

Radical pairs with rotational fluidity in the photochemical reaction of acetophenone and cyclohexane in the zeolite NaY: a ^{13}C CPMAS NMR and product analysis study

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The photochemical reaction of acetophenone and cyclohexane in the zeolite NaY occurs by combination of the geminate radical pairs to give products that reveal a significant amount of rotational fluidity, which was also documented by intermolecular nuclear dipolar interaction measurements using cross polarization ^{13}C NMR (CPMAS) experiments.

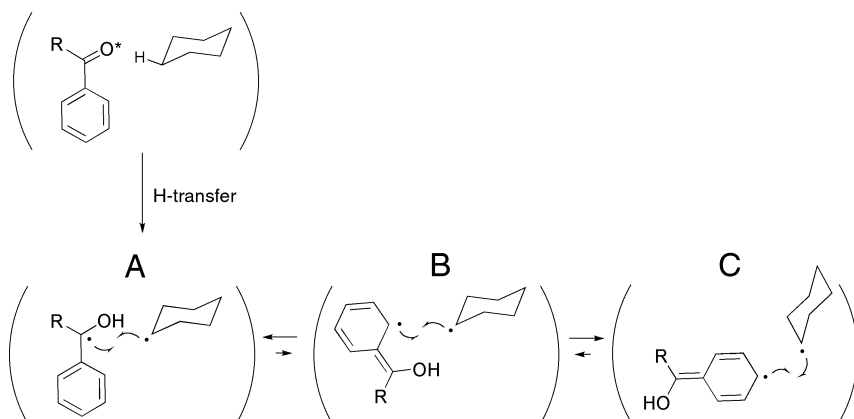
Introduction

During the last few years, a number of organized assemblies have been examined as reaction media to control the product distribution of photochemically generated transients, such as excited states and reactive intermediates.¹ Examples include molecular crystals, zeolites, inclusion complexes (both in the solid state and in solution), liquid crystals, micelles, Langmuir–Blodgett films, and others. The effect of these media varies widely and depends primarily on their influence on the motion of the reactants, generally restricting some reaction pathways and sometimes opening new ones.² Not surprisingly, the largest effects as compared to reactions in solution are seen with reactions carried out in solids. In one extreme, close-packed molecular crystals restrict molecular translation, rotation, and large amplitude conformational motions, so that chemical reactivity is limited to least motion pathways.³ Alternatively, photochemical reactions carried out in zeolites take advantage of most molecular degrees

of freedom, in measures that depend on the sizes and shapes of the reactants as compared to those of the zeolite cavities and channels.^{4,5} The relation between molecular fitting and reaction control has been deduced by product analysis in the MX and MY zeolites by changing the sizes of the cation M,⁶ and by adding molecular “spectators”⁷ and chiral co-adsorbates.⁸ A few years ago, while studying the reaction between benzophenone- d_{10} and cyclohexane in NaX we demonstrated that intermolecular $\{^1\text{H}\}$ - ^{13}C cross polarization in ^{13}C CPMAS⁹ NMR experiments could be used as a measure of close proximity and restricted mobility.¹⁰ A relatively static diphenylketyl–cyclohexyl radical pair ($\text{R} = \text{Ph}$, Scheme 1) formed by intermolecular hydrogen abstraction in the orientation depicted in Scheme 1A led to 1,1-diphenylcyclohexylcarbinol as the only product (as indicated by the half arrows). In this paper we describe an analogous study with acetophenone and cyclohexane in NaY ($\text{R} = \text{Me}$, Scheme 1). We report how the smaller reactant experiences greater mobility, so that the radical pair formed by hydrogen transfer can rotate and explore additional reaction pathways.¹¹ In addition to the product formed from orientation A, products were also obtained from the bonding pathways indicated by orientations B and C. The increased mobility of the reactants was also documented by intermolecular $\{^1\text{H}\}$ - ^{13}C cross polarization measurements, which revealed a weaker dipole–dipole interaction.

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Scheme 1 Alternative forms of C–C bond formation allowed by in-cage rotational motion of the ketyl–cyclohexyl radical pair in the zeolite NaY.

