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NMR Spectra of Organogermanium Compounds. 5.[1] Relaxation Mechanism of Germanium-73 Nuclei in Tetraalkylgermanes

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The ^{73}Ge spin–lattice relaxation time (T_1) and spin–spin relaxation time (T_2) in such alkylgermanes as symmetrical GeR_4 (R = methyl, ethyl, *n*-propyl, *n*-butyl) and the unsymmetrical germacyclohexane derivatives 1,1,3-trimethyl-, 1,1,4-trimethyl-, and 1,1,3,5-tetramethyl-1-germacyclohexane have been measured at several temperatures in order to elucidate the relaxation mechanism of germanium nuclei in organogermanium compounds. Furthermore, the viscosities of the solutions of symmetrical alkylgermanes were measured to obtain the reorientational correlation times. T_1 and T_2 are the same for all the compounds investigated at room temperature, and these become shorter as the molecular radii become larger. The relaxation times of unsymmetrical germacyclohexane derivatives are even shorter than those of symmetrical GeR_4. T_1 and T_2 of germanium nuclei in alkylgermanes were found to be dominated by the quadrupole relaxation. The reorientational correlation times ($(0.69–10.9) \times 10^{-11}$ s) and the activation energies (9.6–13.2 kJ/mol) for GeR_4 are also discussed.

Introduction

Recently considerable attention has been paid to the nuclear magnetic relaxation of group IVB (group 14)[35] elements with $I = {}^1/_2$ (C, Si, Sn, Pb). The relaxation of these nuclei in tetraalkyl compounds of the type XR_4, where X = C, Si, Sn, and Pb and R is an alkyl group, has been particularly well investigated. Thus, the spin–lattice relaxation of ^{29}Si of $Si(CH_3)_4$ is dominated by the spin-rotation mechanism near the boiling point and by the dipole–dipole relaxation mechanism at low temperatures.[2,3] The spin–lattice relaxation of ^{119}Sn and ^{207}Pb in $Sn(CH_3)_4$[4] and $Pb(CH_3)_4$[5] is, however, dominated by the spin-rotation mechanism.

Extensive studies have also been performed on the relaxation of these nuclei in the tetrahalides. The spin–lattice relaxation of ^{13}C in CCl_4 is dominated by the spin-rotation mechanism,[6] while the spin–lattice relaxation of ^{119}Sn in $SnCl_4$ is exclusively dominated by the spin-rotation mechanism while for that in $SnBr_4$ and SnI_4 the spin–lattice relaxation is due to a combination of spin-rotation and scalar coupling.[7,8] The spin–lattice relaxation of ^{207}Pb in $PbCl_4$ is also due to a combination of the spin-rotation and scalar-coupling mechanism, of which the latter is predominant.[9]

Reports on their spin–spin relaxation are rather scarce. Thus, the spin–spin relaxation of ^{119}Sn is predominated by the scalar-coupling mechanism for a variety of tin tetrahalides.[7,8]

As compared with nuclei with $I = {}^1/_2$, the magnetic resonance of ^{73}Ge nuclei has been much less studied chiefly because of the large quadrupole moment associated with this nuclei, which tends to cause excessive broadening of signals. Studies on the chemical shifts and line widths of ^{73}Ge nuclei for alkylgermanes[10–14] and halogermanes[10,13,15,16] have been attempted.

Studies on the relaxation of ^{73}Ge nuclei are even fewer. Thus, there are a few investigations on the spin–lattice relaxation[11,12] and the spin–spin relaxation[10] for a very limited number of compounds. The mechanism of the relaxation of ^{73}Ge nuclei remains virtually unexplored.

