a condenser, addition funnel, and septum). Once the reaction between magnesium and the bromide had started, the remaining cyclopropyl bromide (6.25 g) was dissolved in 50 mL of dry THF and the solution added to the reaction. The total amount of cyclopropyl bromide used was 7.25 g (0.060 mol). Upon completion of addtion of the cyclopropyl bromide/THF solution, the reaction mixture was stirred at room temperature for ~20 min. During this 20-min time period, a suspension of cupric chloride (0.35 g, 2.6 mmol) in 15 mL of THF was prepared in a 250-mL flask. The suspension was cooled with an ice/water bath, and then the previously prepared Grignard was transferred into the same flask by use of a clean, dry cannula and a positive pressure of nitrogen. To this mixture were added 10.75 g (0.06 mol) of HMPA and 7.25 g (0.060 mol) of allyl bromide by syringe. The reaction mixture was then refluxed for 2 h, during which time the color changed from black to red.

After refluxing, the reaction mixture was cooled to room temperature and poured into 150 mL of saturated NH_4Cl solution. This aqueous solution was extracted with 50 mL of ether. The organic phase was separated from the deep blue aqueous phase and extracted with saturated NH_4Cl solution to remove any residual copper species. The organic phase was then washed four times with 100–150 mL of water to remove the HMPA. The ethereal solution was washed three times with saturated sodium chloride solution, dried with anhydrous sodium sulfate/magnesium sulfate, and filtered. The ethereal solution was then fractionally distilled to remove the ether, and the residue was subjected to preparative gas chromatography to yield allylcyclopropane:[27] ^1H NMR ($CDCl_3$) δ -0.1–1.0 (5 H, multiplet), 1.95 (2 H, doublet of doublets (apparent triplet), with fine structure, J = 7 Hz, $J_{allylic}$ ~0.4 Hz), 4.9 (1 H, doublet with much fine structure, J = 10 Hz), 5.1 (1 H, multiplet), 5.7 (1 H, multiplet); infrared spectrum (gas phase, 4.25 torr) 3100 cm^{-1} (CH, cyclopropane), 3020, 2920, 2850, 1640 (C=C), 1450, 1290, 1175, 1020 (cyclopropane ring), and 920 ($C{=}CH_2$, out of plane).

Preparation of *cis*- and *trans*-1-Cyclopropylpropene. Approximately 0.9 mL (0.8 g, 0.008 mol) of 1 cyclopropylpropanol was placed in a 5-mL round-bottom flask and warmed to 100 °C. One drop of concentrated H_2SO_4 was added and the warming continued. A short-path still was attached to the flask, and the products were distilled from the reaction mixture. Analysis of the product mixture by gas chromatography using column A showed two major products produced in equal amounts and two very minor ones. The major products were separated by preparative gas chromatography and determined to be *trans*-1-cyclopropylpropene (first peak) and *cis*-1-cyclopropylpropene (second peak) by NMR spectroscopy. Yield was approximately 50%.

Spectral Data for *trans*-1-Cyclopropylpropene. ^1H NMR ($CDCl_3$) δ 0.1–0.9 (4 H, multiplet), 1.64 (CH_3, 3 H, doublet of doublets, J = 6 Hz, J = 0.5 Hz), 1.70 (1 H, multiplet), 4.93 (1 H, doublet of doublets with fine structure, J = 20 Hz, J = 10 Hz, fine structure $J_{allylic}$ ~ 1 Hz), 5.48 (1 H, doublet of quartets, J = 20 Hz, J = 6 Hz); ^1H NMR ($CDCl_3$, decoupled by irradiating resonant with δ 1.64 (CH_3)) δ 0.1–0.9 (4 H, multiplet), 4.93 (1 H, doublet of doublets, J = 20 Hz, J = 10 Hz), 5.48 (1 H, doublet, J = 20 Hz); ^1H NMR ($CDCl_3$, decoupled by irradiating resonant with δ 5.48) δ 0.1–0.9 (4 H, multiplet), 1.64 (3 H, singlet with fine structure, J = 0.5 Hz), 1.70 (1 H, multiplet), 4.93 (1 H, doublet with fine structure, J = 10 Hz, J = 1 Hz); infrared spectrum (gas phase, GC–FTIR) 3080 cm^{-1} (CH), 3000 (CH), 2940 (CH), 1640 (C=C), 1450 (CH_3), 1380 (CH_3), 1200, 1120, 975, and 800.

