Proximity, Photochemical Reactivity, and Intermolecular ^{1}H−^{13}C Cross Polarization in Benzophenone-d_{10} and Cyclohexane in the Zeolite NaX

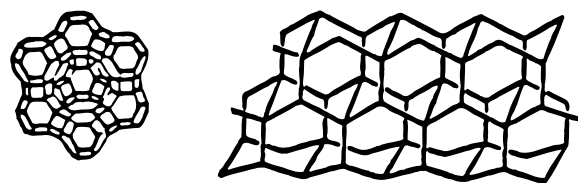**Deniz Cizmeciyan, Laura B. Sonnichsen, and Miguel A. Garcia-Garibay***

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

Received July 8, 1996[⊗]

Abstract: The photochemistry, photophysics, and solid-state ^{13}C CPMAS NMR of benzophenone and cyclohexane in the zeolite NaX have been analyzed to investigate their proximity, relative mobility, and intermolecular reactivity. Photochemical irradiation of benzophenone in pure cyclohexane yields benzopinacol and benzhydrol as the predominant products. In contrast, irradiation in the solid state leads to 1-cyclohexyl-1,1-diphenylmethanol as the only product by collapse of the radical pair formed after hydrogen abstraction from cyclohexane by excited benzophenone. Phosphorescence analysis at 77 K suggests a highly polar environment, but lack of emission at 300 K in the presence of cyclohexane is assigned to triplet decay via an efficient hydrogen abstraction reaction. Spectral analysis by ^{13}C CPMAS NMR reveals that benzophenone and cyclohexane are adsorbed in an approximate 1:2 ratio. Changes observed in spinning and static samples before and after photolysis are interpreted in terms of molecular motions that are capable of affecting the spectral line width. That benzophenone and cyclohexane share the zeolite supercages in a close packed arrangement was shown by a relatively efficient ^{1}H−^{13}C intermolecular cross polarization from cyclohexane to benzophenone-d_{10}. Comparison of the CPMAS intensities measured with deuterated and nondeuterated benzophenone samples under identical conditions suggest that intermolecular C−D···H−R distances between carbon atoms of deuterated benzophenone and hydrogens of cyclohexane have an average value of *ca.* 2.2 Å.

Zeolites are microcrystalline aluminosilicates with periodic structures of interconnecting channels and cages.[1−3] Their ability to include medium size organic chromophores makes them attractive for the study of photochemical processes in nanoscopic containers.[4−9] The zeolites most often used for photochemical studies are those with medium size cavities that allow for intracrystalline complexation and diffusion such as the synthetic faujasites or zeolites X and Y.[1] The internal structure of zeolites X and Y consists of 4-fold interconnected supercages with 15 Å diameter interconnected with each other by pores of 7.4 Å in a network that has the topology of the diamond structure (Figure 1).

Because of their relatively large pores sizes, intracrystalline diffusion in zeolites X and Y is relatively efficient.[9−11] When size and shape requirements are satisfied, there may be several molecules per site allowing for the occurrence of bimolecular reactions.[6,12−21] It is of interest in these reactions to know whether encounters between prospective reactants may occur

Figure 1. Representation of the structure of Zeolite NaX with a supercage as a vertex of a diamond structure where bonds represent interconnecting channels.

within the lifetime of the excited state or whether reaction requires a preorganized arrangement of the two reactants.[9] In this paper, we have studied benzophenone and cyclohexane in the zeolite NaX in search for a correlation between bimolecular reactivity and intermolecular nuclear ^{1}H−^{13}C cross polarization. Several photochemical, photophysical and solid-state ^{13}C CPMAS NMR measurements were carried out in order to investigate their proximity, molecular motion, and relative diffusion.

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1996.

(1) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry and Use*; John Wiley and Sons: New York, 1974.

(2) Dyer, A. *An Introduction to Zeolite Molecular Sieves*; John Wiley and Sons: New York, 1988.

(3) Rabo, J. A. *Zeolite Chemistry and Catalysis*; American Chemical Society: Washington, D.C. 1975.

(4) Weiss, R. G.; Ramamurthy, V.; Hammond, G. S. *Acc. Chem. Res.* **1993,** *26,* 530−536.

(5) Ramamurthy, V. *Chimia* **1992,** *46,* 359−376.

(6) Thomas, J. K. *Chem. Rev.* **1993,** *93,* 301−320.

(7) Yoon, K. B. *Chem. Rev.* **1993,** *93,* 321−339.

