JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 95, NUMBER 11 MAY 30, 1973

Silicon-29 Spin–Lattice Relaxation in Organosilicon Compounds

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Contribution from the General Electric Corporate Research and Development, Schenectady, New York 12301. *Received January 1, 1973*

Abstract: Silicon-29 spin–lattice relaxation and ^{29}Si–^{1}H nuclear Overhauser enhancement measurements are reported for a representative group of organosilicon compounds. Variable-temperature and paramagnetic doping studies are reported for several compounds. In some cases ^{13}C relaxation measurements were also obtained for comparison with the ^{29}Si results. Relaxation for ^{29}Si nuclei occurs *via* competitive dipole–dipole and spin-rotation mechanisms. Evidence was found for minor chemical shift anisotropy contributions. Dipole–dipole interactions between silicon-29 nuclei and directly bonded protons are *ca.* 10 times less effective than analogous ^{13}C–^{1}H interactions, resulting in long ^{29}Si dipole–dipole relaxation times (T_1's). By contrast with ^{13}C relaxation, long-range intramolecular and intermolecular dipole–dipole interactions with protons can be important for ^{29}Si relaxation. Intermolecular ^{29}Si–^{1}H dipole–dipole interactions can contribute up to 15–20% of the relaxation for a ^{29}Si nucleus. T_1 measurements on a series of linear polydimethylsiloxanes demonstrate that localized motions along segments of the oligomer or polymer backbone result in ^{29}Si relaxation that rapidly becomes independent of chain length and solution viscosity at molecular weights >500. The presence of dissolved paramagnetic impurities such as O_2 can lead to significantly shortened T_1's; at pO_2 = 1 atm, $T_1^{O_2} \approx$ 40 sec. Addition of paramagnetic relaxation reagents such as tris(acetylacetonato)chromium can effectively shorten ^{29}Si relaxation times thereby increasing the efficiency of ^{29}Si FT nmr experiments. The quantity of added reagent may be varied in order to obtain T_1's of any desired value down to *ca.* 2–5 sec, limited by the solubility of the paramagnetic reagent in the organosilicon compound. The use of paramagnetic additives in ^{29}Si nmr results in a further benefit; the *negative* ^{29}Si–^{1}H nuclear Overhauser enhancement is effectively suppressed. Quantitative ^{29}Si nmr studies may be performed under these conditions.

Only a few silicon-29 nuclear magnetic resonance studies have been published,[1,2] in strong contrast with the literature of ^{13}C nmr.[3] Two recent communications utilized pulsed Fourier transform (FT) operation and reported ^{29}Si spin–lattice relaxation data.[2a,b]

The 4.7% natural isotopic abundance of ^{29}Si coupled with its magnetogyric ratio, γ (21% smaller than γ for ^{13}C), indicates that unenriched ^{29}Si nmr experiments should have twice the sensitivity of natural abundance ^{13}C experiments. Actually, the situation is more complex[2a,b] and ^{29}Si nmr may be considerably less efficient than predicted from these two factors. First, γ for ^{29}Si is negative. The nuclear Overhauser effect (NOE) which increases integrated ^{13}C peak areas as much as threefold in ^{1}H decoupled ^{13}C experiments (notation: ^{13}C{^{1}H}) is negative in proton decoupled ^{29}Si spectra. ^{29}Si{^{1}H} spectra may have resonance lines of greatly reduced intensity, *negative* peaks, or the signals may be *nulled*, depending on the contribution of the ^{29}Si–^{1}H dipole–dipole (DD) mechanism to relaxation of the ^{29}Si nuclei.[2a,b,4]

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(1) (a) G. R. Holzmann, P. C. Lauterbur, J. H. Anderson, and W. Koth, *J. Chem. Phys.*, **25**, 172 (1956); (b) P. C. Lauterbur, *Determination Org. Struct. Phys. Methods*, **2**, 465 (1962); (c) B. K. Hunter and L. W. Reeves, *Can. J. Chem.*, **46**, 1399 (1968); (d) G. Englehardt, H. Jancke, M. Magi, T. Pehk, and E. Lippmaa, *J. Organometal. Chem.*, **28**, 293 (1971).

(2) (a) G. C. Levy, *J. Amer. Chem. Soc.*, **94**, 4793 (1972); (b) G. C. Levy, J. D. Cargioli, P. C. Juliano, and T. D. Mitchell, *J. Magn. Resonance*, **8**, 399 (1972); (c) H. C. Marsmann, *Chem.-Z.*, **96**, 288 (1972); (d) H. C. Marsmann and H. G. Horn, *ibid.*, **96**, 456 (1972); (e) R. I. Scholl, G. E. Maciel, and W. K. Musker, *J. Amer. Chem. Soc.*, **94**, 6376 (1972).

(3) Recent references are cited in: (a) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance For Organic Chemists," Wiley-Interscience, New York, N. Y., 1972; (b) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972.

(4) G. C. Levy and J. D. Cargioli in "NMR Spectroscopy of Nuclei Other Than Hydrogen," Wiley-Interscience, New York, N. Y., in press.

A second complication results from the fact that ^{29}Si nuclei generally have very long T_1's and thus are easy to saturate. Fourier transform experiments cannot achieve sensitivity improvements comparable to those obtained in FT ^{13}C nmr.[5]

We have investigated in detail ^{29}Si spin-lattice relaxation behavior for several types of organosilicon compounds, with particular emphasis on elucidation of the operant relaxation mechanisms. One goal of this research is to be able to semiquantitatively predict ^{29}Si T_1's for specific silicon nuclei in new compounds, facilitating ordinary ^{29}Si nmr spectroscopic studies. Another objective is to characterize organosilicon molecular processes in the same way that ^{13}C T_1 studies have been used for various kinds of organic molecules.[6]

Silicon-29 Spin–Lattice Relaxation Mechanisms

Four spin–lattice relaxation mechanisms are usually considered for nuclei of spin $^1/_2$: dipole–dipole (DD) interactions, the spin–rotation (SR) interaction, scalar (SC) interaction, and chemical shift anisotropy (CSA). As a result of a lower magnetogyric ratio and changes in molecular characteristics (bond lengths, molecular geometry, etc.) the relative efficiencies of the four mechanisms change in comparisons of ^{29}Si relaxation with ^{13}C relaxation.

The dipole–dipole spin–lattice relaxation rate ($R_1^{DD} \equiv 1/T_1^{DD}$) for a ^{13}C or ^{29}Si nucleus in a molecule which is not subject to severe motional constraints (within the so-called region of extreme spectral narrowing) is described by eq 1 (eq 1 assumes that no high γ nuclei other than protons are present).

$$\frac{1}{T_1^{DD}} = R_1^{DD} = \sum_{i=1}^{n} \hbar^2\gamma_X^2\gamma_H^2 r^{-6}\tau_c \qquad (1)$$

Here $\hbar$ is Planck's constant divided by 2π, γ_X is the magnetogyric ratio for the ^{13}C or ^{29}Si nucleus being relaxed, τ_c is the molecular correlation time, and r is the distance between the ith proton and the x nucleus. In practice the number of protons, n, used for the summations may be restricted, but in principle all nearby protons are included. The molecular correlation time, τ_c, describes molecular tumbling in solution. It approximately equals the time required for the rotation of the molecule through 1 radian. τ_c is strictly defined only for rigid (cubic symmetry) molecules that tumble isotropically. When these conditions do not hold it is sometimes still possible to speak of an effective correlation time, τ_c^{eff}, that may be used to describe molecular motional characteristics.

It has been shown that for protonated ^{13}C nuclei only directly attached ^{1}H nuclei need be considered, eliminating the summation in eq 1.

$$\frac{1}{T_1^{DD}} = R_1^{DD} = N\hbar^2\gamma_X^2\gamma_H^2 r_{XH}^{-6}\tau_c \qquad (2)$$

In eq 2, N is the number of directly attached protons and r_{XH} is equal to 1.09×10^{-8} cm, the C–H bond length. Equations 1 and 2 tell us that the combined effect of the lower γ for ^{29}Si and the longer Si–H bond length (1.48 Å *vs.* 1.09 Å for a C–H bond) is a lowering of the DD relaxation rate, R_1^{DD}, *ca.* tenfold; *i.e.*, T_1^{DD} will be ten times longer for the ^{29}Si nucleus.