Spectral Data for *cis*-1-Cyclopropylpropene. ^1H NMR ($CDCl_3$) δ 0.1–0.8 (4 H, multiplet), 1.30 (1 H, multiplet), 1.70 (CH_3, 3 H, doublet of doublets, J = 7 Hz, J = 1.8–2.0 Hz), 4.71 (1 H, doublet of doublets (apparent triplet) with fine structure, J = 10 Hz, J = 10 Hz, J = 1.8 Hz), 5.35 (1 H, doublet of quartets, $J_{doublet}$ = 10 Hz, $J_{quartet}$ = 7 Hz); ^1H NMR ($CDCl_3$, decoupled by irradiating resonant with δ 1.70 (CH_3)) δ 0.1–0.8 (4 H, multiplet), 4.71 (1 H, doublet of doublets—no fine structure, J = 10 Hz, J = 10 Hz), 5.35 (1 H, doublet, J = 10 Hz); ^1H NMR ($CDCl_3$, decoupled by irradiating resonant with δ 5.35) δ 0.1–0.8 (4 H, multiplet), 1.30 (1 H, multiplet), 1.70 (CH_3, 3 H singlet with fine structure), 4.71 (1 H, doublet, J = 10 Hz; infrared spectrum (gas phase, GC–FTIR) 3080 cm^{-1} (CH), 3030 (CH), 2940 (CH), 1650 (C=C), 1520, 1420, 1375 (CH_3), 1320, 1140, 1025, 960, 920, 820, 720, (cis C=C).

Preparation of 2-Cyclopropylpropene.[28] Sodium hydride (0.05 mol) was placed in a 250-mL three-neck flask and washed several times with petroleum ether. After the system was purged, 25 mL of Me_2SO was added and the suspension stirred while its temperature was raised to approximately 80 °C. At this point 17.9 g (0.05 mol) of methyltriphenylphosphonium bromide dissolved in 50 mL of Me_2SO was added slowly to the Me_2SO anion solution. The color turned from green to brown. Upon completion of the addition, the reaction mixture was stirred for 15 min at a temperature of 0–10 °C. Methyl cyclopropyl ketone (4.62 g, 0.055 mol) was added slowly and the mixtures stirred for 35 min at 0–15 °C, at which time it warmed to room temperature and was stirred for an additional 60 min. Distillation of the mixture provided 2-cyclopropylpropene in a fraction boiling between 70 and 80 °C; yield 35%; ^1H NMR ($CDCl_3$) δ 0.60 (4 H, multiplet), 0.90 (1 H, multiplet), 1.65 (3 H, triplet, $J_{allylic}$ = 2 Hz), 4.70 (2 H, quartet, $J_{allylic}$ = 2 Hz); infrared spectrum (gas phase, GC–FTIR) 3100 cm^{-1}, 3000, 1640 (C=C), 1450 (CH_3), 1375, 1240, 1020, 900. Spectral data consistent with literature values.[29]

Other compounds required for this work were obtained from commercial sources.

Registry No. 1, 5685-46-1; **5**, 4663-23-4; *cis*-**6**, 20479-70-3; *trans*-**6**, 20479-69-0; Br_2bcp, 22975-42-4; cyclopropyl bromide, 4333-56-6; allyl bromide, 106-95-6; 3-cyclopropylpropanol, 5618-01-9; 2-cyclopropylpropene, 4663-22-3; methyl cyclopropyl ketone, 765-43-5; methyltriphenylphosphonium bromide, 1779-49-3.