(8) Abrams, L.; Corbin, D. R.; Turro, N. J. In *Characterization of Porous Solids*; Unger, K. U., Ed.; Elsevier: Amsterdam, 1988; pp 519−529.

(9) Ramamurthy, V.; Garcia-Garibay, M. A. In *Comprehensive Supramolecular Chemistry*; Bein, T., Ed.; Pergamon Press: Oxford, 1996; Vol. 7; pp 693−719.

(10) Garcia-Garibay, M.; Zhang, Z.; Turro, N. J. *J. Am. Chem. Soc.* **1991,** *113,* 6212−6218.

(11) Derouane, E. G.; Gabelica, Z. *J. Catal.* **1980,** *65,* 486−489.

(12) Karger, J.; Ruthven, D. M. *Zeolites* **1989,** *9,* 267−281.

(13) Karger, J.; Pfeifer, H. *Zeolites* **1987,** *7,* 90−106.

(14) Förste, C.; Kärger, J.; Pfeifer, H. *J. Am. Chem. Soc.* **1990,** *112,* 7−9.

(15) Burmeister, R.; Schwarz, H.; Boddenberg, B. *Ber. Bunsenges. Phys. Chem.* **1989,** *93,* 1309−1313.

(16) Iu, K. K.; Thomas, J. K. *Langmuir* **1990,** *6,* 471−478.

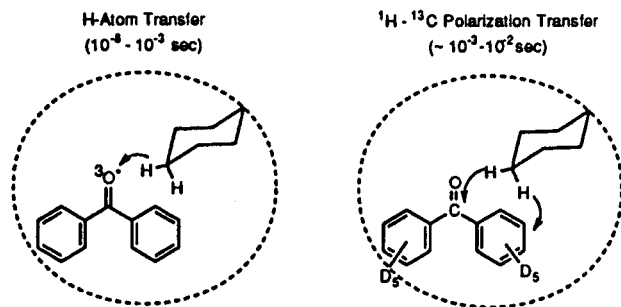(17) Iu, K. K.; Thomas, J. K. *Coll. Surf.* **1992,** *63,* 39−48.

(18) Suib, S. L.; Kostapapas, A. *J. Am. Chem. Soc.* **1984,** *106,* 7705−7710.

(19) Ramamurthy, V.; Corbin, D. R.; Kumar, C. V.; Turro, N. J. *Tetrahedron Lett.* **1990,** *31,* 47−50.

(20) Lei, X.; Turro, N. J. *J. Photochem. Photobiol. A* **1992,** *69,* 53−56.

(21) Ramamurthy, V.; Sanderson, D. R.; Eaton, D. F. *J. Am. Chem. Soc.* **1993,** *115,* 10438−10439.

Benzophenone-d₁₀ and Cyclohexane in the Zeolite NaX

J. Am. Chem. Soc., Vol. 119, No. 1, 1997 185

Scheme 1

Scheme 2

The abstraction of a hydrogen from cyclohexane by triplet benzophenone is a well known reaction which requires close proximity and adequate $C=O \cdots H-R$ alignment that in fluid solution is accomplished by random encounters. In contrast, intermolecular $^1H-^{13}C$ cross polarization depends on nuclear dipolar interactions and requires close proximity and rigidity and cannot occur under conditions of extensive molecular motion where dipolar coupling disappears. Our experiment involves conventional ^{13}C CPMAS NMR measurements with deuterated benzophenone and nondeuterated cyclohexane. The CP part of the experiment involves selective ^1H magnetization followed by dipolar transfer to the less abundant ^{13}C nuclei under Hartman–Hahn matching conditions.[22] Since observation of the carbon spectrum relies on the availability of a polarized ^1H source, deuterated benzophenone cannot be observed unless there is a dipolar-coupled, hydrogen-rich donor source that is relatively rigid and at a relatively close distance. It is expected that the CP efficiency will be best at *the closest distances and under restricted molecular motions*. Finally, it is interesting to point out that polarization transfer is expected to occur within time scales that match the upper limit for triplet state reaction. Thus, efficient polarization transfer from cyclohexane to deuterated benzophenone described below can be taken as evidence for a relatively static bimolecular reaction arrangement during the lifetime of the reactive triplet state.