Experimental

Photochemical experiments

Acetophenone (50 μl) was irradiated using a 400 W medium pressure mercury lamp ($\lambda < 300\text{ nm}$) in dry cyclohexane for 2 h. For photoreactions within NaY zeolite, 50 μl of acetophenone and 3 ml of cyclohexane were mixed in a Pyrex test tube. To this solution was added 200 mg of NaY activated for 3 h at 425 $^\circ\text{C}$ and the resulting suspension stirred for 6 h under an argon atmosphere. The supernatant cyclohexane layer was removed, tested for the removal of acetophenone and the zeolite washed three times with 3 ml fresh cyclohexane. Samples were irradiated as cyclohexane slurries for 1–6 hours in Pyrex test tubes ($\lambda < 300\text{ nm}$) with the 400 W medium pressure mercury lamp. Products were extracted by stirring with ethyl acetate for 6 h. Product analyses were carried by GC and GC-MS with retention times and fragmentation patterns calibrated with those of authentic samples. The identities of products **2**,¹² **3a**¹³ and **3b**¹⁴ and **4**¹⁵ were confirmed by comparing spectral data with that previously reported in the literature.

Solid state NMR measurements

The ^{13}C NMR spectra of all zeolite samples were carried out at 75.47 MHz on a Bruker Avance instrument. The ^{13}C CPMAS experiments were run with the TOSS sequence¹⁶ in order to suppress the spinning sidebands. Adamantane was employed as an external chemical shift reference and the magic angle was adjusted with KBr. The 90° pulse width was 4.25 μs . Adequate cross polarization was achieved using 1.5 ms as contact time in the case of natural abundance samples and 5 ms in the case of acetophenone- d_8 . A rotation rate of 10 kHz was used for all samples. Zeolite samples for ^{13}C -CPMAS studies were prepared with acetophenone labeled with ^{13}C at the carbonyl and methyl carbon to shorten the acquisition times.

Results and discussion

Zeolites X and Y are microcrystalline aluminosilicates made up of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra that form an extended three-dimensional network with an architecture that results in relatively large cavities known as supercages (Fig. 1). With an internal diameter of *ca.* 12 Å , each supercage is connected to four others by openings that have *ca.* 8 Å diameter, so that medium-size organic molecules are able to diffuse through the three-dimensional network. The rate of diffusion, rotation, and conformational motions of the molecules included therein depend on their size and shape, as well as the specific chemical interactions with zeolite walls. Given that each aluminium center carries a negative charge, the structure of the zeolites requires an equivalent number of charge-compensating cations, which are largely responsible for the specific binding interactions with the organic adsorbates. Na-exchanged Y zeolites (NaY) such as the one used in this study have a low Al content, and a smaller number of cations than the analogous X-zeolites. While samples of dried NaY may be considered relatively inert, they are able to remove acetophenone from a cyclohexane solution in as much as 25% of their own dry weight, clearly suggesting a very favorable binding interaction.

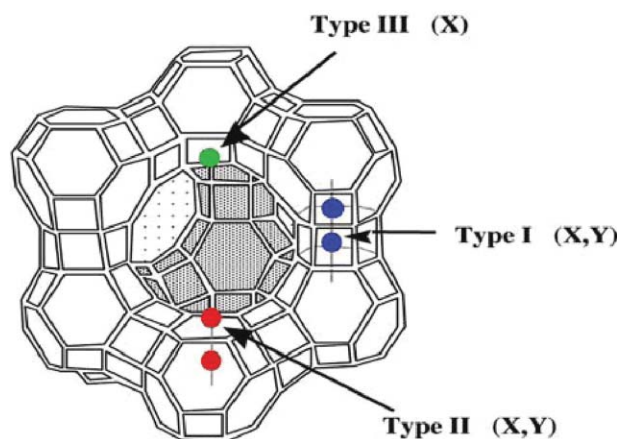
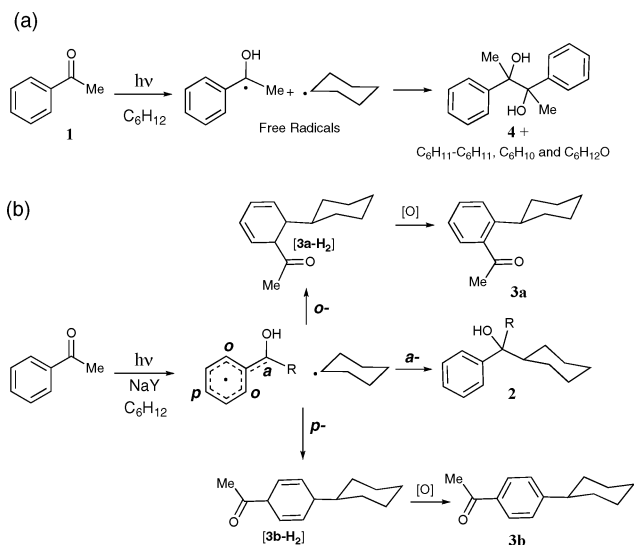


Fig. 1 Structure of the Faujasite X and Y framework illustrating the sites (I–III) of the charge-compensating cations.