This is mostly due to the fact that the relaxation of such a quadrupole nuclei as ^{73}Ge is considered to be predominated by the quadrupole relaxation mechanism. There are, however, some reports that a mechanism other than the quadrupole contributes to the relaxation of quadrupole nuclei such as ^{55}Mn ($I = {}^5/_2$), ^{59}Co ($I = {}^7/_2$), and ^{17}O ($I = {}^5/_2$). It was shown that ^{55}Mn nuclei in $[^{55}Mn(CNCH_3)_6]^+$ or $[^{55}Mn(CNCH_3)_6]^{2+}$ and $[^{55}Mn(CNC_2H_5)_6]^+$ or $[^{55}Mn(CNC_2H_5)_6]^{2+}$ or ^{59}Co nuclei in $[^{59}Co(CN)_6]^{3+}$ relax mostly via the spin-rotation mechanism, not via the quadrupole mechanism.[17–19] ^{17}O nuclei in $Cl^{17}O_3F$ relax predominantly via the scalar coupling at low temperatures.[20]

With this in mind, we initiated an investigation to elucidate the relaxation mechanism of ^{73}Ge nuclei. For this purpose, we have prepared a series of such symmetrical organogermanium GeR_4 compounds (R = methyl, ethyl, *n*-propyl, *n*-butyl). In addition, we also prepared some unsymmetrical organogermanium compounds, i.e., 1,1,3-trimethyl-1-germacyclohexane (113MGC), 1,1,4-trimethyl-1-germacyclohexane (114MGC), and 1,1,3,5-tetramethyl-1-germacyclohexane (1135MGC) because the symmetry often plays an important role in the relaxation of quadrupole nuclei. We determined their relaxation times under various conditions and studied the relaxation mechanism thereof.

Furthermore, as an aid to study the relationship between the relaxation times and molecular motions, we determined the viscosity of chloroform solutions of these symmetrical germanes, from which the reorientational correlation times were determined for germanes.

Experimental Section

Preparation of Compounds. Tetraalkylgermanes GeR_4 (R = methyl, ethyl, *n*-propyl, *n*-butyl) were prepared by the procedures described in the literature.[21] The preparation of germacyclohexanes derivatives, i.e., 113MGC, 114MGC, and 1135MGC, was essentially based on the method of Mazerolles.[22] Details will be described elsewhere. The purity of the compounds prepared was confirmed by ^{1}H NMR spectra (Varian EM-390) and GLC (Shimadzu GC-3BT).

Germanium-73 NMR Spectra. The organogermanium compounds were dissolved in $CDCl_3$ (ca.50 v/v%), and the solution was taken in the egg-shaped cell and degassed by the freeze-and-thaw method. The ^{73}Ge NMR spectra were determined by JEOL FX-90Q equipped with the low-frequency insert NM-IT10LF at 3.10 MHz. The 180° pulse was 540 μs. Typically, the spectral width was 100 or 200 Hz with 2000 or 4000

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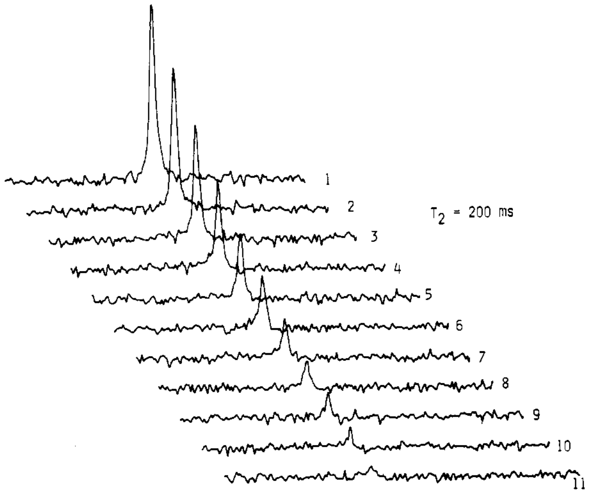

Figure 1. ^{73}Ge T_2 of tetraethylgermane by the CPMG method at room temperature (spectral width 200 Hz; data points 1000; 180° pulse 540 μs). Elapsed time after 90° pulse: (1) 49 ms; (2) 98 ms; (3) 147 ms; (4) 196 ms; (5) 245 ms; (6) 294 ms; (7) 344 ms; (8) 393 ms; (9) 442 ms; (10) 491 ms; (11) 540 ms.

data points. Usually 2500—5000 pulses were accumulated. The temperature of the probe was maintained at the desired temperature with the aid of a variable-temperature unit (NM-VT3C) and was monitored by a thermocouple.