Experimental Section

General Methods. Gas chromatography (GLC) data was obtained on a Hewlett Packard 5890 Series II gas chromatograph, with an HP 3396 Series II integrator. An HP-1 cross-linked methyl silicone gum column and an HP-20M Carbowax 20M column were used. Both are 25 m × 0.20 mm, with a 0.20 μm film thickness. Phosphorescence spectra were acquired at 77 K and 300 K by front face illumination and detection using a Spex Fluorolog Spectrofluorimeter equipped with a pulsed lamp (10 μs width) and a double grating monochromator. Zeolite NaX was obtained from Alfa. Benzophenone was obtained from Fisher Scientific. All solvents were ordered from Fisher Scientific and distilled over sodium and benzophenone under a nitrogen atmosphere. 4-Methoxybenzophenone was bought from Pfaltz and Bauer, Inc. Magnesium turnings were purchased from Malinckrodt Inc. Benzopinacol and benzhydrol were obtained from Aldrich and Eastman Kodak Co., respectively. Bromocyclohexane and *p*-toluenesulfonic acid were ordered from Matheson, Coleman, and Bell. Benzophenone-d_{10} was prepared by hydrolysis of the dichlorodi(phenyl-d_5)methane prepared by AlCl₃-catalyzed Friedel–Crafts reaction of benzene-d_6 with CCl₄.

Preparation of Zeolite Samples. Zeolite NaX was dried at 500 °C prior to use. The adsorption of benzophenone and cyclohexane onto zeolite NaX was achieved by vigorously stirring a suspension with 450 mg of dry zeolite in a solution containing 5 mL of cyclohexane and 40 (45) mg of benzophenone (benzophenone-d_{10}) under argon atmosphere. The amount of benzophenone adsorbed was monitored by GLC analysis of the supernatant solution after adding known amounts of 4-methoxybenzophenone as an internal reference. After
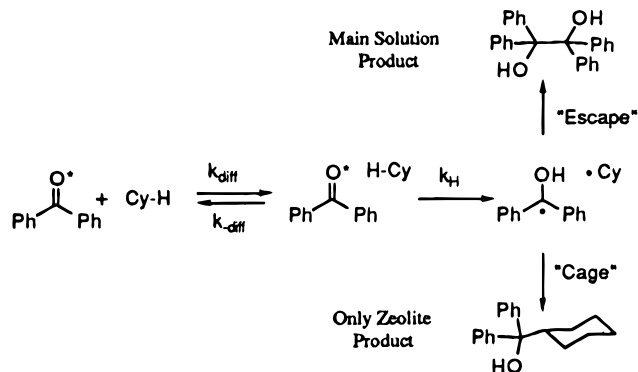
reaching adsorption saturation, the excess solvent was decanted, and the samples were allowed to dry under argon.

Photolyses. Photolyses were carried out under argon with a 400 medium pressure Ace-Hanovia mercury arc lamp, and the products were recovered by dissolving the zeolite in 1 N HCl solution followed by organic extraction. Solution irradiations were carried out in argon-purged cyclohexane with *ca.* 0.029 M benzophenone. Products were analyzed by GLC and GLC-MS and identified by comparison of their retention times and fragmentation patterns with those of authentic samples. Benzhydrol and benzopinacol were commercially available. 1-Cyclohexyl-1,1-diphenylmethanol was prepared by Grignard reaction of benzophenone with cyclohexylmagnesium bromide under argon atmosphere. Benzopinacolone was prepared by refluxing benzopinacol in benzene using *p*-toluenesulfonic acid (TsOH) as catalyst.

NMR Spectroscopy. Solid-state NMR spectra were obtained using a Bruker MSL-300 instrument. ^{13}C (74.8 MHz) spectra were obtained using CPMAS, and the suppression of the spinning side bands was implemented by the TOSS[23] sequence. Hexamethylbenzene (132 ppm) was used as the chemical shift reference, and the magic angle was adjusted with KBr. The 90° pulse width used was 4.9 μs. Adequate cross polarization was achieved using 2.1 ms as a contact time in the case of protonated samples and 5 ms contact time in the case of benzophenone-d_{10}. A recycle delay of 2 s was employed for all zeolite samples. In order to compare intensities, the same number of scans were recorded for similar samples. The spectra of crystalline 1-cyclohexyl-1,1-diphenylmethanol were acquired with a 20 s recycle delay. The rotation rates used were between 3.00 and 3.50 kHz. All solid-state NMR spectra were processed with line broadening of 200 Hz. All solution spectra were obtained with a Bruker ARX 400 MHz spectrometer in deuterated chloroform with TMS as internal reference.