The ^{13}C/^{29}Si DD relaxation differential is not as great for nonprotonated nuclei. Long-range intra- and intermolecular DD interactions, usually negligible for ^{13}C nuclei, can contribute significantly to ^{29}Si relaxation. van der Waals' radii, d, for silicons, carbons, and hydrogens are approximately 1.97, 1.57, and 1.2 Å, respectively.[7,8] The efficiency of non-nearest-neighbor protons in causing DD relaxation of a nucleus, X, relative to DD relaxation by a directly bonded proton, is given by eq 3. N is the number

$$\%\ \text{efficiency} = 100N\left[\frac{d_X + d_H}{r_{XH}}\right]^{-6} \qquad (3)$$

of nuclei at a distance approximately equal to ($d_X + d_H$) from the X nucleus; d_X and d_H are the van der Waals' radii for the X and H nuclei, and r_{XH} is the XH bond length (1.48 Å for silicon; 1.09 Å for carbon). For ^{13}C and ^{29}Si nuclei, the relative efficiency of a single long-range ^{1}H DD interaction operating at the distance ($d_X + d_H$) is 0.37 and 1.0%, respectively. As a result of the larger nonbonded distance between silicon and hydrogen nuclei, a larger number of protons may be accommodated in the van der Waals' "sphere" around a silicon than around a carbon nucleus. Relaxation contributions from long-range DD interactions will be $\lesssim 3$ to 7% for ^{13}C nuclei (corresponding to *ca.* 8–18 nearby nonbonded protons) and $\lesssim 10$–30% for ^{29}Si nuclei (10–30 nearby protons), both relative to the contributions from a single, *bonded* proton. (The ^{13}C estimate is consistent with results obtained on a series of substituted aromatic compounds; see ref 11.) Long-range *intramolecular* interactions may be substantially higher in molecules where steric compression forces protons close to the carbon or silicon nuclei. (See results below for experimental evidences of long-range ^{29}Si–^{1}H DD relaxation.)

^{29}Si dipole–dipole relaxation times are very long, the shortest measured in this study being 26 sec. Thus, relaxation from other mechanisms can contribute significantly for ^{29}Si nuclei.

Recent work by Gibby, Pines, and Waugh[9] indicates that ^{29}Si chemical shift anisotropy is smaller than that observed for ^{13}C nuclei. Nevertheless, CSA relaxation may be able to make minor contributions[10] to relaxation of nonprotonated ^{29}Si nuclei, comparable to CSA contributions for nonprotonated ^{13}C nuclei.[11]

Scalar spin–lattice relaxation requirements are very stringent.[5b,11] The SC mechanism normally should not have to be considered for organosilicon com-

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(5) (a) Reference 3a, Chapters 1 and 2; (b) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, N. Y., 1971.

(6) (a) References cited in G. C. Levy, *Accounts Chem. Res.*, **6**, 161 (1973); see also (b) T. D. Alger, D. M. Grant, and R. K. Harris, *J. Phys. Chem.*, **76**, 281 (1972); and (c) R. A. Komoroski and A. Allerhand, *Proc. Nat. Acad. Sci. U. S.*, **69**, 1804 (1972).

(7) "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing Co., 1964–1965, p F-92.

(8) van der Waals radii may be estimated by adding 0.8 Å to the covalent radii of carbon and silicon: L. Pauling "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(9) M. G. Gibby, A. Pines, and J. S. Waugh, *J. Amer. Chem. Soc.*, **94**, 6231 (1972).

(10) At 23 kG these contributions do not exceed ~5%; at higher magnetic fields they may be substantial.

(11) G. C. Levy, J. D. Cargioli, and F. A. L. Anet, *J. Amer. Chem. Soc.*, **95**, 1527 (1973).

pounds unless the ^{29}Si nuclei are spin–spin coupled to ^{127}I nuclei.[12]

Spin–rotation relaxation[5b] can occur with rapid overall molecular tumbling (*spin overall rotation*) or from free internal spinning of symmetrical groups (*spin internal rotation*). Spin–rotation relaxation can be particularly important for ^{29}Si nuclei where ^{1}H DD relaxation is relatively inefficient.

All of the T_1 and NOE results in this paper were interpreted in terms of relaxation contributions from the DD and SR mechanisms, only in specific cases allowing for minor contributions from the CSA mechanism. Scalar spin–lattice relaxation was assumed nonoperative. Of course, strong dipole–dipole interactions with dissolved paramagnetic materials were taken into account in appropriate cases (see below). The contributions of DD and SR relaxation were calculated by standard methods.[6a,13] The ^{29}Si–^{1}H dipole–dipole T_1 (T_1^{DD}) was determined directly from eq 4 where T_1^{obsd} is the observed T_1 and η is the observed

$$T_1^{\mathrm{DD}} = -2.52T_1^{\mathrm{obsd}}/\eta \qquad (4)$$

NOE ($\eta = -2.52$ is the NOE corresponding to 100% ^{29}Si–^{1}H DD relaxation). The spin–rotation relaxation time T_1^{SR} was calculated from eq 5. As noted

$$\frac{1}{T_1^{\mathrm{obsd}}} = \frac{1}{T_1^{\mathrm{DD}}} + \frac{1}{T_1^{\mathrm{SR}}} + \frac{1}{T_1^{\mathrm{CSA}}} \qquad (5)$$

above, in most cases the CSA term was assumed to be negligible (zero).

Results and Discussion

Before making a thorough examination of ^{29}Si relaxation processes it will be useful to determine some general trends. Representative ^{29}Si spin–lattice relaxation data are given in Table I. All of the ^{29}Si T_1's given in Table I are $\gtrsim$20 sec, in contrast to ^{13}C T_1's for these compounds which are in some cases as short as 3 sec. In small organosilicon compounds (for example, TMS (I) and hexamethyldisiloxane (V)), the T_1's are relatively short and the NOE's are small. Rapid overall tumbling of these molecules results in efficient SR relaxation. The same motion lowers the efficiency of DD relaxation; T_1^{DD} for I and V is >300 sec.

Table I. Silicon-29 Spin–Lattice Relaxation in Some Representative Organosilicon Compounds[a]

Compound	T_1, sec	NOE ($-\eta$)
(I) $Si(CH_3)_4$ (TMS)[b]	19	0.09
(II) Ph_2SiH_2	26	2.5
(III) $PhSi(CH_3)_2H$	46	0.62
(IV) $Si(OCH_2CH_3)_4$	135	1.5
(V) $(CH_3)_3SiOSi(CH_3)_3$	39.5	0.31
(VI) $[(CH_3)_2SiO]_4$	100	1.83

[a] Measurements, 19.9 MHz and 38°. Samples run neat or with 15% acetone-d_6. Oxygen removed with N_2. [b] 25°.

The relatively large molecule diphenylsilane (II) has two protons directly attached to the ^{29}Si nucleus. The observed NOE indicates that within the limits of experimental accuracy ($\pm 0.10\eta$) all of the relaxation arises from ^{29}Si–^{1}H DD interactions. For diphenylsilane T_1^{DD} is therefore ~26 sec (not 16.5 sec, as reported earlier in ref 2a), the shortest ^{29}Si–^{1}H DD T_1 observed in this study.

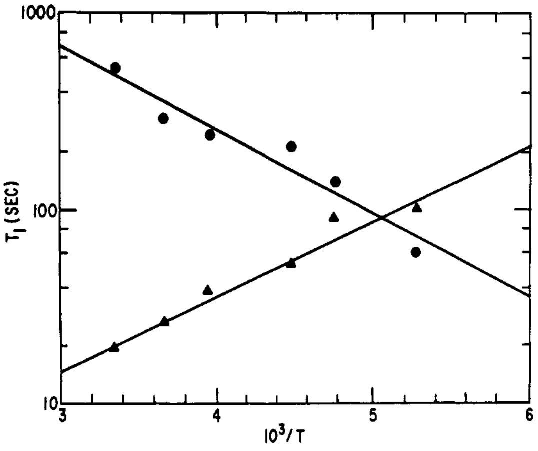

Figure 1. ^{29}Si spin–lattice relaxation in tetramethylsilane: (●) T_1^{DD}, (▲) T_1^{SR} (assumes $T_1^{\mathrm{CSA}} \gg T_1^{\mathrm{DD}}$).