Spin–lattice relaxation time was determined by the inversion–recovery method. Typically, the spectra were recorded for each compound with at least 11 different pulse delays. The error in T_1 was estimated to be about or less than ±5%. The reproducibility of T_1 was very good.

Spin–spin relaxation time was determined by the Carr–Purcell–Meiboom–Gill (CPMG) method. As an example, the stacked CPMG spectra of tetraethylgermane are reproduced in Figure 1. The typical condition of measurement is given in the caption of Figure 1.

The line width was determined under the assumption that the line shape is Lorentzian.

Measurement of Viscosity. Tetraalkylgermanes were dissolved in $CHCl_3$, and the rate of the fall of the solution was determined by an Ubbelohde's viscometer. The viscosity was given relative to water. The density of the solution was determined by a picnometer. For the measurement of viscosity and density, a thermostat regulated at a constant temperature (accuracy of ±0.001 °C) was employed.

The radius of alkylgermanes is defined as the sum of the distance between germanium and the hydrogen atom of the terminal methyl group plus the van der Waals radius of a hydrogen atom. The germanium–hydrogen distance was obtained from the structure of the alkylgermanes optimized by molecular mechanics calculations.[1]

Results and Discussion

Relaxation Time. It is usually taken for granted that the quadrupole nuclei relax exclusively via quadrupole pathway, and hence spin–lattice relaxation time and spin–spin relaxation time are essentially identical.[23] Furthermore, the apparent spin–spin relaxation time as determined from the half-width ($T_2(\nu_{1/2}) = 1/\pi\nu_{1/2}$ where $\nu_{1/2}$ is the half-width of the signals) is practically equal to T_2 determined by the standard procedure such as the CPMG method (T_2(CPMG)).

For such small and symmetrical molecules as tetraalkylgermanes, a possibility of contribution of the relaxation pathway other than quadrupole (e.g., spin rotation) cannot a priori be denied. Hence we determined T_1 (T_1(IR)) of alkylgermanes by the inversion–recovery method, $T_2(\nu_{1/2})$ from the half-width method, and T_2(CPMG) by the CPMG method.

The values obtained, i.e., T_1(IR), T_2(CPMG), and $T_2(\nu_{1/2})$, are tabulated in Table I, which clearly indicates for the alkylgermanes investigated, the assumption

$$T_1 = T_2 = 1/\pi\nu_{1/2}$$

is valid within experimental error.

Table I. Values of T_1(IR), T_2(CPMG) and $T_2(\nu_{1/2})$ of Tetraalkylgermanes at 303 K

compd	T_1(IR), ms	T_2(CPMG), ms	$T_2(\nu_{1/2})$, ms
$GeMe_4$	290	270	280
$GeEt_4$	220	200	240
$GePr_4$	100	100	90
$GeBu_4$	80	80	80
113MGC	16	14	14
114MGC	16	15	15
1135MGC	24	24	24

In the case of tetraalkylgermanes where the half-width is in the order of a few hertz, T_2(CPMG) and $T_2(\nu_{1/2})$ are essentially identical. For narrower signals, the uncertainty in $T_2(\nu_{1/2})$ will be larger because the effect of inhomogeneity of the magnetic field will be large.

As expected, the unsymmetrical (and hence associated with a larger electric field gradient) germacyclohexane derivatives showed much shorter relaxation time as compared with that of symmetrical GeR_4.

Relaxation time of GeR_4 decreases as the molecular radius increases. The relation between the relaxation time and the molecular structure will be discussed in the latter section.