Results and Discussion

Photochemistry in Solution and in the Solid State. Hydrogen abstraction from cyclohexane by triplet benzophenone in fluid media is a very well studied reaction (Scheme 2).[24–26] The triplet state of benzophenone in nonpolar solvents has a lowest energy n,π* configuration, and the hydrogen transfer reaction in neat cyclohexane occurs with a rate of 1.2×10^6 s^{-1} with quantitative quantum efficiency (i.e., $\Phi = 1.0$).[24,25] In fluid solutions, triplet ketone and hydrogen donor encounter each other and react by hydrogen transfer in an activated process (i.e., $k_H < k_{-\text{diff}}$, Scheme 2) with $E_a = 4$ Kcal/mol and log $A = 9$. The resulting triplet radical pair efficiently escapes the solvent cage to form free radicals that combine to form benzopinacol as the main isolable product along with minor quantities of benzhydrol, 1-cyclohexyl-1,1-diphenylmethanol, and other unidentified compounds from the cyclohexyl radical

(22) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042–2053.

(23) Dixon, W. T.; Shaefer, J.; Sefcik, M. D.; McKay, R. A. *J. Magn. Reson.* **1982**, *49*, 341–345.

(24) Topp, M. R. *Chem. Phys. Lett.* **1975**, *32*, 144–149.

(25) Giering, L.; Berger, M.; Steel, C. *J. Am. Chem. Soc.* **1974**, *96*, 953–958.

(26) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048–1054.
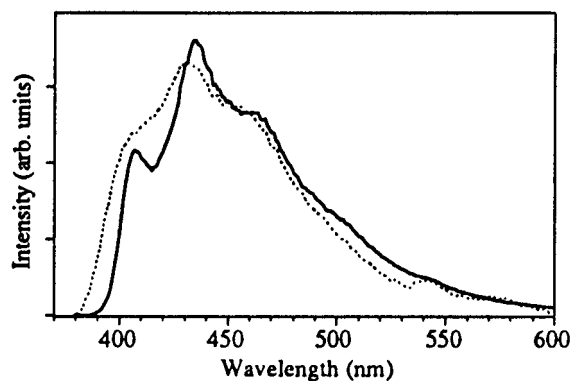
Figure 2. Phosphorescence spectra of (solid line) benzophenone coadsorbed with cyclohexane in Zeolite NaX at 77 K and (dotted line) pure benzophenone in NaX under vacuum at 300 K.

(Scheme 2). The photochemical reaction in the zeolite proceeds in a different manner.

The adsorption of benzophenone and cyclohexane in NaX was accomplished by stirring freshly dried samples of zeolite in cyclohexane solutions of benzophenone (*ca.* 0.05 M). Adsorption analysis showed saturation within 24 h and loading levels of 8.5 to 9.1 w/w corresponding to *ca.* 0.80−0.83 molecules per supercage. It was shown that benzophenone is thermally stable when complexed with NaX at ambient temperatures as it could be recovered in essentially quantitative yields. In contrast, no starting material or products could be retrieved from samples that had been irradiated with λ > 300 nm for 7 h. Failed attempts to adsorb benzopinacol and 1-cyclohexyl-1,1-diphenylmethanol in NaX showed that the expected photoproducts do not fit through the 7.4 Å pores and remain irreversibly trapped when formed inside the zeolite. In fact, extraction of 80% product and 20% unreacted benzophenone could only be accomplished after destructive dissolution of the zeolite in a 1 N HCl solution. The only product obtained in the zeolite was identified as 1-cyclohexyl-1,1-diphenylmethanol. Results obtained with benzophenone-d_{10} were identical to those observed with non deuterated ketone, and formation of 1-cyclohexyl-1,1-di(phenyl-d_5)methanol was confirmed.[27] The formation and exclusive coupling of cyclohexyl and diphenylketyl radicals indicates that the radical pair cannot escape such that reaction proceeds under a very efficient cage effect (Scheme 2).[10]