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^{13}C CP/MAS NMR Study of Molecular Motion in *n*-Alkylsilanes Bonded to the Silica Surface

Dean W. Sindorf and Gary E. Maciel*

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received September 29, 1982*

Abstract: Motional dynamics in long-chain aliphatic phases bonded to silica gel were studied using CP/MAS ^{13}C relaxation measurements. Differences in cross-polarization rates and proton $T_{1\rho}$ and T_1 values observed for samples prepared by silylation of silica gel with dimethyloctadecylchlorosilane (DMODCS) and dimethyloctylchlorosilane (DMOCS) identified methyl group rotation as a likely principal source of proton spin–lattice relaxation. Cross-polarization rates for carbons located at equidistant positions from the surface-attached silicon atom were similar for DMODCS and DMOCS systems. In general, cross-polarization efficiency was observed to decrease with increasing distance from the surface along the alkyl chain. However, for distances greater than roughly eight carbon units cross-polarization rates are essentially the same.

Introduction

Recent studies of normal and chemically derivitized silica gels using ^{29}Si and ^{13}C cross-polarization (CP)[1] and magic-angle spinning (MAS) NMR[2-5] have proven highly useful in extracting qualitative and in certain cases quantitative information about

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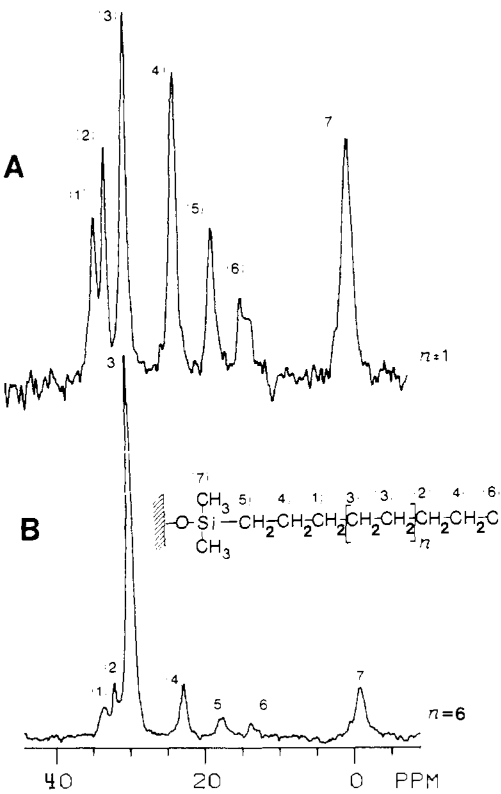

Figure 1. CP/MAS ^{13}C spectra and chemical shift assignments of silica gel reacted with DMOCS (A) and DMODCS (B).

the surface structural environments of these systems. Such studies have relied for the most part on the analysis of chemical shift and intensity data obtained from the CP/MAS NMR spectra. The potential capabilities of the solid-state NMR technique in the study of such systems is further extended in the present report, which examines the use of ^{13}C relaxation measurements for elucidating motional dynamics in long-chain aliphatic silane phases bonded to silica gel. The silica–silane systems examined are reaction products of silica gel with dimethyloctylchlorosilane (DMOCS) and dimethyloctadecylchlorosilane (DMODCS).

Experimental Section

Samples. High-purity Fisher S-662 silica gel (surface area = 510 m^2/g by N_2 adsorption) was used in the silane bonding reactions. Silyating reagents, DMOCS and DMODCS, were obtained from Petrarch Systems, Inc. (P.O. Box 141, Levitown, PA 19059) and were used as received (i.e., without purification). The DMOCS–silica reaction was carried out by refluxing 7 mL of pure liquid reagent with a 3-g sample of silica gel (predried under vacuum at 185 °C) at 180 °C for a period of 36 h. Following the reaction, the sample was washed repeatedly with toluene and then was evacuated at 100 °C. A silane loading of 185 mg/g was measured for this sample by use of gravimetric methods. For the DMODCS–silica reaction, 15 mL of a 30% (by weight) solution of the solid reagent in toluene was added to 3 g of dry silica. The resulting slurry was heated at 130 °C for a period of 48 h. As in the case of DMOCS, purification involved repeated washing with toluene and evacuation at 100 °C. A silane loading of 212 mg/g was measured for this sample.