Relaxation Mechanism. It is generally accepted that the quadrupole relaxation times, T_1^q and T_2^q, of nuclei with $I > {}^1/_2$ and $\zeta \neq 0$ are related to the reorientational correlation time τ_c at the extreme-narrowing limit as given in eq 1,[24] where e^2Qq/h

$$\pi\Delta\nu_{1/2} = \frac{1}{T_1} = \frac{1}{T_2} = \frac{3\pi^2}{10}\,\frac{2I+3}{I^2(2I-1)}\left(\frac{e^2Qq}{h}\right)^2\left(1+\frac{\zeta^2}{3}\right)\tau_c \qquad (1)$$

is the quadrupole coupling constant and ζ is the asymmetry parameter. The correlation time is usually well represented by an Arrhenius-type equation (eq 2), where τ°_c is a constant, and ΔE

$$\tau_c = \tau^\circ_c \exp(\Delta E/RT) \qquad (2)$$

an activation energy for the reorientation and R the gas constant. If relaxation occurs solely via the quadrupole mechanism, ln $(1/T_1^q)$ and ln $(1/T_2^q)$ are proportional to the reciprocal of the absolute temperature, $1/T$ (K); i.e., the plot of ln $(1/T_1)$ or ln $(1/T_2)$ against $1/T$ (K) should give a straight line with a positive slope.

It has been shown that $1/T_1$ or $1/T_2$ for the symmetrical molecules is proportional to τ_s, where τ_s is a correlation time for the reorientation of solvent molecules or for the translational diffusion of the ions or the correlation time of deformation of the electronic shells by collisions.[25]

It was found that for the relaxation of ^{73}Ge nuclei in $Ge(CH_3)_4$ and $Ge(C_2H_5)_4$, the plot of ln $(1/T_1)$ against $1/T$ gave a straight line with a positive slope.[12] This fact is in agreement with the general assumption that the spin–lattice relaxation is predominantly quadrupole (i.e., $T_1 = T_1^q$) since other possible mechanisms (e.g., spin-rotation) show a reverse temperature dependency as discussed below.

In Figure 2 plots of ln $(1/T_1)$ and ln $(1/T_2)$ for $Ge(CH_3)_4$ and $Ge(C_2H_5)_4$ against $1/T$ are given. Both of the two plots give straight lines with positive slopes which are nearly equal for each compound in the temperature range of +50 to −50 °C. These results indicate that the spin–spin relaxation of ^{73}Ge nuclei in $Ge(CH_3)_4$ and $Ge(C_2H_5)_4$ occurs also solely via the quadrupole mechanism. The relaxation mechanism of ^{73}Ge nuclei in other compounds listed in Table I proved similar to that for the two compounds above.

The possibility of contribution of relaxation other than quadrupole is excluded as discussed below. ^{73}Ge signal strength was not changed by the Overhauser effect within experimental error

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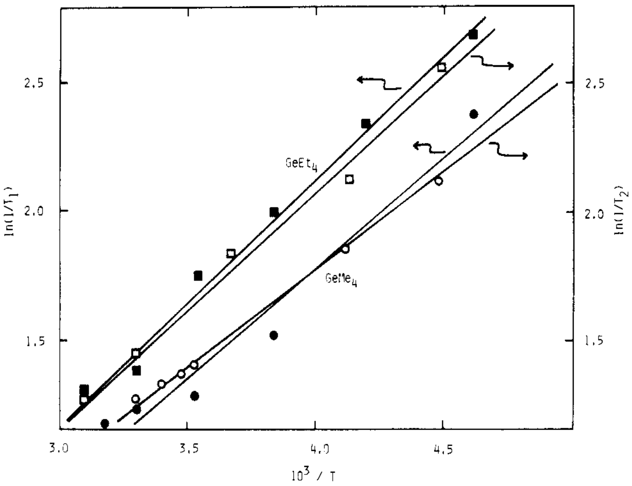