Photochemical results

Our observations on the solution and zeolite photochemical reactivity of acetophenone and cyclohexane are summarized in Scheme 2. Photochemical excitation in solution results in formation of pinacol **4** and several low molecular weight products, including bicyclohexane and cyclohexene. It is well known that the reaction occurs by intermolecular H-abstraction from the rapidly formed triplet excited state to form a triplet radical pair that separates to become free radicals.¹⁷ The results suggest that the kinetics of termination for the ketyl and cyclohexenyl radicals are very different as no coupling between them is observed in solution.¹⁸ In contrast, the reaction in NaY is characterized by a very efficient cage effect. While 1-cyclohexyl-1-phenylethanol **2** is formed by coupling the cyclohexyl and acetophenone-derived radicals at the ketyl carbon, 2'-cyclohexylacetophenone **3a** and 4'-cyclohexylacetophenone **3b** are formed by coupling at the *ortho*- and *para*-positions, respectively. It is interesting that pinacol **4** and bicyclohexyl were completely absent (by GCMS) when the photoreaction was conducted in the zeolite.



Scheme 2 Photochemical reactivity of acetophenone and cyclohexane in (a) dilute solution, and (b) co-adsorbed in the zeolite NaY.

It has been previously established that radical combination is the dominant reaction pathway for ketyl and alkyl geminate radical pairs generated by intermolecular hydrogen abstraction with the zeolite supercage.^{19,10} Some examples include the reactions of benzaldehyde, *p*-methylbenzaldehyde, acetophenone, and benzophenone with toluene,¹⁹ and benzophenone with cyclohexane.¹⁰ All these reactant pairs favor the coupling of the corresponding alkyl and ketyl radicals to give a tertiary alcohol. Based on this precedent, the absence of pinacol **4** and the formation of the tertiary alcohol **2** from acetophenone and cyclohexane within NaY come as no surprise. The results suggest: (1) that having two reacting acetophenone molecules in the same supercage is very unlikely, (2) that reacting ketones share the supercages with cyclohexane molecules and, (3) that the resulting radical pairs are unable to separate and become free radicals. However, the formation of 2'-cyclohexylacetophenone **3a**, and 4'-cyclohexylacetophenone **3b** suggest that radical pairs are able to explore several orientations for the *ortho*- and *para*-coupling reactions to occur (Scheme 1).

It should be noted that formation of **3a** and **3b** requires ketonization and oxidation of the initially formed coupling products. The initial coupling at the *ortho*- and *para*-positions followed by ketonization of resulting enols leads to 2,4- and 1,4-cyclohexadienone intermediates **3a-H₂** and **3b-H₂** (Scheme 2). While no evidence could be obtained for these intermediates by solid state ¹³C CPMAS NMR (*vide infra*), control experiments with samples of commercial 1,4-cyclohexadiene in NaY showed that oxidation and aromatization takes place spontaneously within the time scale of the photochemical reaction and analysis. The results from a series of runs under various experimental conditions are shown in Table 1. Notably, photochemical experiments carried out for 6 h with aerated, O₂-purged, and Ar-purged samples showed relatively modest differences, suggesting that chemisorbed oxygen may be the oxidant.²⁰ Given that the spin density at the *ortho*- and *para*-positions are relatively similar,²¹ the yields of **3a** and **3b** suggest that *ortho*-coupling is sterically hindered as compared to *para*-coupling. One may also speculate that *ortho*-coupling should be kinetically disfavored with respect to coupling with the nearby ketyl position. Although the uncertainty of our measurement is relatively high at low conversion values (17%), the relative yields of **3 (a and b)** as compared to **2** are relatively constant for conversion values of 56% and 95%. Combination at the ketyl radical center to form **2** accounts for *ca.* 42% and combination at the *ortho*-

and *para*-carbons to form **3a** and **3b** accounts for *ca.* 48% of the products formed.

