cage effect of approximately 20% on both NaY and NaX at the 2% loading level of DBK justifies this assumption [5].

A loading study with *d,l*-DPP on NaY showed that there was no effect on either the stereoselectivities of DPB formation or the s parameter (akin to the results obtained with DBK). However, on NaX, unlike DBK, *d,l*-DPP again displayed no effect of loading in the 0.5%–5% range. Two possible hypotheses may be considered to explain the lack of any loading effect on the s value: a very small diffusional mobility of the radicals generated from DPP relative to those generated from DBK and/or an enhanced rate of decarbonylation for the α -methylphenylacetyl radical, due to the presence of the methyl group, relative to the phenylacetyl radical obtained from DBK. In solution, it is known that the rate of decarbonylation of the α -methylphenylacetyl radical is about eight times faster than the rate of decarbonylation of the phenylacetyl radical [14]. Thus if decarbonylation occurs before the radicals can diffuse apart, collide with another DPP molecule (the frequency of this collision will increase at larger loading levels) and return for recombination, then the percentage of the diastereomer formed will be independent of the loading level (for loadings of less than one molecule per supercage). Similarly, if the radicals generated from DPP have very small self-diffusion coefficients, then the zeolite cavity will act as the perfect cage and each cavity will essentially behave as an "isolated system" for loadings of less than one molecule per cavity.

The implication of the small self-diffusion coefficient hypothesis is the prediction of extremely large cage effects of the secondary pair even at very small loading levels. This prediction was borne out by our cage effect studies using unsymmetrically labelled *d,l*-DPP- d_6 . At the 2% loading level, cage effects of 18% and 22% were observed on

NaY and NaX respectively with DBK- d_5 . Using DPP as the substrate, we observed a cage effect of 100% at the 2% level on both NaY and NaX: no d_0 or d_{12} substrates were detected in either the DPB products or the diastereomerized starting material. The presence of the extra methyl group is apparently sufficient to decrease the self-diffusion coefficient to a value small enough to preclude any significant diffusional motion prior to recombination.

The strength of the electronic interactions between the cations and the radical fragments obtained from either DBK or DPP is probably very similar (the *sec*-phenethyl radical is probably slightly more basic than the toluyl radical due to the presence of the additional methyl group). However, the steric interactions are likely to be much more severe in the case of the radicals obtained from DPP. It is this fact, coupled with a faster rate of decarbonylation, that is probably responsible for the lack of detection of any ortho or para coupling products in the photolysis of DPP isomers as opposed to results seen with DBK. Our observation of the lack of formation of a significant amount of PPA is consistent with the observation of Ramamurthy *et al.* [15] who did not detect any aldehydic products in their photolysis of monoalkyl-substituted DBKs. A possible explanation for this behavior may be that the presence of the alkyl substituent at the benzylic position of the benzylic radical prevents the relative motion of the two radical fragments, within the confines of the zeolite cage, to achieve a geometry suitable for the disproportionation reaction to occur.

5. Conclusions

The photolysis of isomerically pure *d,l*- and *meso*-DPP adsorbed onto lithium- and sodium-exchanged X and Y zeolites results in diastereoselective induction in the DPB products formed. The lithium- and sodium-exchanged Y zeolites show a larger selectivity for *d,l*-DPB formation than the lithium- and sodium-exchanged X zeolites. This larger selectivity of the Y zeolites over the X zeolites is greater when *d,l*-DPP is the substrate than when *meso*-DPP is the substrate. The lack of selectivity with either KX or KY is a manifestation of the existence of extremely subtle stereo-electronic interactions between the cations present in the zeolite cavities and the adsorbed DPP molecules.

Unlike the *d,l*-/*meso*-DPB ratio, the *s* parameter is independent of substrate configuration. In the Y series, the *s* parameter falls within a narrow range and this is in complete analogy with the results obtained with DBK. However, in the X series the *s* parameter is non-monotonic with respect to cation size, and NaX reveals smaller *s* values than either LiX or KX. The *s* parameter is completely insensitive to loadings of up to 5% on both NaX and NaY. These results may be attributable to either an enhanced rate of decarbonylation and/or to severely restricted diffusional motion of the radicals. The latter hypothesis is supported by the observation that a 100% cage effect is found for both NaX and NaY with *d,l*-DPP- d_6 as the substrate, whereas DBK under similar conditions shows a cage effect of only 20%.

The effect of benzene as an added spectator molecule, on NaX and NaY, is to reduce the selectivity in *d,l*-DPB formation and to increase the *s* value due to increased steric congestion.

This report is the first example, to the best of our knowledge, of diastereoselective induction in radical coupling reactions in zeolites. This diastereoselectivity may be modified by changing the nature of the zeolite (X or Y) and the associated cations.

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