Figure 2. Plots of ln $(1/T_1)$ and ln $(1/T_2)$ vs. $1/T$ in tetraalkylgermanes: (■) ln $(1/T_1)$ of $Ge(C_2H_5)_4$ ($R = 0.997$); (□) ln $(1/T_2)$ of $Ge(C_2H_5)_4$ ($R = 0.914$); (●) ln $(1/T_1)$ of $Ge(CH_3)_4$ ($R = 0.873$); (○) ln $(1/T_2)$ of $Ge(CH_3)_4$ ($R = 0.921$). R is the correlation coefficient.

in the $^{73}Ge\{^1H\}$ experiment, which excludes the dipole–dipole mechanism. The shielding anisotropy mechanism is also excluded because the germanium atom has a tetrahedral environment in the symmetrical GeR_4. The spin-rotation mechanism shows a reverse temperature dependency to that of the quadrupole relaxation. Figure 2 suggests the absence of the spin-rotation mechanism in the temperature range studied. The scalar-coupling mechanism contributes to the spin–spin relaxation mechanism as the temperature is increased; on the other hand, it contributes to the spin–lattice relaxation mechanism in the lower temperature region. The scalar-coupling mechanism is also absent from Figure 2.

Origin of the Quadrupole Relaxation Mechanism in the Symmetric Nuclei. Since tetraalkylgermanes of the type GeR_4 have tetrahedral symmetry, the electric field gradient at the germanium nuclei must be zero, which is expected to make the relaxation time of germanium nuclei infinitely long. The fact is, however, that the relaxation time is shorter than what is expected if relaxation mechanisms other than the quadrupole relaxation mechanism are operative. For instance, in OsO_4 having tetrahedral symmetry, the relaxation time of ^{189}Os ($I = {}^3/_2$) is 230 μs, whereas for ^{187}Os ($I = {}^1/_2$) it is about 5 s.[26] The relaxation of ^{189}Os apparently occurs through the quadrupole relaxation mechanism.

Several explanations have been proposed to account for the relaxation of highly symmetric nuclei by the quadrupole relaxation mechanism. In order to explain splittings due to quadrupole couplings observed for $^{189}OsO_4$ by laser saturation spectroscopy, Hougen and Oka[27] presented an idea that, in many excited vibrational and/or rotational states of a totally symmetric electronic state, the high symmetry is broken and a small electric quadrupole coupling is produced. Brown and Colpa[28] related the results of molecular spectroscopy to those of nuclear spin relaxation and showed that the vibrational distortion of very symmetrical molecules corresponding to certain normal modes can generate the electric field gradient at the center, which does not average to zero over the vibrational motion. Osten and Jameson[29] presented an alternative mechanism, the collisional deformation by long-range van der Waals interactions and by fields induced by octopole moments. They found that the quadrupole relaxation rates calculated by the vibrationally induced electronic field gradients were much too small compared to experiment. The collisional-deformation model is also based on the generation of the instantaneous electronic field gradient, which averages to zero but has a nonvanishing mean square, i.e., $(e^2Qq/h)^2 \neq 0$.

Table II. Values of τ_c and ΔE for Tetraalkylgermanes

compd	$10^{11}\tau_c$(30 °C), s	ΔE, kJ mol^{-1}
$GeMe_4$	0.69	9.6
$GeEt_4$	2.2	11.4
$GePr_4$	4.5	11.9
$GeBu_4$	10.9	13.2

