it is perfectly possible, for example, that elimination of Li_2O from A is followed by reaction with CO_2 to give Li_2CO_3.

Further experiments are in progress to elucidate the mechanisms of these reactions, to explore their generality, and to develop catalytic variants. We are also investigating the electrochemical implications.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Exxon Educational Foundation, and the National Science Foundation (partial support to J.M.—Grant No. CHE 78-25699) for financial support. We thank Dr. J. S. Bradley of Exxon Research and Engineering for valuable discussions.

John M. Maher,* N. John Cooper*
Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

Received June 3, 1980

Silicon-29 Nuclear Magnetic Resonance Study of the Surface of Silica Gel by Cross Polarization and Magic-Angle Spinning

Sir:

The properties of silica gels, especially their surface characteristics, have been the subject of much research and interest for several years.[1-3] A variety of physical and spectroscopic techniques have been applied to the study of this interesting system.[2-10] One of the more important aspects of chemical research on silica gels recently has been the development of stationary phases for catalysis and for chromatography by covalent attachment of appropriate moieties to the silica gel surface. As part of a program of study of such systems by NMR,[11] we have addressed the structure of the silica gel surface by ^{29}Si NMR, using cross polarization and magic-angle spinning (CP/MAS).[12-16] Lippmaa and co-workers have very recently reported a ^{29}Si NMR study of solid silicates.[12]

By using CP/MAS techniques, one can obtain ^{29}Si NMR spectra on silica gel in reasonable times (minutes to hours) and with a highly useful level of resolution. The ^{29}Si–^{1}H cross polarization restricts detection to silicon nuclei that are near protons, i.e., at or near the surface. Figure 1 shows a typical ^{29}Si CP/MAS spectrum, obtained on a JEOL FX-60QS spectrometer, of SG-2 silica gel, prepared by the method of Peri and Hensley (without the autoclave step).[3] The spectrum shows peaks at −109.3, −99.8, and −90.6 ppm (relative to liquid Me_4Si), which can be identified with silicon sites in a reasonable surface model.

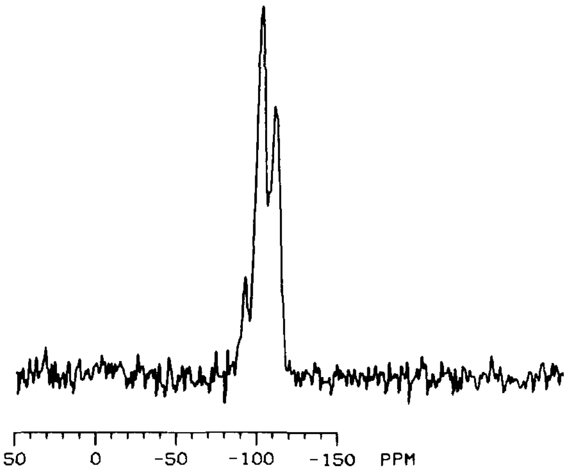


Figure 1. ^{29}Si CP/MAS spectrum of silica gel (SG-2) obtained at 11.88 MHz (1014 scans, 20-ms contact times, 1-s repetitions).

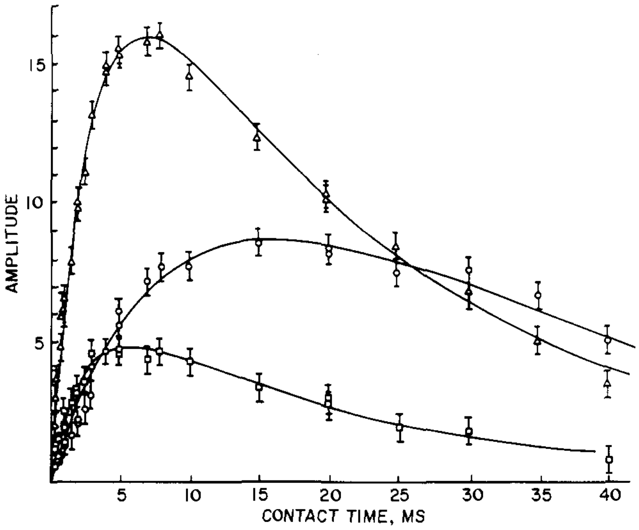


Figure 2. Plot of ^{29}Si CP/MAS amplitudes (relative scale) as a function of Hartmann–Hahn contact time. Similar results were obtained from integrated areas. (△) Data for −99.8-ppm resonance; (○) data for −109.3-ppm resonance; (□) data for −90.6-ppm resonance.