The ^{29}Si T_1 for diphenylsilane can be compared with ^{13}C T_1's obtained for the phenyl ring carbons in the same sample at 25.2 MHz. Those T_1's should be *ca.* 5.3 times shorter than the ^{29}Si T_1 observed for the same sample (allowing for the differences between ^{13}C and ^{29}Si nuclear characteristics and the two protons bonded to the silicon; see eq 2). The average ring carbon (dipole–dipole) T_1 is *ca.* 5 sec (5.5, 5.5, and 3.1 sec for the ortho, meta, and para carbons, respectively). Multiplying 5 sec by 5.3 predicts $T_1^{\mathrm{DD}} = 26.5$ sec, in excellent agreement with the observed value. (This is partly accidental since anisotropic molecular motion affects the ^{13}C and ^{29}Si values differently.)

The ^{29}Si nucleus in compound III, with one directly attached proton, might be expected to have T_1^{DD} approximately twice that observed for the silicon in II. Instead, T_1^{DD} is ~187 sec while T_1^{SR} is ~61 sec. Compound III would appear to be tumbling more rapidly, with τ_c for III being ~$^{1}/_{3}\tau_c$ for II. The ^{13}C T_1's for the ring carbons in III largely confirm this. In III, T_1 for the ortho and meta carbons is 13 sec, and T_1 para is 8 sec. (Exact comparisons of the T_1 data cannot be made since II and III may have different anisotropic tumbling characteristics.)

Very long ^{29}Si T_1's coupled with high experimental NOE's (see, for example, compounds IV and VI) characterize nonprotonated ^{29}Si nuclei in molecules undergoing relatively slow molecular motion. SR relaxation is inefficient in these cases.

The competition between DD and SR relaxation can be observed from ^{29}Si T_1 measurements made over a range of temperatures. The SR relaxation rate, R_1^{SR}, is proportional to the *spin–rotation correlation time*, τ_j (the complete equation for SR relaxation is given in ref 5b). For spherical top molecules in the small step diffusion limit, the spin–rotation correlation time, τ_j, and the reorientational correlation time, τ_c (eq 1 and 2), are related according to eq 6, where I is the

$$\tau_c\tau_j = I/6kT \qquad (6)$$

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[12] ^{127}I has a Larmor frequency close to ω for ^{29}Si. In some cases this condition may not be necessary, when the scalar coupling is very large and when the coupled nucleus has a very short T_1: R. R. Sharp, *J. Chem. Phys.*, 57, 5321 (1972).

[13] J. R. Lyerla, Jr., D. M. Grant, and R. K. Harris, *J. Phys. Chem.*, 75, 585 (1971).

Table II. Silicon-29 Spin-Lattice Relaxation Times and Nuclear Overhauser Effects in TMS[a]

Temp, °C[b]	T_1, sec[c]	NOE ($-\eta$)[d]	T_1^{DD}, sec[e]	T_1^{SR}, sec[e]
+25	19	0.09	522	19.7
0	23.3	0.205	286	25.4
−20	32.5	0.35	234	37.8
−50	42.0	0.495	213.8	52
−62.5[f]	55[g]	1.0	139[g]	91[g]
−64[f]		1.03		
−83[f]	37	1.59	58.6	100

[a] Data from ref 2a; sample 85% TMS, 15% acetone-d_6. Oxygen removed with N_2. [b] ±2–3°. [c] Inversion-recovery pulse sequence. Estimated errors <10%. [d] Theoretical maximum, $-\eta \equiv 2.52$. Determined directly from the decoupled and undecoupled spectra, estimated error <0.1. [e] Estimated error in $T_1^{DD} \lesssim 25\%$. [f] Sample: 75% TMS, 25% CD_2Cl_2. [g] $^{29}Si\{^1H\}$ signal nulled. T_1 determined from undecoupled pulsed Fourier transform resonance spectra.

Table III. Silicon-29 Relaxation in Linear Polydimethylsiloxanes[a]

	T_1, sec[b,c]					NOE ($-\eta$)[b,c]				
Compd[a]	M	D^1	D^2	D^3	D^4	M	D^1	D^2	D^3	D^4
MM	39.5					0.31				
MDM	35	54				0.36	0.55			
MD_2M	38	78				0.53	1.2			
MD_3M	46	82	77			0.57	1.1	1.2		
MD_6M	42	64	55	59		0.7	1.6	1.9	1.9	
MD_8M	44	67	60	55	55	0.7	1.5	1.8	2.0	2.0
MD_xM[e]										
$\bar{x} \sim 10$			35							
$\bar{x} \sim 50$			28					1.7		
$\bar{x} \sim 3000$[f]			27.3					1.7		
	T_1^{DD}, sec[d]					T_1^{SR}, sec[d]				
MM	320					45				
MDM	245	247				41	69			
MD_2M	181	164				43	149			
MD_3M	203	188	162			59	146	147		
MD_6M	151	101	73	78		58	175	224	240	
MD_8M	158	112	84	69	69	61	166	210	266	266

[a] Samples: 90% siloxane, 10% acetone-d_6; N_2 degassed. [b] T_1 at 38°. [c] D units numbered from each end, *e.g.*, $MD^1D^2D^1M$. [d] Derived quantities ±10–25%. [e] Undegassed. [f] Run neat, as a gum rubber.

molecular moment of inertia, k is Boltzmann's constant, and T is the absolute temperature. Equation 6 indicates that τ_j becomes longer as the sample temperature increases, the opposite dependence observed for τ_c. The effect of increased temperature is to shorten T_1^{SR} and lengthen T_1^{DD}. Relaxation data for TMS over the temperature range +25 to −83° are given in Table II and Figure 1.

Clearly SR relaxation dominates for TMS near room temperature (near the boiling point vapor-phase SR relaxation of the continually evaporating and condensing molecules is very efficient). Even at low temperatures SR relaxation in the liquid is quite significant. Figure 1 shows the anticipated (from eq 5) quantitatively similar but opposite in direction temperature dependences for T_1^{SR} and T_1^{DD}. The activation energies (E_a) corresponding to the data in Figure 1 are *ca.* −1.8 kcal mol^{-1} (for T_1^{SR}) and *ca.* +1.9 kcal mol^{-1} (for T_1^{DD}). Substantial experimental scatter is evident in Figure 1, preventing more accurate determinations of the activation energies. No differentiation between E_a for relaxation in the gas and liquid phases was possible because of limitations imposed by the observed temperature range, number of data points, and the experimental accuracy. The ^{29}Si T_1 activation energies found in this study can be compared with −1.3 kcal mol^{-1} observed for the ^{13}C T_1^{SR} in CS_2[14] and +1.63 kcal mol^{-1} found for the predominantly DD ^{13}C T_1 in $CHCl_3$.[15] Also, the TMS activation energies may be contrasted with larger E_a's for proton DD relaxation in associated liquids such as BuOH[16] (9.2 kcal mol^{-1}) and aniline-d_2[17] (4.5 kcal mol^{-1}).

Polydimethylsiloxanes. Linear polydimethylsiloxanes are important commercial materials and thus they have been extensively characterized.[18] In a study of proton spin-lattice and spin-spin relaxation times for a series of fractionated polydimethylsiloxanes Cuniberti[18b] was able to treat the results in terms of the Woessner anisotropic reorientation model,[19] separating the effects of internal CH_3 group rotation from chain reorientation motions. With ^{29}Si T_1 measurements it is possible to look at the motional processes along the chains themselves. Table III gives ^{29}Si relaxation data for several trimethylsiloxy terminated polydimethylsiloxanes. For convenience the M–D nomenclature is used in Table III and for further discussion. M units refer to the trimethylsiloxy end groups while D^1, D^2, D^3, etc., refer to the outermost and successive inner dimethylsiloxy groups, respectively (see Table III).