The effect of the zeolite on the photophysical properties of benzophenone was investigated by phosphorescence measurements (Figure 2). While zeolites stabilize ketone triplets to the extent that phosphorescence may be observed at ambient temperatures,[28−31] no emission could be detected from benzophenone in NaX in the presence of cyclohexane at 300 K. However, spectra obtained at 77 K showed a broad emission similar to that observed at ambient temperatures in the absence of cyclohexane and in good agreement with spectra previously reported in zeolite Na-ZSM-5.[28] Phosphorescence decays were not monoexponetial but reasonably good double exponential fits were obtained with lifetimes of 6.5 and 46.6 ms for benzophenone and 7.2 and 45.2 ms for benzophenone-d_{10}. These lifetimes suggest a predominant π,π^* configuration and like other diarylketones show essentially no isotope effect.[32−35] While it is known that π,π^* states are not reactive toward hydrogen abstraction,[36,37] the efficient reaction at 300 K indicates that the reactive n,π^* state may be populated at ambient temperatures. Reactive quenching in the presence of cyclo-
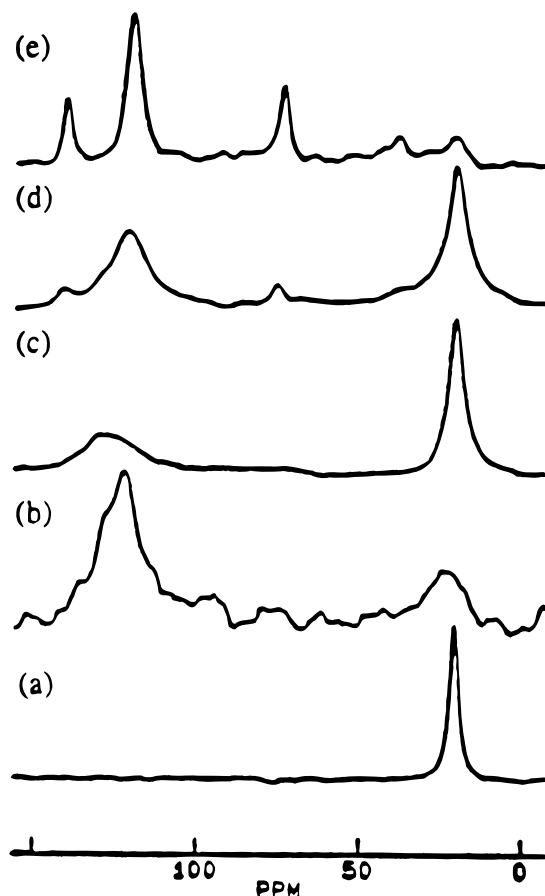
Figure 3. ^{13}C NMR (74.8 MHz) CPMAS spectra of (a) pure cyclohexane adsorbed on Zeolite NaX, (b) pure benzophenone in NaX, (c) cyclohexane and benzophenone coadsorbed on Zeolite NaX, (d) cyclohexane and benzophenone coadsorbed on Zeolite NaX after photolysis (spectrum recorded with a spinning sideband suppression sequence), and, (e) pure polycrystalline 1-cyclohexyl-1,1-diphenylmethanol.

hexane was also suggested by the observation of ambient temperature phosphorescence emission in evacuated samples of pure benzophenone in NaX which has a decay that was fit to double exponential values of 0.13 and 2.3 ms.

Solid State. ^{13}C CPMAS NMR Studies. Although the use of solid-state NMR to study molecular motion in zeolites includes line shape analysis, relaxation,[38] and pulse field gradient measurements,[12,13] a large amount of qualitative information may be obtained by simple examination of CP-MAS and static spectra. Initial measurements and assignments were carried out with cyclohexane and benzophenone followed by measurements with samples prepared with cyclohexane and benzophenone-d_{10}.

From bottom to top, Figure 3 shows the ^{13}C CPMAS spectra of cyclohexane (3a), benzophenone (3b), cyclohexane coad-

(27) Arnold, R. T.; Liggett, R. W. *J. Am. Chem. Soc.* **1942**, *64*, 2875−2877.

(28) Okamoto, S.; Nishiguchi, H.; Anpo, M. *Chem. Lett.* **1992**, 1009−1012.

(29) Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1985**, *63*, 1308−1314.

(30) Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 628−629.

(31) Scaiano, J. C.; Casal, H. L.; Netto-Ferreira, J. C. *ACS Symp. Ser.* **1985**, *278*, 211−222.

(32) Miller, J. C.; Borkman, R. F. *J. Chem. Phys.* **1972**, *56*, 3727−3729.

(33) Borkman, R. F. *Mol. Photochem.* **1972**, *4*, 1−19.

(34) Okamoto, Y.; Teranishi, H. *J. Am. Chem. Soc.* **1986**, *108*, 6378−6380.

(35) Garcia-Garibay, M. A.; Gamarnik, A.; Bise, R.; Jenks, W. S. *J. Am. Chem. Soc.* **1995**, *117*, 10264−10275.