Solid state ¹³C-CPMAS NMR studies

Reaction progress was documented *in situ* by solid state NMR measurements by comparing the spectra before and after several irradiation periods. Samples were prepared with acetophenone labeled with ¹³C at the carbonyl and methyl carbons in order to have sufficient signal intensity and chemical resolution to detect the starting material, potential intermediates, and final products. The ¹³C-CPMAS spectra of acetophenone and cyclohexane co-adsorbed in NaY acquired before photolysis, and after 2.0 and 5.5 hours of UV irradiation are illustrated in Fig. 2. The spectrum of acetophenone and cyclohexane before photolysis exhibits ¹³C peaks at 27 ppm and 208 ppm. Independent measurements with samples of the two components (Fig. 2) confirmed that high field peak belongs to the overlapping signals of cyclohexane and the methyl group of acetophenone (Fig. 1a). The signal at 208 ppm corresponds to the carbonyl carbon and the natural abundance aromatic signals are not visible in this experiment. Evidence of reaction is clearly visible after 2.0 h of irradiation (Fig. 2b) with a signal belonging to the tertiary alcohol of 2-cyclohexyl-2-phenylethanol **2** clearly visible at 78 ppm along with some broadening of the methyl and carbonyl signals. Further irradiation increased the intensity of the carbinol carbon in **2** and led to changes in the carbonyl region.

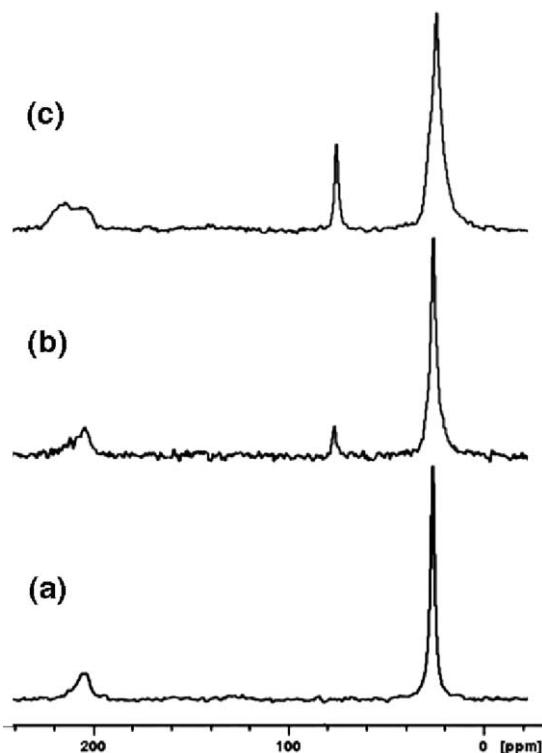


Fig. 2 ¹³C CPMAS NMR spectra (75.47 MHz) of ¹³C CO- and Me-labelled acetophenone and cyclohexane co-adsorbed in zeolite NaY (a) before photolysis, (b) after 2 hours of photolysis (17% conversion), (c) after 5.5 hours of photolysis (40% conversion).

A decrease in the intensity of the signal at 208 ppm was accompanied by the appearance of a broad peak at *ca.* 216 ppm, which

Table 1 Photoproduct distribution from acetophenone and cyclohexane in solution and in the zeolite NaY

Reaction medium	Irradiation time/h	% Conversion	Photoproducts (%) ^a		
			2	3a, 3b	4
Cyclohexane	2	10	—	—	10
NaY, aerated	3	17	4	1, 12	—
NaY, aerated	6	56	22	5, 29	—
NaY, aerated	9	95	41	7, 45	—

^a % Photoproducts are based on the relative ratio obtained from the GC data with an estimated error ± 3 . The photoproduct **2** was characterized based on comparison of retention time values with those of a sample independently synthesized. The photoproducts **3a**, **3b** and **4** were characterized by comparing the GC-MS data with the literature (ref. 13–15). Mass balances are typically in the 65–85% range.