Table I. Summary of Cross Polarization Relaxation Results on Silica Gel

structural type[a]	δ_{Si}[b]	T_{SiH},[c] ms	$T_{1\rho H}$,[d] ms	$M_{\alpha e}$[e]
$(HO)_2Si^*(OSi\leqslant)_2$	−90.6	2.3 ± 0.2	20.3 ± 1.4	6.3 ± 0.2
$HOSi^*(OSi\leqslant)_3$	−99.8	2.9 ± 0.1	22.1 ± 0.8	21.7 ± 0.4
$Si^*(OSi\leqslant)_4$	−109.3	12.7 ± 1.7[f]	21[g]	18.8 ± 0.5

[a] The silicon nucleus of interest is indicated by an asterisk. The structural assignments are based on chemical shift arguments given in the text. [b] Chemical shifts in ppm with respect to liquid Me_4Si; higher numbers correspond to lower shieldings. [c] ^{29}Si–^{1}H cross polarization relaxation time in milliseconds. [d] Proton spin-lattice relaxation time in the rotating frame in milliseconds. [e] Magnitude of the maximum available magnetization in arbitrary, relative units. [f] As the cross polarization time for $^*Si(OSi\leqslant)_4$ is rather large, an accurate measure requires that the radiofrequency fields be extremely well matched over the entire sample. Hence, the value 12.7 ms should be considered qualitative. [g] This value was chosen as an average of the other two $T_{1\rho H}$ values and used as a constraint on the least-squares analysis for this peak. In an unconstrained analysis the value 33 ± 9 was obtained for $T_{1\rho H}$; the corresponding T_{SiH} and $M_{\alpha e}$ values were 9.0 ± 2.1 ms and 13.9 ± 1.7, respectively.

The studies of Marsmann[17] on silicate–water glass solutions provide the following ^{29}Si chemical shifts for the relevant structural types of interest here: −107.2 ppm, $Si^*(OSi<)_4$; −94.6 ppm, $HOSi^*(OSi<)_3$; −86.6 ppm, $(HO)_2Si^*(OSi<)_2$. Considering bulk susceptibility differences (for which corrections were not made),

---

(1) J. A. Hockey, *Chem. Ind.* (*London*), 57 (1965).
(2) H. P. Boehm, *Angew. Chem., Int. Ed. Engl.*, **5**, 533 (1966).
(3) J. B. Peri and A. L. Hensley, Jr., *J. Phys. Chem.*, **72**, 2926 (1968).
(4) M. R. Basila, *J. Chem. Phys.*, **35**, 451 (1961).
(5) A. J. VanRoosmalen and J. C. Mol, *J. Phys. Chem.*, **83**, 2485 (1979).
(6) W. Hertl and M. L. Hair, *J. Phys. Chem.*, **72**, 4676 (1968).
(7) D. Fiat, J. Reuben, and M. Holman, *J. Chem. Phys.*, **46**, 4453 (1967).
(8) L. R. Snyder and J. W. Ward, *J. Phys. Chem.*, **70**, 3941 (1966).
(9) H. Pfeifer, *Phys. Lett. C*, **26**, 296 (1976).
(10) L. B. Schreiber and R. W. Vaughan, *J. Catal.*, **40**, 225 (1975).
(11) G. E. Maciel, D. W. Sindorf, and V. J. Bartuska, *J. Chromatogr.*, in press.
(12) E. Lippmaa, M. Magi, A. Samoson, G. Englehardt, and A.-R. Grimmer, *J. Am. Chem. Soc.*, **102**, 4889 (1980).
(13) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973).
(14) J. Schaefer and E. O. Stejskal, *Top. Carbon-13 NMR Spectrosc.*, **3** (1979).
(15) J. Schaefer and E. O. Stejskal, *J. Am. Chem. Soc.*, **98**, 1031 (1976).
(16) F. P. Miknis, V. J. Bartuska, and G. E. Maciel, *Am. Lab.*, (*Fairfield, Conn.*), **11**, 19 (1979).
(17) H. C. Marsmann, *Z. Naturforsch., B*, **29**, 495 (1974).