Several trends can be observed from the data in Table III. The somewhat different relaxation behaviors observed for the trimethylsiloxy (M) and dimethylsiloxy (D) silicon nuclei result from group symmetry considerations, as well as from the end-of-chain location of the M units. An M unit is able to freely spin

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(14) J. R. Lyerla, D. M. Grant, and R. D. Bertrand, *J. Phys. Chem.*, **75**, 3967 (1971).

(15) R. R. Shoup and T. C. Farrar, *J. Magn. Resonance*, **7**, 48 (1972).

(16) Y. Margalit, *J. Chem. Phys.*, **55**, 3072 (1971).

(17) E. Bock, J. Czubryt, and E. Tomchuk, *Can. J. Chem.*, **48**, 2814 (1970).

(18) H. I. Waterman, W. E. R. Van Herwijnen, and H. W. Den Hartog, *J. Appl. Chem.*, **8**, 625 (1958); (b) C. Cuniberti, *J. Polym. Sci., Part A-2*, **8**, 2051 (1970); (c) J. A. Barrie, M. J. Fredrickson, and R. Sheppard, *Polymer*, **13**, 431 (1972).

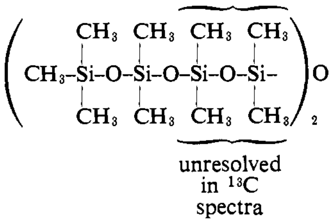
(19) D. E. Woessner, *J. Chem. Phys.*, **36**, 1 (1962).

internally around its threefold axis, whereas a D unit may easily rotate only through a restricted angle. Because of this, SR relaxation is favored for the M units. Even in the decasiloxane MD_8M, SR relaxation dominates for the M silicons (note that all of the D silicons in MD_8M are relaxed primarily by the ^{29}Si–^1H DD mechanism; see Table III). SR relaxation of the M silicons is only weakly dependent on the size of the molecule; *i.e.*, T_1^{SR} varies from 41 to 61 sec in the series MM to MD_8M. For the D silicons T_1^{SR} is more strongly a function of molecular size and also of the position of the D unit along the chain. Near the ends of the chains increased freedom of motion is evident. This is also indicated in the T_1^{DD} data, particularly for the four types of D units in MD_8M. In this case *segmental motion*[6a, 20] along the chain results in longer ^{29}Si DD T_1's near the chain ends.

In polydimethylsiloxanes local segmental motions control ^{29}Si relaxation; overall molecular reorientation does not directly affect the observed T_1's. This is evident from T_1 data for several polydimethylsiloxanes where the degree of polymerization varies from *ca.* 10 to 3000 (data for three of these polymers are given in Table III). These polymers have macroscopic viscosities that range from approximately 5 to 2 × 10^7 cP while their microviscosities, *as measured by* T_1^{DD}, vary only slightly. Analogous behavior has been observed in ^{13}C T_1 studies of some synthetic organic polymers[21] but in those cases the minimum molecular weights required to reach a "limiting microviscosity"[6a] were very high.

Methyl carbon relaxation times determined from ^{13}C T_1 spectra of MD_6M also show increased motion of the chain-end CH_3 groups resulting from internal CH_3 group rotation and overall rotation of the $Si(CH_3)_3$ groups.

$T_1(^{13}C)$	9.2	6.2	5.6
$T_1^{DD}(^{13}C)$	12.3	7.8	7.5



$$\left(\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}}\right)_2\mathrm{O}$$

With the cyclic dimethylsiloxanes (Table IV) molecular size is a more important factor for determining ^{29}Si relaxation parameters. No apparent trend is clear from the observed T_1's in Table IV. By contrast, both T_1^{DD} and T_1^{SR} are strongly dependent on molecular structure. In dodecamethylcyclohexasiloxane (D_6) dipole–dipole relaxation increases significantly, while the efficiency of SR relaxation is markedly lower (see Table IV). In these cyclics simple segmental motion is not as important as in the case of linear siloxanes. Large changes in molecular conformations that would affect T_1 processes appear to vary with the specific cyclic structure.

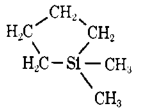
Table IV. ^{29}Si Relaxation Data for Cyclic Polydimethylsiloxanes[a]

Compd[a]	Visc, cP	T_1, sec	NOE ($-\eta$)	T_1^{DD}, sec	T_1^{SR}, sec
$[(CH_3)_2SiO]_3$[b]	≈0.51	80	1.1	183	142
$[(CH_3)_2SiO]_4$	0.982	100	1.83	138	365
$[(CH_3)_2SiO]_6$	1.968	91	2.24	102	820

[a] Samples: 85% siloxane, 15% acetone-d_6; N_2 degassed. [b] 75% siloxane, 25% CD_2Cl_2.

Dipole–Dipole Relaxation with Dissolved Oxygen. Table V gives some ^{29}Si T_1 data obtained under three sets of conditions: (1) degassed, where the partial pressure ($p(O_2)$) above the solution and the dissolved O_2 concentration is ≈0; (2) O_2 gassed, where the solution is saturated with O_2 at $p(O_2)$ = 1 atm; and (3) undegassed, where $p(O_2)$ above the solution is 0.21 atm. The relaxation from DD interactions with the paramagnetic oxygen molecules can be calculated from the relaxation rates in the presence and absence of O_2. Table V lists T_1^e ($1/R_1^e$), the ^{29}Si T_1 contribution resulting from DD interactions with unpaired electrons defined at $p(O_2)$ = 1 atm. For ^{13}C nuclei, $T_1^{e(O_2)}$ values have been found to be *ca.* 20–25 sec.[11] The observed nuclear–electron DD relaxation rates for ^{29}Si nuclei are in close agreement with the ^{13}C values, since all dipole–dipole interactions are proportional to γ^2 for the interacting spins $(\gamma_{^{13}C}/\gamma_{^{29}Si})^2 = 1.6$.[22]

Table V. Effect of Dissolved Oxygen on Silicon-29 Relaxation[a]

Compound	$p(O_2)$, atm	T_1, sec	T_1^e, sec[b]
	0 0.21 1.0	52 43 20.5	 52 34
$[(CH_3)_2SiO]_x$	0 0.21	33 28	 39
MD_8M (see also Table III)			
M_1	1.0	20	37
D	1.0	23	35
D^2	1.0	23	37
D^3 D^4	1.0	22	37

[a] Calculated from R_1^{obsd}(degassed) − $R_1^{obsd}(O_2)$. [b] For solutions at $p(O_2)$ = 0.21 atm, T_1^e is extrapolated to 1 atm of O_2.

Paramagnetic Relaxation Reagents. Chemical additives that can shorten spin–lattice relaxation times without causing extensive line broadening and without affecting spectral chemical shifts have been used to facilitate both ^{13}C[23] and ^{29}Si[2b] nmr studies. In ^{29}Si nmr these reagents are particularly useful because ^{29}Si spectral signal-to-noise usually gains from both shortening of T_1's and loss of (negative) NOE's whereas ^{13}C spectral sensitivity is helped only by the shortening of T_1's. Suppression of the (positive) ^{13}C–^1H NOE is a necessary, but not always desirable, product of the paramagnetic doping experiment.

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(20) (a) D. Doddrell and A. Allerhand, *J. Amer. Chem. Soc.*, **93**, 1558 (1971); (b) G. C. Levy and G. L. Nelson, *ibid.*, **94**, 4897 (1972); (c) Y. K. Levine, N. J. M. Birdsall, A. G. Lee, and J. C. Metcalfe, *Biochemistry*, **11**, 1416 (1972).

(21) (a) A. Allerhand and R. K. Hailstone, *J. Chem. Phys.*, **56**, 3718 (1972); (b) J. Schaefer and D. F. S. Natusch, *Macromolecules*, **5**, 416 (1972).

(22) A more complete treatment of DD interactions with dissolved paramagnetic materials will be presented elsewhere: G. C. Levy and J. D. Cargioli, *J. Magn. Resonance*, in press; G. C. Levy and E. B. Whipple, unpublished results.

(23) (a) G. N. LaMar, *J. Amer. Chem. Soc.*, **93**, 1040 (1971); (b) R. Freeman, K. G. R. Pachler, and G. N. LaMar, *J. Chem. Phys.*, **55**, 4586 (1971); (c) S. Barza and N. Engstrom, *J. Amer. Chem. Soc.*, **94**, 1762 (1972); (d) O. A. Gansow, A. R. Burke, and W. D. Vernon, *ibid.*, **94**, 2550 (1972).