is consistent with the formation of 4'-cyclohexylacetophenone **3b** along with a small amount of the *ortho*-isomer **3a**. Deconvolution of the carbonyl signals in terms of two Lorentzian functions revealed that the reactant carbonyl had broadened from 516 Hz before photolysis (Fig. 2a) to 944 Hz after 5.5 h irradiation (Fig. 2c). This broadening is indicative of an increased heterogeneity, which leads us to suggest that molecular motion within the zeolite cage is more restricted once the products are formed. We analyzed the peak at 27 ppm in the spectrum obtained after 5.5 h of irradiation using the program dmfit²² as a superposition of lines in order to account for the two major products (**2** and **3a**) and the two reactants. The cyclohexane peak in Fig. 3b can be fitted to a Lorentzian with a shift of $\delta = 27.56$ ppm and a line width of 34.95 Hz. Keeping those parameters for cyclohexane constant, and modeling the peak around 27 ppm in Fig. 2a (corresponding to cyclohexane and acetophenone) as a superposition of two Lorentzians, we obtained a shift of $\delta = 25.91$ and width of 197 Hz for acetophenone. We found that the experimental spectrum could not be reproduced by these values as well as the literature values of the chemical shift product **3b** ($\delta = 26.55$) constant. A satisfactory fit was obtained by fitting co-added cyclohexane and acetophenone with a line width of 299 ppm, and the two products with line widths of 533 and 234 Hz, respectively. The estimated errors in this model are relatively small (± 0.01 – 0.2 ppm and ± 8 – 30 Hz) and the spectrum is relatively well simulated. While highly tentative, this analysis suggests a nearly 10-fold increase in the line width of cyclohexane and a 50% increase in the line width of the methyl group of acetophenone, as expected for a highly anisotropic sample. In further agreement with this conclusion we determine that the approximate line width of the static spectra increases from 486 Hz before photolysis to 782 Hz after 40% reaction.

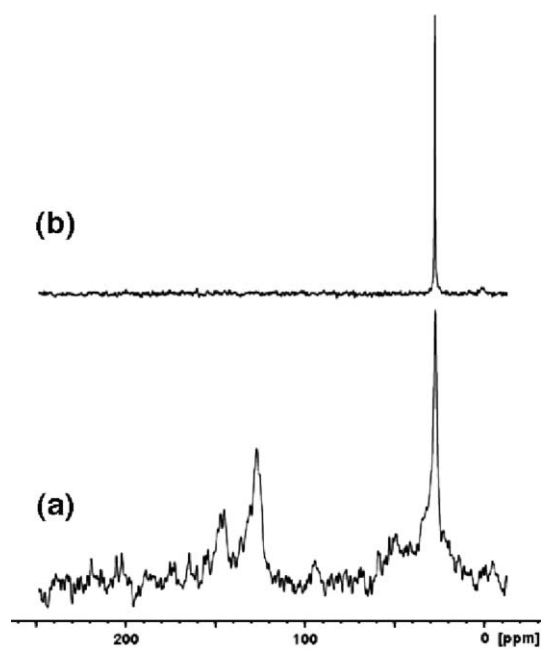


Fig. 3 ¹³C CPMAS spectra (75.47 MHz) of (a) acetophenone and cyclohexane co-adsorbed in zeolite NaY obtained with a contact time of 1.5 ms and 7200 scans, (b) acetophenone-*d*₈ and cyclohexane co-adsorbed in zeolite NaY obtained with a contact time of 5 ms and 31 900 scans.

The relative rigidity and mobility of the two reactants within the cavity of the zeolite NaY was probed in a qualitative manner with ¹³C CPMAS NMR measurements using acetophenone-*d*₈ and natural abundance cyclohexane. The cross polarization (CP) experiment involves the selective excitation of the ¹H nuclei followed by dipolar magnetization transfer to the less abundant ¹³C. A reasonable analogy may be drawn between the dipolar interactions in the nuclear CP experiment and those that dictate the Forster type energy transfer mechanism (FRET).^{9,10} The rate and efficiency of cross polarization rely on the strength of the ¹H-¹³C dipolar coupling, which depends on their distances and orientations. The most interesting difference between the magnetic and electronic experiments is that a dismal spectral overlap between ¹H and ¹³C, with resonance frequencies at 300 and 75 MHz (in our instrument), is converted into a perfect frequency match at fields that correspond to *ca.* 40 kHz by using the spin-locking RF pulse established by Hartmann and Hahn.²³ Under these conditions, isoenergetic ¹H-¹³C coupled transitions transfer the magnetization from the abundant ¹H to the rare ¹³C over time scales that vary from 0.1 to 10 ms. While most ¹³C CPMAS experiments involve intramolecular magnetization transfer, our experiment relies on the transfer of magnetization from one molecule to the other.