NMR Experiments. ^{13}C CP/MAS spectra were obtained at 37.6 MHz on a modified Nicolet NT-150 spectrometer using 3.9-kHz MAS and 0.75-cm^3 Delrin rotors. Solid-state ^{13}C NMR spectra obtained on the samples prepared from DMOCS and DMODCS are shown in Figure 1. Also included in this figure is a structural model that shows tentative chemical shift assignments. These assignments were made on the basis of differences in relative integrated intensities measured from the two spectra of Figure 1 and observed[6] and previously reported[3,7] ^{13}C chemical shifts of related materials, assuming additivity relationships.[6,8]

Proton T_1 values for reacted materials were measured by a pulse sequence involving inversion-recovery of the proton magnetization, followed by cross-polarization to ^{13}C and observation of the resultant ^{13}C signal amplitude.[9] Proton $T_{1\rho}$ values were obtained by first spin-locking the proton magnetization in the rotating frame, waiting a variable time period (τ), and then cross-polarizing to ^{13}C.[9] Cross-polarization time constants (T_{CH}) were measured from observed amplitude changes in the ^{13}C resonances as a function of the contact time (CT). Intensity data were fit using a nonlinear least-squares algorithm to an equation given previously[10] for the case of an isotopically dilute observe-spin species (^{13}C) in the presence of a large excess of isotopically abundant spins ^1H, with nonnegligible rotating-frame spin–lattice relaxation. In principle, both T_{CH} and $T_{1\rho H}$ can be obtained from this variable CT experiment. However, because of the difficulty of maintaining a close Hartmann–Hahn match over the lengthy CT period required for $T_{1\rho}$ behavior to manifest itself (i.e., tens of milliseconds), T_{CH} values were obtained in these studies by constraining $T_{1\rho H}$ to the value determined using the more direct proton spin lock-τ-CP experiment described above. In this way meaningful T_{CH} results could be extracted from experiments with a relatively narrow range of contact times (0 to 5 ms).

Results and Discussion

A stacked plot of ^{13}C spectra obtained for the DMODCS-reacted sample at different values of CT is shown in Figure 2. Unlike the T_{1H} and $T_{1\rho H}$ results, individual values of T_{CH} determined for the various ^{13}C resonances are substantially different, ranging from 0.2 ms to over 1.5 ms. In agreement with previous solid-state NMR results, carbons associated with methyl groups (peaks 1 and 2) were observed to cross-polarize at a significantly slower rate than methylene carbons in similar chemical environments (e.g., peaks 3, 7). This behavior can be attributed to rapid molecular rotation of the methyl group about the CH_2–CH_3 C–C bond, which partially decouples methyl carbons from methyl protons. (Without such motion one would expect methyl carbons to cross-polarize faster than methylene carbons, since there are 50% more directly attached protons available for this purpose.)

In both DMDCS- and DMODCS-reacted samples resonances associated with carbons near the silane atom (i.e., near the silica surface) were observed to cross-polarize significantly faster than resonances associated with similar carbon atoms located near the end of the alkyl chain. This behavior is illustrated in Figure 3, where T_{CH} values measured for methyl and methylene carbons are plotted vs. carbon position (from the silane silicon atom). For the nonresolved resonances 4 and 5 an average carbon position was computed on the basis of the chemical shift assignments given in Figure 1.

Proton T_1 values measured on the silylated silicas prepared from DMODCS and DMOCS are 300 ± 10 ms and 199 ± 9 ms, respectively. All of the carbons except the CH_3–Si carbons reflected these T_{1H} values, but the latter yielded T_{1H} values that were somewhat lower (10 to 20%). $T_{1\rho H}$ values were found to be 15 ± 3 and 24 ± 1 ms for the DMODCS-reacted and DMOCS-reacted samples, respectively.