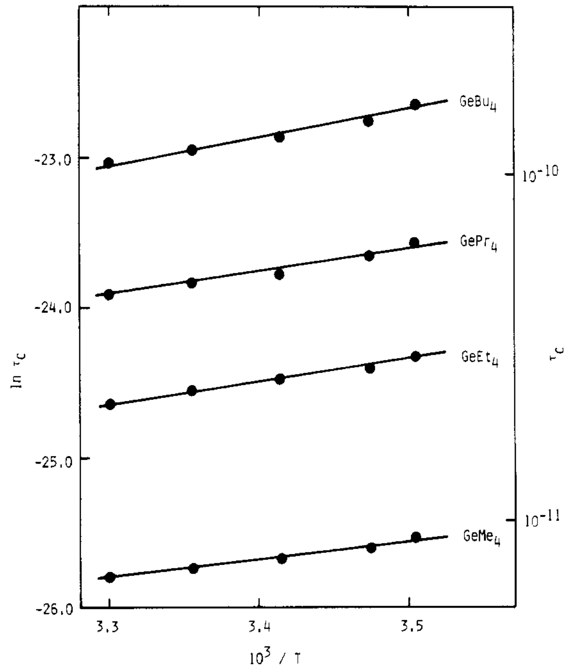

Figure 3. Relationship between the correlation times of alkylgermanes and the reciprocal of the temperatures: $Ge(CH_3)_4$ ($R = 0.996$); $Ge(C_2H_5)_4$ ($R = 0.999$); $Ge(C_3H_7)_4$ ($R = 1.000$); $Ge(C_4H_9)_4$ ($R = 1.000$).

Reorientational Correlation Time. To elucidate the relationships between the molecular motion and the molecular structure or the molecular motion and the relaxation time, the reorientational correlation times were obtained from the viscosity measurements of solutions.

The correlation time, τ_c, in eq 1 is generally used in the rotational diffusion model of a liquid, which is concerned with the reorientational motion of a molecule as being impeled by a viscosity-related frictional force (Stokes–Einstein–Debye model). Gierer and Wirtz have introduced the idea of a microviscosity, f.[30]

The reorientational correlation time τ_c is given by eq 3, where

$$\tau_c = 4\pi r^3 \eta f / 3kT \qquad (3)$$

r is the molecular radius, η the solution viscosity, k the Boltzmann constant, T the absolute temperature, and f a microviscosity, which is defined by

$$f = [6a_s/a + (1 + a_s/a)^{-3}]^{-1} \qquad (4)$$

We determined τ_c at various temperatures from viscosity measurement. In Table II, τ_c at 30 °C and the activation energies are listed.

In Figure 3, plots of ln τ_c of symmetrical tetraalkylgermanes against $1/T$ are given. The plots gave straight lines. With τ_c thus obtained, ΔE was estimated on the basis of eq 2.

The correlation times become longer and the activation energies increase as the molecular radius increases in accordance with eq 2 and 3. In Figure 4, a plot of ln τ_c vs. the molecular radius (r) is given. The correlation coefficient R is unity. In Figure 5 a plot of the activation energy of reorientation ΔE vs. r is given.

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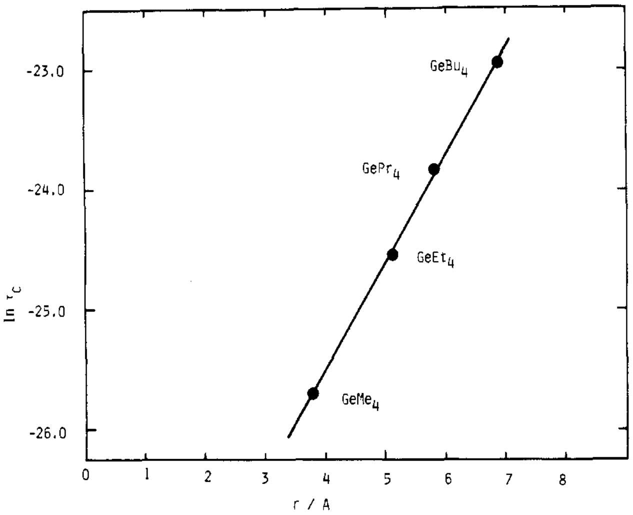

Figure 4. Relationship between the correlation times and the molecular radii of alkylgermanes (R = 1.000).