0002-7863/80/1502-7606$01.00/0

effects of different degrees of hydrogen bonding, and other subtle structural differences between the local silicon environments of silica gel and silicate–water glass, these values are in reasonable qualitative agreement with the values found by ^{29}Si CP/MAS for silica gel. Thus, the −109.3-ppm shift is assigned to the silicon atoms bound to four other $\mathrm{OSi{<}}$ moieties at the silica gel surface, the −99.8-ppm resonance is assigned to the surface silicon atoms attached to three $\mathrm{OSi{<}}$ moieties and one OH group, and the −90.6-ppm resonance is assigned to surface silicon atoms bonded to two $\mathrm{OSi{<}}$ groups and two hydroxyl groups.

Corroboration of these assignments is obtained from the cross polarization relaxation data summarized in Figure 2. This figure shows the dependence of the amplitude of each of the three ^{29}Si NMR signals as functions of the cross polarization contact time under Hartmann–Hahn conditions in a single-contact experiment.[13] The initial rise on the left side of each plot is due to the growth of ^{29}Si magnetization due to cross polarization by protons (with a characteristic time T_{SiH}), and the later decline is a manisfestation of relaxation of the spin-locked ^{1}H magnetization (characterized by the ^{1}H spin–lattice relaxation time in the rotating frame, $T_{1\rho\mathrm{H}}$). The data were analyzed by a least-squares treatment based on a previously reported theory for the case in which the abundance of protons is much greater than that of the nuclide being cross polarized (4.7% natural abundance for ^{29}Si).[18] The results are summarized in Table I.

From Table I, we see that the proton $T_{1\rho}$ values measured from the three resonance peaks are essentially the same, within experimental error.[19] The more interesting parameter is the ^{1}H–^{29}Si cross polarization relaxation parameter, T_{SiH}. By far the largest value of T_{SiH} is for the peak at −109.3 ppm, which we have assigned to $\mathrm{Si^*(OSi{<})_4}$; the Si* atom in this environment is removed by at least four bonds from the nearest hydroxyl proton.[20] The peaks assigned to $\mathrm{(HO)_2Si^*(OSi{<})_2}$ and $\mathrm{HOSi^*(OSi{<})_3}$ structures (at −90.6 and −99.8 ppm, respectively) have similar T_{SiH} values (2.3 and 2.9 ms) and correspond to silicon positions removed by two bonds from the nearest hydroxyl proton. The shorter of these two T_{SiH} values is assigned to the Si moiety with two hydroxyl groups attached, the longer with only one attached hydroxyl group. Thus, the assignments based upon chemical shift analogies agree with what one would derive from the cross polarization relaxation times.

In conclusion, the three peaks observed in the ^{29}Si CP/MAS spectra of silica gel can be assigned to particular silicon environments at the surface. This makes possible a variety of interesting studies of the influence of preparation methods on the structure of silica gel and of the nature of adsorption and covalent attachment of silica gel surfaces. Such studies are under way.

Acknowledgment. We are grateful to the National Science Foundation for partial support of this work under Grant No. CHE74-23980 and to Dr. V. J. Bartuska for invaluable instrumental assistance. We also gratefully acknowledge use of the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. 78-18581, in obtaining ^{29}Si spectra of related liquid samples.

---

(18) M. Mehring, "High Resolution NMR Spectroscopy in Solids", Springer-Verlag, New York, 1976, p 138.

(19) In the least-squares and analysis for the $\mathrm{Si^*(OSi{<})_4}$ data, the analysis was constrained by assuming that $T_{1\rho\mathrm{H}}$ must be a weighted average of $T_{1\rho\mathrm{H}}$ values for $\mathrm{(HO)_2Si^*(OSi{<})_2}$ and $\mathrm{HOSi^*(OSi{<})_3}$ because presumably these moieties represent the types of protons available for cross polarizing $\mathrm{Si^*(OSi{<})_4}$; an average of 21 ms was used.

(20) There may be some contribution from silicon nuclei imbedded more deeply in the silica structure (at least five bonds from hydroxyl hydrogen), which would cause significant deviation from a single-exponential behavior.