As proton spin diffusion in solids is normally a very efficient process, one can usually assume that all or most of the protons in a homogeneous sample have common or similar T_1's. Except for perhaps T_{1H} values of the methyl group (for which rapid rotational motion attenuates the dipolar interactions responsible for spin diffusion), this appears to be the case for the present data. The relatively shorter proton T_1 values and longer proton $T_{1\rho}$ values measured from the DMOCS-reacted sample relative to the DMODCS-reacted sample suggests a spectral density distribution that includes a larger fraction of motional components in the

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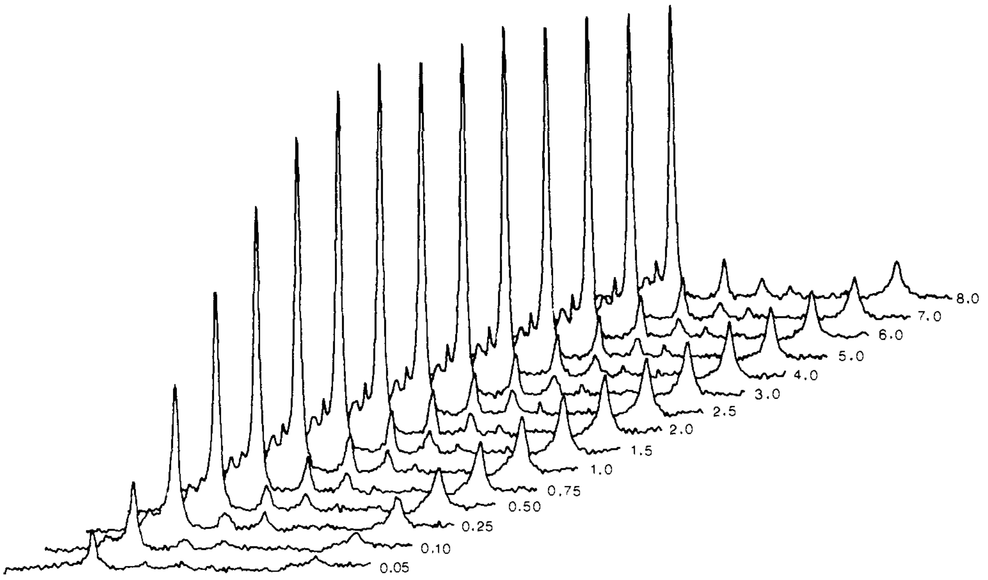

Figure 2. CP/MAS ^{13}C spectra of silica gel reacted with DMODCS obtained at increasing contact times (ms).

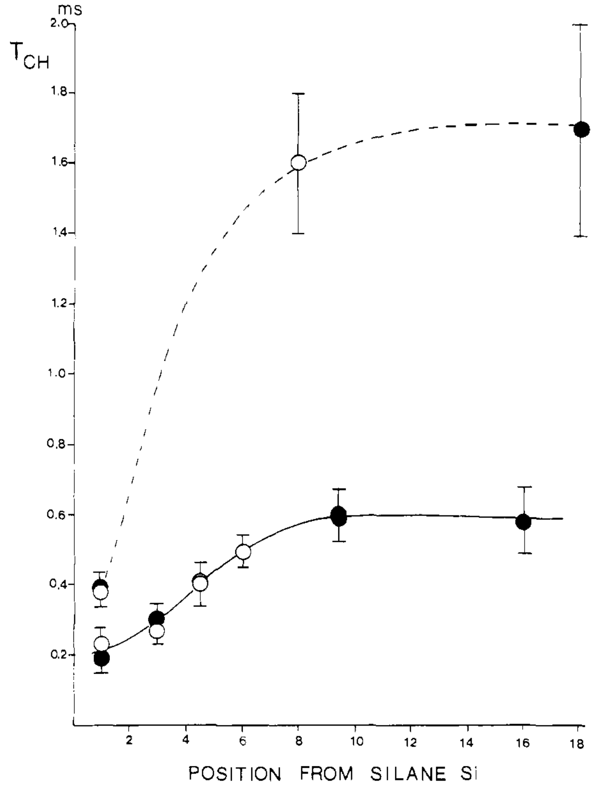

Figure 3. Dependence of cross-polarization time constants (T_{CH}) on the average carbon distance from the point of surface attachment: (●) results obtained for DMODCS-reacted sample; (○) results obtained for DMOCS-reacted sample. Error bars show the standard deviation observed for T_{CH} values measured in three separate experiments.