(36) Wagner, P.; Park, B.-S. In *Organic Photochemistry*; Padwa, A. Ed.; Marcel Dekker: New York, 1991; pp 227−366.

(37) Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1973**, *95*, 8474−8475.

(38) Lechert, H.; Basler, W. D. *J. Phys. Chem. Solids* **1989**, *50*, 497−521.

sorbed with benzophenone (3c), a spectrum of the latter sample after photolysis for 6.5 h (3d), and the spectrum of crystalline 1-cyclohexyl-1,1-diphenylmethanol (3e). The spectra in Figure 3a−d were recorded with a 90° pulse of 4.9 μs, a contact time of 2.1 ms, and a recycle delay of 2.0 s. The spectrum in Figure 3e was acquired with a 20 s recycle delay. The spectrum of pure cyclohexane in NaX displays a symmetric peak at 20 ppm and relatively sharp line width of 230 Hz (Figure 3a). Pure benzophenone in NaX gives a broad signal (983 Hz) centered at 122 ppm that is assigned to the aromatic carbons. Coadsorption of benzophenone and cyclohexane broadens the cyclohexane signal relative to that of pure cyclohexane from 230 to 469 Hz and the signal of the benzophenone ring carbons at 135 ppm relative to that of pure benzophenone from 983 to 1516 Hz. The integrated areas of the aromatic and aliphatic signals in Figure 3c show an approximate cyclohexane to benzophenone ratio of the order of 2:1 suggesting a fairly packed, if disordered, structure. Several variations in contact times and recycle delays failed to produce the signal of the carbonyl group, which was expected in the range of 160−180 ppm. This is a reminder that integration on solid samples must only be taken as a rough approximation. CPMAS analysis of the photolyzed sample (Figure 3d) gave a spectrum consistent with that expected for 1-cyclohexyl-1,1-diphenylmethanol (Figure 3e) which cannot be independently adsorbed in the zeolite, presumably because of its large kinetic diameter. The spectrum of the photoproduct within the zeolite consists of aromatic peaks at 120 and 141 ppm, a carbinol carbon at 75 ppm, and a broad aliphatic signal assigned to the cyclohexyl group and to unreacted cyclohexane. This is consistent with the spectrum obtained from pure crystalline samples of the same compound shown in Figure 3e. We interpret the systematic broadening of the cyclohexyl signal in the spectra of Figure 3a,c,d in terms of changes in molecular motion. Since all spectra are obtained under high power ¹H dipolar decoupling, the 2-fold increase in line width in going from 3a to 3c is a strong indication of spectral heterogeneity resulting from restricted molecular motion which limits spectral averaging in a highly heterogeneous environment. This interpretation is supported by the further 30% increase in the line width of the cyclohexyl peak, up to 616 Hz, after the sample was photolyzed to form the product. Appearance of spinning side bands in the aromatic region of the spectrum of 1-cyclohexyl-1,1-diphenylmethanol (which were removed with TOSS[23] in Figure 3) also suggests a decrease in motion as radicals from benzophenone and cyclohexane become bound to form the photoproduct. Accordingly, static sample measurements shown in Figure 4 reveal a considerable increase in the chemical shift anisotropy of the aromatic region of the photoproduct as expected for a molecule unable to undergo rapid molecular tumbling. The static line widths of the aromatic peaks change from 3.63 to 8.15 kHz, and those of cyclohexyl groups change from 1.21 to 2.40 kHz before and after photolysis. These line widths are close to those of the static polycrystalline sample of the photoproduct.