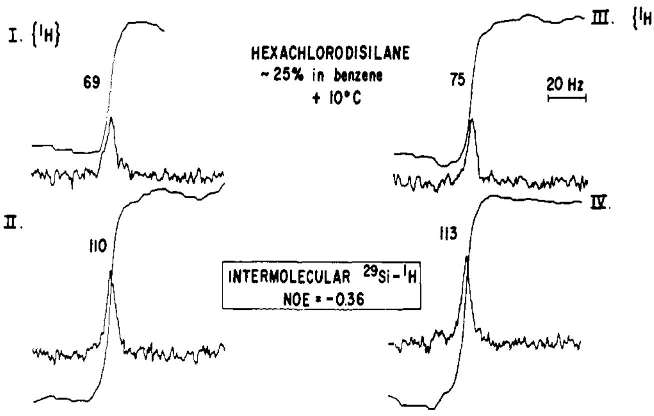


Figure 2. Intermolecular ^{29}Si-^{1}H NOE in hexachlorodisilane. Spectra: (I and III) benzene protons decoupled; (II and IV) no ^{1}H decoupling.

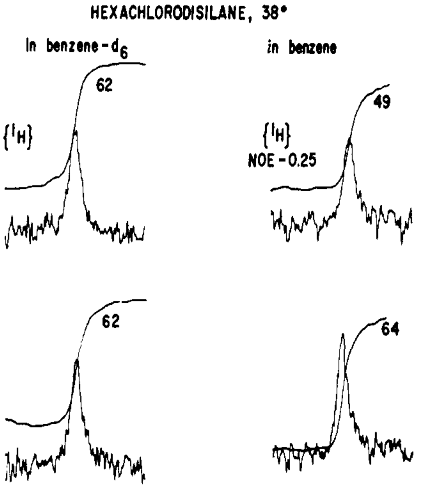
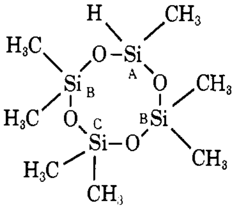


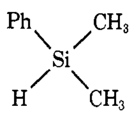
Figure 3. Confirmation of internuclear ^{29}Si-^{1}H NOE in hexachlorodisilane, 30% solutions in benzene and benzene-d_6. Upper spectra obtained with proton decoupling.

Chromium(III) acetylacetonate (Cr(acac)$_3$) has been successfully used for both ^{13}C and ^{29}Si nmr. As with dissolved oxygen, the limiting ^{29}Si T_1 depends on the concentration of the additive. The limited solubility of Cr(acac)$_3$ restricts its maximum soluble concentration in many organosilicon compounds (especially siloxanes) to $\sim 10^{-2}$ M. Use of cosolvents such as ethyl acetate or acetone can increase the Cr(acac)$_3$ solubility to $\sim 5 \times 10^{-2}$. Table VI shows the approximate value for a ^{29}Si T_1 as a function of Cr(acac)$_3$ concentration, and lists several experimental cases. The expectation values in Table VI should be used with caution, since the effect of Cr(III) depends on the solution viscosity.[22] It is important to note that it does not matter if the ^{29}Si nucleus has directly attached protons. The effect of the added Cr(III) will be equivalent for all ^{29}Si nuclei with undoped T_1's $\gg T_1$ with Cr(III) (as long as there are no weak interactions between the Cr(III) and organosilicon compounds[22]). At concentrations greater than 3×10^{-2} M, $T_1^{e} \ll T_1$ for any ^{29}Si nucleus observed in this study.

Table VI. ^{29}Si Relaxation with Cr(acac)$_3$



VIII



IX

Compound	Cr(III), M	T_1^{e}, sec^a
Expectation values	5×10^{-3}	20
	1×10^{-2}	10
	5×10^{-2}	2
IX	3.6×10^{-2}	2.9
VIII	3.2×10^{-2}	A 4.5
		B 4.5
		C 4.3
MD$_6$M	1×10^{-3} all nuclei	76.5
	5×10^{-3}	14.5

^{a} Calculated from $R_1^{obsd}[Cr] = 0 - R_1^{obsd}[Cr] \neq 0$.

Preliminary experiments[22] have indicated that Fe(acac)$_3$ may be even more useful for ^{29}Si nmr studies, as a result of (a) higher solubility and (b) greater efficiency at a given concentration.

Evidences for Long-Range Intramolecular and Intermolecular ^{29}Si-^{1}H Dipole–Dipole Relaxation. Specific T_1 and NOE experiments can be performed to separate long-range from directly bonded ^{29}Si-^{1}H DD interactions and to identify *intermolecular* contributions from intramolecular long-range interactions. Figures 2 and 3 show intermolecular ^{29}Si-^{1}H NOE data for a compound containing no protons, hexachlorodisilane. Figure 2 shows four experiments on a 25% sample of the disilane in benzene at +10°. The experiments were run in the order I → IV. For experiments I and III the benzene protons were irradiated; no proton irradiation was used in II and IV. The NOE observed in I and III, $\eta = -0.37$ and -0.33, is clear evidence of intermolecular ^{29}Si-^{1}H dipole–dipole interactions.[24] Another set of experiments were run at 38° on two samples of 35% hexachlorodisilane in benzene and benzene-d_6 (Figure 3). Here, the intermolecular NOE *observed only* in the protio-benzene solvent was somewhat smaller than that observed for the more dilute sample at 10°. In addition to the dilution effect, at 38° spin–rotation relaxation can more effectively compete with intermolecular DD interactions. The NOE observed at +10° (*ca.* 14% of the theoretical maximum) is a minimum contribution; the efficiency of SR relaxation at +10° is unknown (only an approximate T_1 was obtained for this sample, ≈ 115 sec).

It is extremely difficult to separate *intermolecular* from *intramolecular* NOE's in compounds containing protons. Solutions of octamethylcyclotetrasiloxane (D$_4$) in cyclohexane and cyclohexane-d_{12} and benzene and benzene-d_6 show *ca.* 10% differentials in observed T_1's, having shorter T_1's in the protio solvents, where the NOE's are marginally higher (typically 0.1–0.2). The observed differences between solutions in protio and deuterio solvents are too small to be reliably used. They are consistant, however, with *ca.* 15–20% dipolar relaxation contributions from intermolecular ^{29}Si-^{1}H DD interactions (relative to total ^{29}Si-^{1}H DD

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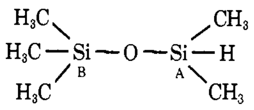
[24] Attempts in this laboratory to observe ^{13}C-^{1}H intermolecular NOE's have failed: G. C. Levy and F. A. L. Anet, unpublished results.

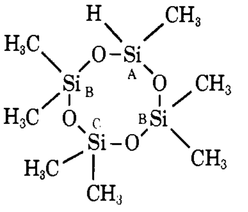
relaxation contributions; corresponding to intermolecular T_1^{DD} contributions of between 700 and 1000 sec).

Table VII summarizes T_1 and NOE data for two compounds that have *both* protonated and nonprotonated ^{29}Si nuclei. Assuming that the tumbling motions of the molecules are isotropic (this is partly confirmed for the larger molecule, VIII, where the two kinds of nonprotonated ^{29}Si nuclei have nearly identical T_1's), T_1^{DD} for the nonprotonated ^{29}Si nuclei can be used to evaluate long-range DD interactions. For the small molecule pentamethyldisiloxane, VII, SR relaxation dominates, lowering the accuracy for determinations of T_1^{DD}. The relaxation data for the cyclic tetrasiloxane, VIII, are more favorable. A complete dissection of the relaxation processes for VIII is given in Table VII. These were calculated as follows. T_1^{DD} for the nonprotonated carbons was made up of intra- and intermolecular contributions. The intermolecular contribution was estimated to be approximately 15% of the total long-range DD relaxation contribution. T_1^{DD} for the protonated silicon A contained both one-bond and long-range contributions. Long-range contributions for the A silicon were assumed to be equivalent in seconds to those for the B and C nuclei.