higher-frequency regions (ca. 150 MHz) than in the case for the DMODCS-reacted sample (with shorter $T_{1\rho H}$ values and longer T_{1H} values). This could be interpreted as indicating more restricted overall motion for the alkyl chains in the DMODCS-reacted sample than in the DMOCS-reacted sample, as might be depicted in spectral density curves such as B and C, respectively, in Figure 4. However, in this situation one would also expect to observe smaller T_{CH} values for carbons in the DMODCS-reacted case, since cross-polarization is most efficient for static or near-static C–H dipole–dipole interactions. (Note the larger value of $J(\omega)$ at $\omega = 0$ for curve B.) However, Figure 3 shows that cross-polarization rates are quite similar for corresponding carbons in these two systems (i.e., carbons at the same distance from the surface), decreasing with increasing numbers of bonds separating a CH_2 group from the surface. This latter behavior could be discussed in terms of curves A and D of Figure 4, which represent spectral density functions for motion of the C–H vectors of methylenes close to and far from the silica surface, respectively.

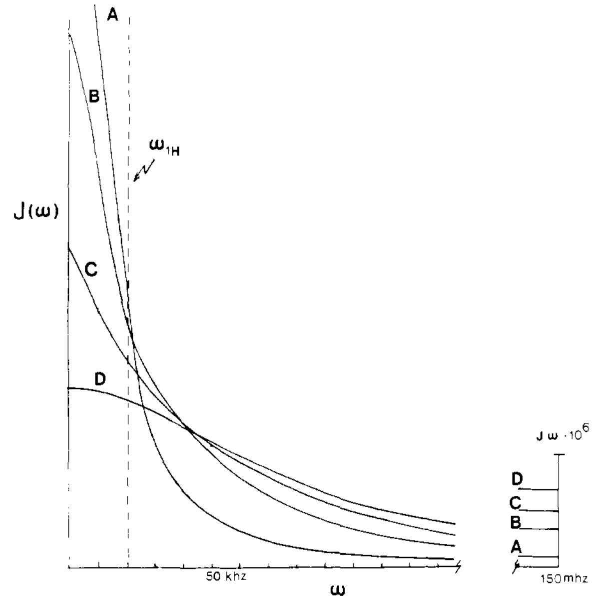

Figure 4. Hypothetical spectral density curves: (A) motion of CH_2 groups near the silica surface; (B) representing lower-mobility motion; (C) representing higher-mobility motion; (D) motion of CH_2 groups far from the silica surface. The frequency scale is not linear. Note the expanded scale for $J(\omega)$ at the right extreme.

The observed increase in T_{CH} as a function of carbon position in Figure 3 is a clear indication that molecular motion increases (and/or becomes less anisotropic) in both the DMOCS-reacted and DMODCS-reacted samples in moving outward from the surface along the alkyl chain. In the case of DMODCS one observes also a leveling off of T_{CH} after a carbon position number of about 8 or 9. This behavior indicates that motion does not become completely liquid-like for carbons far removed from the surface; a trend toward liquid-like behavior for increasing separation from the surface would manifest itself as a continuing increase in T_{CH} to very large values (ultimately much larger than $T_{1\rho H}$, making the CP experiment impractical). The leveling suggests that as-yet-undefined interactions, possibly with the silica surface or to other attached silane moieties, may place restrictions on the modes of motion available to these groups.

The approximate equivalence of T_{CH} values for corresponding methylene groups in the DMODCS-reacted and DMOCS-reacted samples leads one to challenge the suitability of spectral density curves B and C of Figure 4 to explain the proton relaxation data of the DMODCS-reacted and DMOCS-reacted samples, respectively. The T_{CH} results, together with "chemical intuition," lead to the conclusion that *on the average* the methylene C–H bond vectors must be *more* mobile for larger attached alkyl chains (a smaller fraction of methylenes near the surface); this is opposite to what is implied in identifying curve B with the DMODCS-reacted case and curve C with the DMOCS-reacted case.