The signals of benzophenone in Figures 3b and 4 result primarily from *intra*molecular magnetization transfer. It is expected that hydrogens directly attached to benzophenone transfer magnetic polarization to benzophenone carbons much more efficiently that those of cyclohexane. In contrast, the aromatic signals in spectra obtained with benzophenone-d₁₀ coadsorbed with cyclohexane must originate from *inter*molecular polarization transfer. Our expectations from *intra*molecular and *inter*molecular ¹H−¹³C polarization (CP) transfer are based on analysis of the cross polarization experiment as originally presented by Schaefer and Stejskal.[39] For our purposes, a
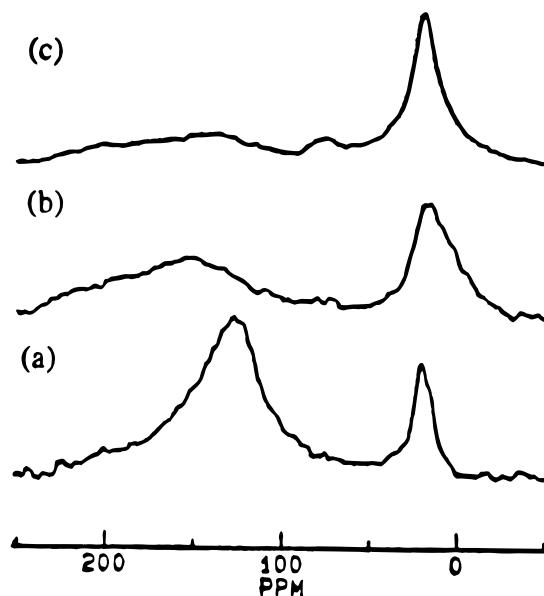
Figure 4. ¹³C NMR (74.8 MHz) CP spectrum of (a) stationary samples of cyclohexane and benzophenone adsorbed on Zeolite NaX, (b) stationary samples of cyclohexane and benzophenone adsorbed on Zeolite NaX after photolysis, and (c) stationary sample of polycrystalline 1-cyclohexyl-1,1-diphenylmethanol.

reasonable analogy may be drawn between the nuclear CP experiment and the dipolar interactions that are familiar to photochemists in the Forster type energy transfer mechanism.[40] Both depend on the distance and orientation between the donor and the acceptor as well as on their spectral overlap. The main difference with optical experiments is that spectral overlap in the magnetic CP experiment can be artificially optimized within a spin-locking RF-field where the Hartman−Hahn condition has been satisfied.[22] A dismal spectral overlap with ¹H and ¹³C resonance frequencies at 300 and 75 MHz, respectively, can be converted into a perfect frequency match at fields of *ca.* 40 kHz of the spin-locking RF pulse. Under these conditions, isoenergetic ¹H−¹³C coupled transitions transfer magnetization from abundant ¹H to rare ¹³C, thus providing the well-known sensitivity advantage.[41]

The efficiency of cross polarization depends on geometric factors and on the strength of the ¹H−¹³C dipolar coupling. It is inversely proportional to the ¹H−¹H homonuclear dipolar coupling.[39] Experimentally, ¹³C signals grow during ¹H−¹³C contact times (T_{CT}) of a few milliseconds and then they decay (usually in slightly longer times) by virtue of their spin−lattice relaxation in the rotating frame ($T_{1\rho}$). For samples with randomly oriented molecules where many orientations and distances are possible, the strength of the dipolar interactions and the rate of cross polarization (T_{CT}^{-1}) are maximized when molecules are relatively static. It has been documented that cross polarization can occur if the average ¹H−¹³C distances in different molecules are of the order of 10 Å.[42,43] Experiments demonstrating ¹H−²⁹Si cross polarization across silicate interfaces have also been carried out to distances up to 3−5 Å.[44,45] Thus, it may be expected that intracavity intermolecular cross

(39) Schaefer, J.; Stejskal, E. O. *Topics Carbon-13 NMR Spectrosc.* **1979**, *3*, 283−324.

(40) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co.: Menlo Park, 1978.

(41) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569−590.

(42) Parmer, J. F.; Dickinson, L. C.; Chien, C. W.; Porter, R. S. *Macromolecules* **1987**, *20*, 2308−2310.

(43) Gobbi, G. C.; Silvestri, R.; Russel, T. P.; Lyerla, J. R.; Fleming, W. W.; Nishi, T. *J. Polym. Sci. Part C: Polym. Lett.* **1987**, *25*, 61−65.
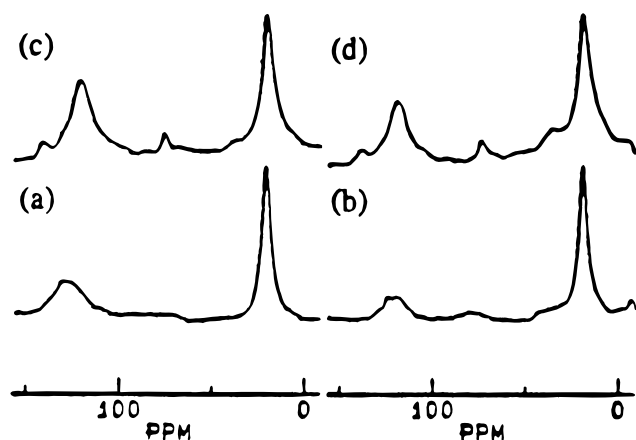
Figure 5. ^{13}C NMR (74.8 MHz) CPMAS spectrum of (a) cyclohexane and benzophenone adsorbed on Zeolite NaX obtained with a contact time of 2.1 ms and 9.5K scans, (b) cyclohexane and benzophenone-d_{10} adsorbed on Zeolite NaX obtained with a contact time of 5.0 ms and 9.5K scans, (c) cyclohexane and benzophenone adsorbed on Zeolite NaX after photolysis, obtained with a contact time of 2.1 ms and 85K scans, and (d) cyclohexane and benzophenone-d_{10} adsorbed on Zeolite NaX after photolysis, obtained with a contact time of 5.0 ms and 85K scans.