Table VII. Dissection of Dipolar Relaxation Terms[a]



VII



VIII

	Silicon	T_1^{obsd}	NOE (η)	T_1^{DD}	T_1^{SR}
VII	A	34	0.56	150[b]	50
	B	43	0.35	310[c]	44
VIII	A	31	1.8	43.4	108
	B	66	1.45	115	155[b]
	C	67	1.40	121	151[b]

		T_1^{DD} One bond	$T_1^{DD\,b}$ Long-range intra-molecular	$T_1^{DD\,c}$ (est[d]) Inter-molecular
VIII	A	69	(140)	(750)
	B		140	750
	C		140	750

[a] All T_1's in sec. T_1^{xx} terms calculated as relaxation rates, ±10–15%; see eq 5 and text; samples degassed. [b] ±20–30% (estimated). [c] ±30–40% (estimated). [d] From NOE and T_1 data on hexachlorodisilane and octamethylcyclotetrasiloxane.

The ^{29}Si DD relaxation behavior observed for the two compounds in Table VII is in sharp contrast with that observed for ^{13}C–^{1}H DD relaxation in organic compounds that have been investigated to date. Nonprotonated ^{13}C nuclei have DD relaxation times much longer (typically 20 times longer) than T_1^{DD} for protonated carbons in the same molecule. The reason for the disparity between ^{13}C and ^{29}Si relaxation is the difference in bond lengths and van der Waals' distances for silicon and carbon nuclei (as discussed in the initial section on ^{29}Si relaxation mechanisms).

Calculation of the Molecular Correlation Time, τ_c, from ^{29}Si T$_1$ Data. It is possible to roughly calculate τ_c for many organosilicon compounds by inserting appropriate parameter values into eq 1 or 2. In each case, rigid, isotropic molecular tumbling is assumed; significant deviation from this condition will greatly restrict the accuracy of the calculation.

For protonated ^{29}Si nuclei: SiH = 1.48×10^{-8} (cm); $\gamma_H = 26{,}750$ (radians sec^{-1} G^{-1}); $\gamma_{Si} = -5319$; $\hbar = 1.054 \times 10^{-27}$ (erg sec). Substitution of these values into eq 2 gives correlation times of *ca.* 9×10^{-12} and 2.5×10^{-12} sec for diphenylsilane (II) and phenyldimethylsilane (III), respectively. Correlation times of 1.6×10^{-11} and 5.8×10^{-12} sec can be calculated from the para ^{13}C T_1's for these two compounds. Inclusion of the effect of long-range ^{29}Si–H DD interactions into the calculation would give somewhat shorter correlation times, especially in the case of III (*ca.* 15–20% shorter). Nevertheless, the ^{29}Si and ^{13}C calculated τ_c's are in reasonable agreement, especially considering that motional anisotropy is probably present.

For nonprotonated ^{29}Si nuclei, summing all neighboring proton interactions (eq 1) for likely molecular conformers can be a very difficult task, making calculations of τ_c impractical in most cases.

Variable-Temperature Studies. In order to separate and identify major and minor contributions from the chemical shift anisotropy and spin–rotation relaxation mechanisms it is necessary to perform variable field or variable-temperature T_1 experiments.

Variable-field experiments directly identify CSA relaxation contributions from their second power dependence on the magnetic field indicated for axially symmetrical molecules in eq 7.[5b]

$$R_1^{CSA} \equiv \frac{1}{T_1^{CSA}} = \frac{2}{15}\gamma^2 H_0^2(\sigma_\parallel - \sigma_\perp)^2\tau_c \qquad (7)$$

In eq 7 H_0 is the static magnetic field used in the experiment and $\sigma_\parallel$ and $\sigma_\perp$ are the chemical shieldings along and perpendicular to the symmetry axis; γ is the magnetogyric ratio and τ_c is the molecular correlation time. Unfortunately no superconducting solenoid spectrometer equipped for ^{29}Si T_1 experiments was available for this work.

Variable temperature T_1 experiments isolate SR relaxation contributions since the spin–rotation correlation time τ_j varies inversely with τ_c (eq 6). It is possible to indirectly determine CSA relaxation contributions from variable temperature T_1 experiments, using eq 5. Both DD and CSA relaxations are proportional to τ_c. Assuming isotropic motion, the ratio T_1^{DD}/T_1^{CSA} remains constant over a wide range of temperatures. Anisotropic overall tumbling or internal motion will not in general change the T_1^{DD}/T_1^{CSA} ratio greatly. By contrast, a sample temperature change of 50–100° (around room temperature) changes ^{29}Si T_1^{SR}/T_1^{DD} or T_1^{SR}/T_1^{CSA} ratios drastically. Table VIII summarizes some ^{29}Si T_1 data obtained over the temperature range -78 to $+127°$. The T_1^{other} relaxation contributions in Table VIII are calculated from eq 5, combining all non DD contributions.

While the T_1^{DD} relaxation terms clearly increase as a function of increasing temperature, the T_1^{other} contributions exhibit a complex temperature dependence. Above ambient temperatures, T_1^{other} exhibits an inverse

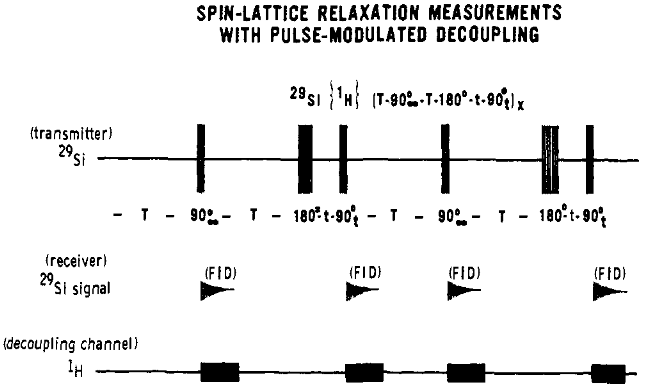


Figure 4. Pulse sequence for obtaining ^{29}Si spin–lattice relaxation times from ^{29}Si{^{1}H} spectra while simultaneously suppressing the ^{29}Si–^{1}H NOE (using pulse-modulated proton decoupling).

Table VIII. Variable-Temperature T_1 Studies[a]

	Temp, °C[b]	T_1^{obsd}	NOE $(-\eta)$	T_1^{DD}	T_1^{other}	E_a T_1^{DD}, kcal mol^{-1}
$[(CH_3)_2SiO]_6$	+127	93	0.87	269	142	
D_6	+78	110	1.29	215	225	
Neat	+39	73.3	2.12	87.1	462	
	0	30.7	2.22	34.8	258	
	−27	17.0	2.27	18.9	171	
						3.7
MD_xM	+127[c]	55	1.38	100	122	
($\bar{x} \approx 50$)	+74	69	1.75	99	226	
	+38	46	2.16	53.7	322	
(Sample:	0	31.5	2.25	35.3	294	
25%	−20	21.2	2.26	23.6	205	
toluene-d_8	−35	12.3	2.27	13.6	124	
						2.6
$(CH_3CH_2O)_4Si$	+60	140	0.8	441	205	
Sample:	+38[d,e]	135	1.5	227	334	
30%	−58	31.5	2.28	34.8	331	
acetone-d_6[d]	−78	16.6	2.25	18.6	155	
						2.6

[a] All T_1's in sec. Determined at 19.86 MHz. Samples vacuum degassed. T_1^{other} terms ±25%. [b] ±2–3°. [c] Neat polymer sample. [d] N_2 degassed. [e] Sample: 15% acetone-d_6; see Table I.

dependence on temperature, as expected for SR relaxation. Below room temperature T_1^{other} decreases with decreasing temperature. This behavior can be explained by postulating that CSA relaxation is *ca.* 5–10% as effective as DD relaxation. Just below room temperature, where DD relaxation is more effective than SR relaxation, the CSA contribution becomes significant. At very low temperatures CSA relaxation is much more effective than SR relaxation, even though it is still only a minor contribution to the total ^{29}Si relaxation.