The apparent dilemma can be explained as follows. If proton spin–lattice relaxation, sensitive to motional frequency components at 150 MHz, is due primarily to methyl group rotation, then the CH_3 group serves as a "T_1 sink." In this case, the system with more methylene protons has a larger Zeeman heat capacity and will manifest less efficient overall ^1H spin–lattice relaxation (larger T_{1H}). In this case one could identify curve C of Figure 4 with the average chain motion of CH_2 groups in the DMODCS-reacted sample (having greater average methylene mobility) and curve B with methylene motion in the DMOCS-reacted sample (with less average mobility of methylene C–H vectors).

In summary, ^{13}C relaxation measurements have shown that motional behavior is quite heterogeneous for methyl and methylene environments in silica-attached alkylsilane phases. Future studies can be expected to elucidate more fully the nature of the interactions responsible for such behavior in these and other surface-immobilized systems.

Acknowledgment. The authors gratefully acknowledge partial support of this research by the U.S. Department of Energy (Contract No. DE-AT20-81LC0652 from the Laramie Energy Technology Center) and the assistance of the Colorado State University Regional NMR Center, funded by National Science Foundation Grant CHE 78-18581.

Registry No. DMOCS, 18162-84-0; DMODCS, 18643-08-8.

Photoresponsive Crown Ethers. 8. Azobenzenophane-Type "Switched-On" Crown Ethers Which Exhibit an All-or-Nothing Change in Ion-Binding Ability[1]

Seiji Shinkai,* Takahide Minami, Yumiko Kusano, and Osamu Manabe*

Contribution from the Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan. *Received July 14, 1982*

Abstract: Three new azobenzenophane-type crown ethers, cr(O_7), cr(O_8), and cr(O_9), in which 4,4′ positions of azobenzene are linked by a polyoxyethylene chain, were synthesized. The trans isomers were isomerized by UV light to the cis isomers, and the cis isomers were isomerized thermally or by visible light to the trans isomers, the interconversion being completely reversible. The solvent extraction showed that the trans isomers totally lack affinity toward metal ions, whereas the cis isomers are able to bind considerable amounts of alkali metal cations. The result is in accord with the prediction by the CPK model building that the polyoxyethylene chains of the trans isomers are linearly extended, whereas those of the cis isomers form the crown-like loops. The cis isomers showed spheric recognition patterns in the binding of alkali metal cations, typical of crown ethers in solution; the metal cations which provided the maximum extractability are Na^+ for *cis*-cr(O_7), K^+ for *cis*-cr(O_8), and Rb^+ for *cis*-cr(O_9). The rate of the thermal cis-to-trans isomerization was significantly suppressed by added alkali metal cations, indicating that the additional energy is required to disrupt the crown–metal interaction. The order of inhibitory effect is well correlated with that of extractability. From plots of the rate constant against metal concentration, we estimated association constants (K) and rate constants for the crown-metal complexes (k_{CM}). Conceivably, the increment in free energy of activation in the presence of metal cations reflects the magnitude of the "template effect" of metal ions. This is the first example for photoresponsive crown ethers which exhibit an "all-or-nothing" change in ion-binding ability.

Photoresponsive systems are ubiquitous in nature, and light is frequently the trigger for subsequent life processes. As a first step to mimic natural photoresponsive systems, one has to design a molecule (or system) which combines a photoantenna to capture a photon with a functional group to mediate some subsequent event. Photoresponsive crown ethers have azobenzene or anthracene as a photoantenna and crown ether as a functional group and change their chemical and physical functions in response to photoirradiation.[2-8] Similarly, azobenzene derivatives have been utilized as a light trigger to control the functions of metal ligands,[9] β-cyclodextrin,[10] membranes,[11] micelles,[12] and microemulsions.[13]

In spite of these efforts, few examples have ever attained an "all-or-nothing" photoregulation. Shiga et al.[8] synthesized azobenzenophane-type crown ethers in which the 2,2′ positions of azobenzene are linked by a polyoxyethylene chain. Although the

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