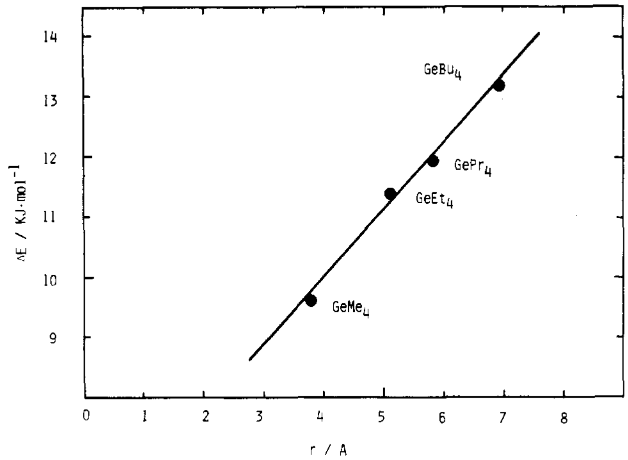

Figure 5. Relationship between the activation energies and the molecular radii of alkylgermanes (R = 0.996).

The linearity is also excellent. As T_1 decreases, τ_c proportionally increases.

The correlation time of $Ge(CH_3)_4$ was found to be 6.9×10^{-12} s. For the correlation time of a molecule of this size, the value we obtained seems reasonable since, for instance, the correlation times of transition metals in aqueous tetrahedral oxo anions MO_4^{x-} (M = ^{51}V, ^{53}Cr, ^{97}Mo, etc.; x = 1–3) obtained by viscosity measurements and eq 3 were in the range (0.5–1.5) $\times 10^{-11}$ s.[31]

Sekatsis et al. determined, however, the correlation time of $Ge(CH_3)_4$ in $CDCl_3$ at 23 °C as 0.5×10^{-12} s from the dipole–dipole relaxation of the methyl group by assuming the complete reorientation time of the $Ge(CH_3)_4$ molecule was longer than that of the methyl group by a factor of 9.[11] The assumption used by Sekatsis et al. that the methyl group rotates faster than the $Ge(CH_3)_4$ molecule by a factor of 9 is questionable, which was indicated by the relaxation time of the ^{13}C NMR spectrum of cholesteryl chloride.[32] Thus the Stokes–Einstein–Debye model may be strictly inapplicable to a GeR_4 solution. The two methods give τ_c values different from each other by a factor of 10. Hence, the discrepancy between our τ_c (from the viscosity measurement) and that of Sekatsis (dipole–dipole relaxation) seems to arise from the difference of the method.

The activation energies for reorientation of tetraalkylgermanes are found in the range 9.6–13.2 kJ/mol. The activation energy of reorientation for $Sn(CH_3)_4$ is estimated to be 9.2 kJ/mol from the slope of ln $T_1(^{119}Sn)$ against $1/T$.[4] For CCl_4, the activation energy is 7.6 kJ/mol from the temperature dependency of T_2 of the chlorine nuclei.[33] Furthermore, the activation energy of 13 kJ/mol for rotation of the sulfate ion was obtained from a plot of the correlation time at infinite dilution, $\tau(0)$, against the ratio of viscosity to temperature, (η/T).[34]

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(35) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Chemical Species in Solutions of Sulfur in Liquid Ammonia

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New results are given for absorption and Raman spectra of solutions of sulfur in liquid ammonia. These spectra have been obtained in a wide range of concentrations and temperatures. Our results give evidence that sulfur solubilization in liquid ammonia is in fact a redox dismutation, giving mainly the oxidized species S_4N^- and the reduced species S_6^{2-}, which is in equilibrium with the radical anion $S_3^{\bullet-}$. The identification of these species from absorption and Raman spectra is discussed. The redox dismutation equation is also discussed. It is indicated that the chemical species in these solutions are pH-dependent.

Introduction

It has been known for a long time that sulfur dissolves in liquid ammonia to give very colored solutions.[1] At the beginning of this century, the interpretation[2,3] of these solutions was misled by the identification of tetrasulfur tetranitride, S_4N_4, after addition of silver iodide and evaporation of ammonia. It was not before the mid-1960s that the interpretation of Ruff and Geisel[2,3] was recognized as incorrect by Zipp[4,5] and by Nelson and Lagowski.[6-8]

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