polarization may be possible given the fact that intermolecular distances between donor and acceptor should be much less than 15 Å, which is the diameter of the supercages in zeolite NaX.

The optimized CPMAS spectra of the benzophenone-d_{10}–cyclohexane samples before and after photolysis are shown in Figure 5 (b and d) along with the optimized spectra of the nondeuterated ketone (spectra 5a and 5c). The first thing to notice is that the relatively strong signal for the benzophenone-d_{10} carbons clearly demonstrates the occurrence of intermolecular cross-polarization. As expected, the most important difference between deuterated and nondeuterated samples comes from their cross polarization efficiencies. The optimum signal intensity for the *intra*molecularly cross-polarized aromatic carbons of benzophenone, and its photoproduct were obtained with a contact time of 2.1 ms (Figure 4). In contrast, identical spectral acquisition with benzophenone-d_{10} and its photoproduct under these conditions failed to produce the aromatic signals along with the strong cyclohexyl peak. When the contact times were increased, up to 5 ms, the appearance of aromatic signals was observed at the same time that the cyclohexyl peak de-

creased by about 40% as a result of spin−lattice relaxation in the rotating frame ($T_{1\rho}$). That the shape of the spectra of benzophenone-d_{10}−cyclohexane samples are essentially identical to those with nondeuterated benzophenone suggests that all carbons are on average equally accessible to cyclohexane hydrogens. Spectra obtained after photolysis showed similar trends.

Based on analysis by Klein Dowel *et al.*,[44−46] one may propose that cross polarization to benzophenone carbons in deuterated [$I_{(D)}$] and nondeuterated [$I_{(H)}$] samples is related to the inverse sixth power of the average C−H and C−D···H−R distances responsible for *intra-* and *inter*molecular polarization transfer. These efficiencies may be roughly estimated from the intensity of signals obtained under identical conditions. Thus, using the relations $[d_{(C-D\cdots H-R)}/d_{(C-H)}] = [I_{(H)}/I_{(H)}-I_{(D)}]^{1/6} \sim [I_{(H)}/I_{(D)}]^{1/6}$,[46] the intensities obtained with 2.1 ms contact times (i.e., $I_{(H)}/I_{(D)} \sim 8$), and a C−H bond distance of 1.54 Å, one can estimate an average carbon-hydrogen C−D···H−R distance of the order of 2.2 Å. It is interesting to note that this is the value expected for a C−D···H distance where benzophenone and cyclohexane are within their van der Waals distances,[47] which is a reasonable result given the loading of benzophenone and cyclohexane present in the zeolite. Thus, the proximity and rigidity suggested by the photochemical results is strongly supported by the ^{13}C CPMAS measurements. This study shows that the ^{13}C CPMAS NMR can be used as a qualitative tool for probing the proximity and mobility of distinct molecules within the confined environment of a zeolite and may be used to complement studies involving intermolecular reactivity. The line shape similarities between intra- and intermolecular cross polarization reflect the nearly spherical symmetry of the supercages in the zeolite NaX. It may be expected that polarization transfer in zeolites with less spherical sites may result in different transfer efficiencies to different nuclei if less isotropic contact between donor and acceptors are enforced by the structure. Studies in progress in our group are currently addressing this and other aspects of zeolite complexation and photochemistry.

(44) Zumbulyadis, N.; O'Reilly, J. M. *Macromolecules* **1991**, *24*, 5294−5298.

(45) Zumbulyadis, N. *J. Chem. Phys.* **1987**, *86*, 1162−1166.

(46) Klein Douwel, C. H.; Maas, W. E. J. R.; Veeman, W. S.; Werumeus Buning, G. H.; Vankan, J. M. J. *Macromolecules* **1990**, *23*, 406−412.

(47) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.