This small relaxation contribution from the CSA mechanism would become quite significant for experiments run on superconducting solenoid spectrometers (such experiments are planned). For protonated ^{29}Si nuclei, on the other hand, the CSA contributions at 23 kG would be insignificant, as in ^{13}C relaxation.[11]

For an arbitrary molecular correlation time of 1×10^{-11} sec, substitution into eq 2 and 7 (using values of 50–100 ppm for the shielding anisotropy[9] of silicon and 23 kG in eq 7) implies that CSA relaxation will only be 0.25–1% as efficient as DD relaxation for a ^{29}Si–^{1}H nucleus. For nonprotonated ^{29}Si nuclei the theory would give estimates of 1–5% for the CSA contributions, in reasonable agreement with the experimental evidence.

The variable-temperature studies also allowed calculation of activation energies for T_1^{DD}, which are given in Table VIII. All of these values were higher than E_a for TMS, presumably as a result of increased internal motional freedom or anisotropy of overall motion. It is not clear to us why E_a for the cyclic hexamer was significantly higher than the other activation energies.

Discussion of Experimental Procedures

Pulse-modulated (interrupted) proton wide-band decoupling was used to obtain most of the ^{29}Si–^{1}H NOE's and ^{29}Si T_1's reported in this paper. In this decoupling scheme the noise-modulated irradiation of the protons is operating only *during the periods of* ^{29}*Si data acquisition.* During the long intervals between pulses (that are required for *both* NOE and T_1 measurements) the ^{1}H decoupler power is gated off. The computer controls decoupler gating, on command from the teletype in the same way as other initialization parameters can be specified for the experiment.

In direct NOE determinations two spectra are obtained, one with pulse-modulated wide-band ^{1}H decoupling and one with continuous wide-band ^{1}H decoupling. In order to prevent appreciable NOE from building up during the data acquisition periods in the pulse-modulated experiments the following condition was met or exceeded, if possible

condition 1 $\quad T_1/\mathrm{AP} \gtrsim 20$

(where AP = data acquisition period; T_1 = the T_1 for the fastest relaxing silicon in the molecule). Furthermore, the usual requirement for direct NOE determinations was met

condition 2 $\quad \mathrm{PI}/T_1' \gtrsim 5$

(where PI = the pulse interval; T_1' = the T_1 for the slowest relaxing silicon in the molecule).

This automatically resulted in a third relationship

condition 3 $\quad \mathrm{PI/AP} \gtrsim 100$

which completely ensured against cumulative build-up of NOE in the repetitive pulse experiments. (Condition 3 corresponds to a 1% duty cycle for ^{29}Si{^{1}H} irradiation. In some situations, duty cycles as high as 3–5% were used, with some loss of accuracy.)

In early ^{29}Si T_1 experiments[2a] that did not utilize pulse-modulated decoupling spectral sensitivity suffered. In some cases where the ^{29}Si–^{1}H NOE was ≈ -1 (η) the T_1's could only be obtained from the undecoupled spectra.

We devised the pulse-modulated decoupling scheme shown in Figure 4, to allow T_1 measurements on the simpler, ^{1}H decoupled spectra, while still eliminating the negative NOE.

Spin–lattice relaxation times obtained by the pulse scheme shown in Figure 4 are essentially equivalent to T_1's determined without decoupling. Grant and others have shown that ^{13}C T_1's determined in ^{1}H decoupled and undecoupled experiments may be significantly different.[25] Furthermore, the time function of the

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(25) T. D. Alger, R. Freeman, and D. M. Grant, *J. Chem. Phys.*, 57, 2168 (1972); T. D. Alger, S. W. Collins, and D. M. Grant, *ibid.*, 54, 2820 (1971); T. Maruyama, M. Imanart, S. Shimizu, and K. Ishibitsu, *Proc. Congr. AMPERE, 16th*, 299 (1970).

^{13}C magnetization in the undecoupled case was found to be somewhat nonexponential.

More recently it has been postulated by R. Freeman[26] that this nonexponential relaxation as well as the quantitative differences between T_1's obtained with and without decoupling *will be very small* under certain circumstances: (a) if the dipolar contribution is negligible or (b) if the undecoupled nucleus (^{1}H in this case) has a much shorter T_1 (due to external mechanisms) than the ^{29}Si dipolar T_1. For organosilicon compounds $T_1(^{29}\mathrm{Si}) \gg T_1(^1\mathrm{H})$ (generally). Thus in ^{29}Si relaxation measurements the presence or absence of ^{1}H decoupling should not quantitatively affect the results. To test Freeman's hypothesis, we performed ^{29}Si T_1 experiments on samples of several organosilicon compounds under both ^{1}H decoupled and pulse-modulated $\{^1\mathrm{H}\}$ conditions. Figure 5 shows the two magnetization recovery curves for a linear polydimethylsiloxane, SE-30 ($\bar{x} \sim 3000$). These data were particularly accurate because of the large sample size (run as a solid gum rubber in a 10-mm o.d. tube with a surrounding annulus of D_2O) and extended time averaging. The ^{29}Si T_1's indicated in Figure 5 are experimentally identical, confirming Freeman's hypothesis (in this case T_1 for the protons is *ca.* 0.7 sec). Furthermore, both magnetization recoveries are completely exponential within experimental accuracy limitations. (Results similar to these were obtained for ^{29}Si relaxation in diphenylsilane, II, and hexamethyldisiloxane, V.)

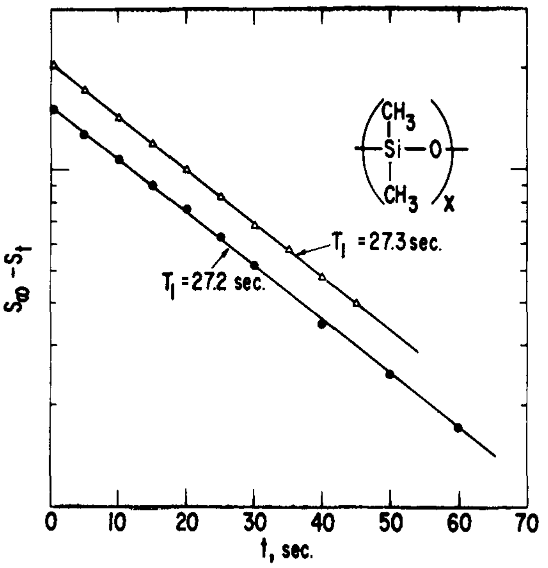

Figure 5. Magnetization recovery curves from two ^{29}Si T_1 experiments on a single sample of MD_xM ($\bar{x}$ — 3000): (●) continuous wide-band proton decoupling; (△) pulse-modulated wide-band decoupling (see Figure 4 and text).

Experimental Section

Materials. The following compounds were obtained from PCR, Inc., and used as received: diphenylsilane, II, Catalog No. 01-25170-09, and phenyldimethylsilane, III, Catalog No. 01-25010-05.

Hexamethyldisiloxane (MM) and octamethylcyclotetrasiloxane (D_4) were obtained from the Silicone Products Business Department, General Electric Co., Waterford, N. Y. These compounds were purified by fractional distillation from calcium hydride: MM, bp 99° (760 mm) [lit.[27] bp 98.5° (760 mm)]; D_4, bp 175° (760 mm) [lit.[28] bp 175° (760 mm)]. Gas–liquid phase chromatography, glpc (6 ft columns, SE-30-10% on Chromosorb W, H-P 5750 with dual TC detectors) showed >99% purity.

Octamethyltrisiloxane, MDM, bp 98° (159 mm) [lit.[29] bp 91° (106 mm)], decamethylpentasiloxane, MD_2M, bp 115° (60 mm) [lit.[29] bp 113° (57 mm)], and dodecamethylpentasiloxane, MD_3M, bp 112° (10 mm) [lit.[30] bp 229° (1 atm)], were obtained from a fractional distillation of the products of an acid (H_2SO_4)-catalyzed equilibration of MM and D_4.[30] Octadecamethyloctasiloxane, MD_6M, bp 105° (0.2 mm) [lit.[31] bp 186° (20 mm)], and docosamethyldecasiloxane, MD_8M, bp 131° (0.2 mm) [lit.[31] bp 182° (4 mm)], were obtained from a careful fractional distillation (Nester-Faust NT-51 Adiabatic Annular Still) of a commercial polydimethylsiloxane fluid, SF-96(5) G.E., Silicone Products Business Department. All of the distilled polydimethylsiloxanes were >98% pure by glpc. Two other polydimethylsiloxanes were obtained from the same source and were used as received: SF-96 (100), $MD_{\bar{x}}M$, $\bar{x} \cong 50$[32] and SE-30, $MD_{\bar{x}}M$, $\bar{x} \cong 3400$.[33]

Pentamethyldisiloxane, VII, was obtained from a low-temperature (5–10°) cohydrolysis of trimethylchlorosilane and dimethylchlorosilane in diethyl ether. The ether layer was washed with an aqueous sodium bicarbonate solution, dried over anhydrous magnesium sulfate, concentrated, and fractionally distilled. The water white product, bp 83° (755 mm) [lit.[34] bp 85° (760 mm)], was >99% pure by glpc.