Gary E. Maciel,* Dean W. Sindorf

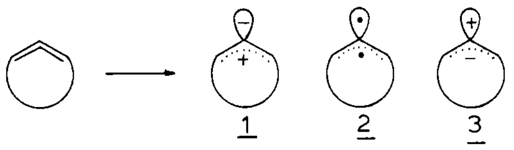
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

Received August 8, 1980

Chirality as a Probe for the Structure of 1,2-Cycloheptadiene and 1,2-Cyclohexadiene

Sir:

An allene incorporated in a carbocyclic ring of nine or more carbons is relatively unstrained.[1] However, if the ring size is decreased, the linear perpendicular allene will be twisted and bent until at some point the energy gained by π bonding in the two double bonds should be insufficient to offset the increased strain. At that point the allene moiety would be expected to prefer a bent, planar structure with electrons distributed as in **1**, **2**, or **3**.[2] For unsubstituted 1,2-dienes, the concensus seems to be that eight- and seven-membered rings are sufficiently large to accommodate the strain of the twisted diene and therefore should prefer two double bonds, albeit certainly distorted and strained.[1] On the other hand, opinions on the preferred structure of singlet 1,2-cyclohexadiene are mixed. On the basis of extensive studies of its chemistry, Bottini[3] and co-workers prefer initial formation of a bent, twisted allene which rapidly isomerizes to the diradical, which is the active agent in both 2 + 2 and 2 + 4 cycloadditions.[3,4] They also contend that the species with electrons distributed as in **3** is responsible for some of the chemistry of this diene.[3] In contrast, Moore and Ward[5] and, more recently, Greenberg and Liebman[1] prefer **8** for the structure of 1,2-cyclohexadiene, a contention that has found support in an INDO–MO study by Dillon and Underwood.[2]



At this time we report experimental results that lead us to conclude that the species initially generated from dehydrohalogenation of both 1-bromocycloheptene[6-8] and 1-bromocyclohexene[3,4,9-12] are nonplanar and are therefore best represented as bent allenes. Our results also require that these are the species that are responsible for 2 + 4 cycloaddition to 1,3-diphenylbenzo[*c*]furan[7,9,10] and further suggest that, at around 80 °C, conversion of the nonplanar form of 1,2-cyclohexadiene to a symmetrical isomer (presumably **8**)[2] competes with its reaction with the allene trap. The latter probably is not the case for 1,2-cycloheptadiene.

Our strategy for probing this problem was based on the chirality that is inherent in the allene structures **6** and **7** but is absent in planar allene forms such as **8** and **9**. Starting materials for chirality studies were optically active 1-bromo-6-deuteriocyclohexene (**4**) and 1-bromo-7-deuteriocycloheptene (**5**), which were synthesized as shown in Schemes II and III (absolute configurations are unknown). Activity was introduced by reduction of the enones with lithium aluminum hydride–quinine complex.[13]

Base-induced elimination of HBr from **4** and **5** with potassium *tert*-butoxide in tetrahydrofuran[7,8] gave the desired intermediates. Enantiomeric enrichment was expected if nonplanar allenes **6** and **7** were initially formed because elimination of HBr and DBr, which

---

(1) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; pp 126–30.

(2) Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* **1974**, *92*, 779–87.

(3) Bottini, A. T.; Corson, F. P.; Fitzgerald, R.; Frost, K. A., II *Tetrahedron* **1972**, *28*, 4883–904.

(4) Bottini, A. T.; Hilton, L. L.; Plott, J. *Tetrahedron* **1975**, *31*, 1997–2001.

(5) Moore, W. R.; Moser, W. R. *J. Am. Chem. Soc.* **1970**, *92*, 5469–74.

(6) Ball, W. J.; Landor, S. R. *Proc. Chem. Soc.* **1961**, 143–4. *J. Chem. Soc.* **1962**, 2298–304.

(7) Wittig, G; Meske-Schuller, J. *Justus Liebigs Ann. Chem.* **1968**, *711*, 76–81.

(8) Bottini, A. T.; Frost, K. A., II; Anderson, B. R.; Dev, V. *Tetrahedron* **1973**, *29* (14), 1975–81.

(9) Wittig, G.; Fritze, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 846.

(10) Wittig, F.; Fritze, P. *Justus Liebigs Ann. Chem.* **1968**, *711*, 82–7.

(11) Bottini, A. T.; Corson, F. P.; Fitzgerald, R.; Frost, K. A., II *Tetrahedron Lett.* **1970**, 4753–6, 4757–60.

(12) Bottini, A. T.; Cabral, L. J.; Dev, V. *Tetrahedron Lett.* **1977**, 615–8.

(13) Wynberg, H.; Marsman, B. *J. Org. Chem.* **1980**, *45*, 158–61.

0002-7863/80/1502-7607$01.00/0