As a reference point we first acquired a ¹³C CPMAS spectrum of natural abundance acetophenone and cyclohexane coadsorbed in zeolite NaY. A relatively noisy spectrum was obtained in 7200 scans with a cross polarization time (contact time) of 1.5 ms (Fig. 3b). The peak at 27 ppm is attributed to the methyl group of acetophenone and the equivalent carbons of cyclohexane. Although the two signals overlap, they have significantly different line widths. Two broad signals at 127 ppm and 145 ppm correspond to the aromatic carbons but the signal of the carbonyl carbon is not visible with the unlabeled samples. The spectrum in Fig. 3b was obtained with a sample prepared with acetophenone-*d*₈ and natural abundance cyclohexane using a cross polarization time of 5 ms and 31 900 scans. Since no signals from acetophenone were observed despite the longer contact time and the greater number of transients, we conclude that there is no significant dipolar coupling between acetophenone and cyclohexane, and that intramolecular dipolar coupling in the cyclocarbon is very weak. Given that the two molecules share the same supercages for the reaction to take place, we conclude that the local environment must be highly fluid so that the lifetime of a given acetophenone-cyclohexane pair must be sufficiently long for hydrogen transfer in the excited state (*ca.* $> 10^{-9}$ s), but shorter than the timescale needed for magnetization transfer, which is *ca.* 10^{-3} to 10^{-2} seconds. A great deal of rotational freedom is also suggested by the sharp line width of cyclohexane in Fig. 3 and by the low intensity of its signal, even after 31 900 scans, as expected for a very inefficient *intramolecular* cross polarization.

When the photochemical and CPMAS results obtained with acetophenone are compared to those previously determined for benzophenone, one may conclude that a relatively small difference in the volume of the two ketones translates in substantial fluidity changes in the zeolite. To support this, one can estimate the average number of reactant molecules that can fit within a supercage by considering their van der Waals volume with respect the volume of the supercage. The molecular volumes (V_m) of benzophenone, acetophenone and cyclohexane can be estimated with a van der Waals increment approach first suggested by Bondi²⁴ with the

values later refined by Gavezzotti.²⁵ The method assigns van der Waals volume to different molecular components (methyls, methylenes, aromatic methines, carbonyls, hydroxyls, halides, *etc.*), which are added together to approximate the total volume of the molecule.^{24,25} Values (V_M) of 177 Å³ and 120 Å³ are obtained for benzophenone and acetophenone, respectively, and a value of 101 Å³ for cyclohexane. The average free volume of the supercages of NaY is reported²⁶ to be $V_{SC} = 839$ Å³. To estimate the number of molecules that may be accommodated within a supercage, we assume the known packing coefficient of benzene in NaY as an upper limit. The packing coefficient, C_K , was defined by Kitaigorodskii²⁷ as the ratio between the filled volume, based on the van der Waals molecular volume, and the total available volume. In the case of benzene, it has been determined that, on average, there are 5.4 benzene molecules per supercage.²² With a van der Waals volume of 85.4 Å³ per benzene molecule, the packing coefficient of benzene becomes $C_K = (5 \times 85.4)/839 = 0.55$. Assuming the same packing coefficient for the reactants in our study, one may expect that supercage occupancies will occur with a number of molecules that have a total added volume $V_{TOT} \approx V_{SC} * C_K = 462$ Å³. While this volume is surpassed slightly with one benzophenone and three cyclohexane molecules for a $V_{TOT} = 478$ Å³, an analogous occupancy in the case of acetophenone would occur with a $V_{TOT} = 421.4$ Å³, which could help explain the significantly higher molecular and radical pair rotational fluidities.

Conclusions

Photochemical reactions in zeolites take place under conditions where the time scales for molecular and intermolecular degrees of freedom are strongly reorganized as compared to solution and most other reaction media. While slow diffusion allows for reactants and product to enter and exit the zeolite interior, bimolecular reactions take advantage of relatively long-lived cage effects. While reactions derived from random encounters of free radicals are efficiently prevented, the options available to the geminate radical pair depend on how the latter fits within the rigid environment of the zeolite supercages. Intermolecular cross polarization experiments indicate that acetophenone and cyclohexane have a significantly enhanced rotational freedom as compared with that of benzophenone and cyclohexane. The greater rotational fluidity allows the radical pair derived from the former reactant couple to explore reaction pathways that are not available to the latter.

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