2,4,4,6,6,8,8-Heptamethylcyclotetrasiloxane (VIII) was prepared in a two-step procedure. The first intermediate, 1,7-dichloro-1,3,3,5,5,7,7-heptamethyltetrasiloxane, was obtained from a room-temperature ring-opening reaction of hexamethylcyclotrisiloxane with lithium chloride in tetrahydrofuran in the presence of dimethylchlorosilane. This product was fractionally distilled, then treated with ZnO in dry ethyl acetate (high dilution–5% product) to effect cyclization[35] to the desired 2,4,4,6,6,8,8-heptamethylcyclotetrasiloxane. After water work-up to remove the by-product $ZnCl_2$, the ethyl acetate layer was dried (anhydrous $MgSO_4$), concentrated, and fractionally distilled through a spinning band column; bp 64° (20 mm) [lit.[36] bp 66° (20 mm)].

Nmr Measurements. All ^{29}Si Fourier transform spectra were obtained on a Varian XL-100-15 spectrometer system. The system computer (Varian 620-i; 16K core) allowed acquisition of 8192 spectral data points, resulting in 4096 output data points in the phase corrected absorption spectra (limiting spectral resolution to $\cong$0.5 Hz only for the widest spectral widths used). The computer was interfaced to a Computer Operations, Inc. (Beltsville, Md.) magnetic tape unit to allow storage and retrieval of the individual transformed spectra in T_1 experiments and to allow rapid interchange of computer programs.

In most cases wide-band proton (noise) decoupling was used, provided by the spectrometer Gyrocode decoupler. Internal field frequency control was obtained from deuterium solvents or from an annulus of D_2O in a 12-mm tube, with the ^{29}Si sample contained in a coaxial 10-mm tube. Sample temperature was determined to better than ±2–3° by substitution with similar sample tubes containing thermometers. The sample temperature in routine studies was 38°.

The rf pulse power of our XL-100 was limited to $\lesssim$2 G ($\pi/2$ pulse $\cong$175 μsec). Therefore, spectral widths were restricted to $\lesssim$1000 Hz.

Spin–Lattice Relaxation Measurements. Spin-lattice relaxation times (T_1) for all ^{29}Si nuclei were determined simultaneously by the inversion-recovery pulse method. The pulse sequence utilized in these measurements was

$$(-T-90_\infty-T-180°-t-90°_t-)_x$$

where t is experimentally varied and T is set greater than three to four times the longest T_1 to be measured.

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In this sequence, the log of ($S_\infty - S_t$) is plotted against t where S_∞ and S_t are the transformed signals from the $90°_\infty$ and $90°_t$ pulses, thus yielding only positive peaks in the spectral display. T_1 is the time, t, at which the linear trace of ($S_\infty - S_t$) reaches 0.368 ($\equiv 1/e$) of ($S_\infty - S_t$) for $t = 0$ ($\equiv 2S_\infty$). For each determination 6–10 sets of measurements were taken. Some determinations were repeated on different samples of the same compound. Reproducibility of T_1 values was considerably better than ±15% in most cases. Accuracy limitations depend in each instance on solute concentration and the length of data acquisition. In the higher accuracy studies (stated probable error limits <10%) very high signal-to-noise ratios were achieved. Repetitive experiments on separate, equivalent samples yielded T_1 values within one-third to one-half the stated maximum probable error limits.

NOE Measurements. Direct ^{29}Si–^{1}H NOE determinations were obtained from continuous wide-band and pulse-modulated[2a,37] wide-band proton decoupled ^{29}Si spectra. Using the technique of decoupling just before the short ^{29}Si pulses and during short (<2 sec) acquisitions of the free-induction decays while leaving the decoupler off for the long ($\gtrsim 4T_1$) pulse intervals allowed direct measurements of the NOE's from all of the ^{1}H decoupled spectra (where ^{29}Si T_1's > 20 sec). A few of the early NOE determinations were obtained from decoupled and coupled spectra.[2a] Most NOE's are reported to an accuracy of $\pm 0.1\eta$.

Acknowledgments. We thank Charles S. Peters for writing supplementary computer software and Craig D. Robertson for experimental assistance. We also thank Professor F. A. L. Anet for several helpful discussions.

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Decomposition Kinetics of Chemically Activated Dimethylsilane and Ethylsilane[1]

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Abstract: An experimental study of the decomposition kinetics of chemically activated dimethylsilane and ethylsilane produced by reaction of singlet methylene with methylsilane is reported. Rate constants for various possible decomposition paths are deduced and a RRKM theoretical treatment of CH_3–Si bond rupture is given. Revised theoretical calculations for previous studies of CH_3–Si bond rupture are presented.

The relative importance of possible primary decomposition paths of ground electronic state silanes and alkylsilanes is an important question toward which a few recent pyrolysis[2] and chemical activation[3] studies have been directed. Some possible indications of criteria for decisions on the relative contributions of radical production (bond rupture) and molecular elimination have resulted.[4] In view of the major difficulties which have plagued thermal decomposition studies in the past, namely heterogeneous effects and complicating secondary reactions, chemical activation studies of these decomposition processes are of value. The relatively low temperature, at which chemical activation studies can be carried out, tends to minimize many heterogeneous complications and homogeneous secondary reactions.

The production of chemically activated dimethylsilane and ethylsilane by Si–H and C–H insertion respectively of singlet methylene with methylsilane has been reported.[5] That work is extended here, with more complete product analyses, to lower pressures.

Experimental Section

Materials. The acquisition and handling procedures for diazomethane (DM), methylsilane (MS), *n*-butane (nB), 1,3-butadiene (Bd), and oxygen have been described in earlier work.[3,5]

Apparatus. The gas handling vacuum system, photolysis radiation source, and Pyrex reactors have been described.[3]

Procedure. The following mixtures were photolyzed at 3660 Å and 25° for various times depending on the total pressure: $CH_2N_2/CH_3SiH_3/O_2$, 1/10/1; $CH_2N_2/CH_3SiH_3/n\text{-}C_4H_{10}/O_2$, 1/7.5/2.5/1; $CH_2N_2/CH_3SiH_3/n\text{-}C_4H_{10}/1,3\text{-}C_4H_6$, 1/2/2/4; and $CH_2N_2/CH_3SiH_3/1,3\text{-}C_4H_6$, 1/3/6. Total pressures ranged from 1 to 200 cm. After photolysis the reaction mixtures were fractionated by vacuum distillation at −196°. The noncondensibles were collected with a Toepler pump and analyzed by glpc or mass spectrometry. The condensibles were analyzed by glpc.

Analytical. In the early experiments the noncondensibles were analyzed by glpc on a 10-ft molecular sieve (5 A) column. This proved unsatisfactory since quantitative transfer of the noncondensibles to and from sample tubes and to the glpc was difficult. Consequently a mass spectrometric analysis was devised which did not require quantitative transfer in order to get complete product ratios. A sample of a known mixture of argon and *n*-butane was added to each product plus reaction mixture just prior to removal of the noncondensibles. This procedure was used only for those reactions in which *n*-butane was not initially added as an internal monitor of total $^{1}CH_2$ insertion. The noncondensibles at −196° (H_2, CH_4, N_2, Ar, O_2) were quantitatively collected with a Toepler pump and analyzed mass spectrometrically which quantitatively gave H_2 and CH_4 relative to argon. The

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