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Exchange reactions between trimethylsilyl azide and hexamethyldigermoxane

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Abstract

Trimethylsilyl azide and hexamethyldigermoxane undergo exchange at room temperature to stoichiometrically yield trimethyl(trimethylsiloxy)germane and trimethylgermyl azide. The rates of this second order reaction have been measured at several temperatures between 21 and 53° C. An Arrhenius plot of this data gives the following activation parameters: $\Delta G^{\ddagger} = 20.8 \pm 1.7$ kcal/mol, $\Delta H^{\ddagger} = 9.0 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -40 \pm 2$ eu. The large negative entropy of activation implies a highly ordered transition state for this reactions.

We would like to report a novel exchange reaction between trimethylsilyl azide and hexamethyldigermoxane. This quantitative reaction proceeds in chloroform at room temperature in the absence of catalysts to yield trimethyl(trimethylsiloxy)germane and trimethylgermyl azide.

$$(CH_3)_3SiN_3 + [(CH_3)_3Ge]_2O \rightarrow (CH_3)_3GeN_3 + (CH_3)_3SiOGe(CH_3)_3$$

On the other hand, no further exchange between trimethyl(trimethylsiloxy)germane and excess trimethylsilyl azide to yield hexamethyldisiloxane and a second equivalent of trimethylgermyl azide occurs. Similar exchange reactions have been carried out between trimethylsilyl azide and hexaethyldigermoxane to give triethyl(trimethylsiloxy)germane and triethylgermyl azide stoichiometrically. Neither hexamethyldisiloxane nor a second equivalent of triethylgermyl azide is formed even in the presence of excess of trimethylsilyl azide. Apparently a germanium oxygen bond in a digermoxane (Ge–O–Ge) is significantly different in chemical reactivity from a germanium oxygen bond in a siloxygermanium compound (Si–O–Ge). Similar selectivity has been observed previously in exchange reactions of n-butyl trimethylsilyl sulfide and hexaethyldigermoxane which give n-butyl triethylgermyl sulfide and triethyl(trimethylsiloxy)germane [1] as well as in the reaction of tris(trimethylsilylamino)-*s*-triazine with hexaethyldigermoxane which gives triethyl(trimethylsiloxy)germane and tris(triethylgermylamino)-*s*-triazine [2]. On the other hand, in the

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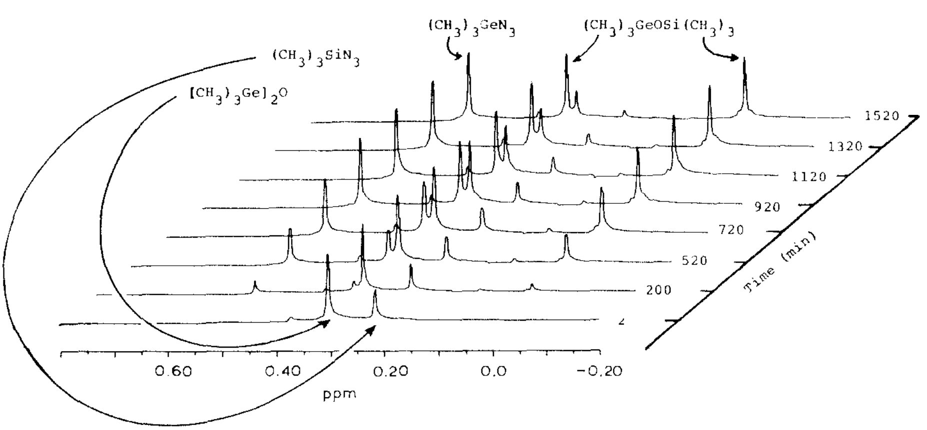
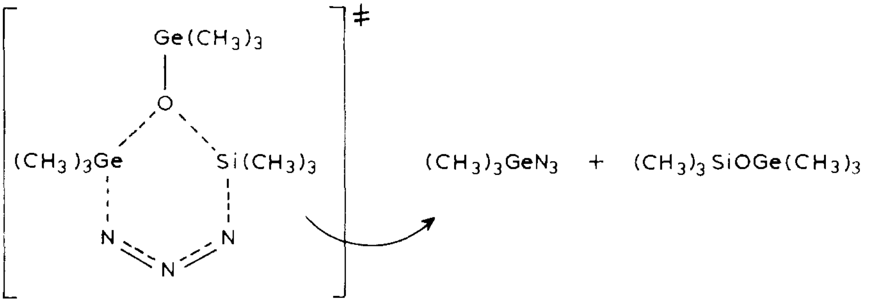


Fig. 1. ^1H NMR kinetics of reaction of trimethylsilyl azide and hexamethyldigermoxane.

exchange reaction between hexamethyldigermoxane and triethylchlorosilane no such selectivity was observed. Hexaethyldisiloxane and two equivalents of trimethylchlorogermane were the only products obtained [3]. For comparison, no exchange reaction is observed between either trimethylsilyl azide and hexamethylcyclotrisiloxane [4,5] or triethylsilyl azide and hexamethyldisiloxane [6].

We have followed the rate of this unusual exchange reaction between trimethylsilyl azide and hexamethyldigermoxane by ^1H NMR (see Fig. 1) at various temperatures between 21 and 53° C. The reaction is found to be second order, (first order in each reactant). The activation parameters for this reaction at 22° C have been determined to be: $\Delta G^{\ddagger} = 20.8 \pm 1.7$ kcal/mol, $\Delta H^{\ddagger} = 9.0 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -40 \pm 2$ eu. The large negative entropy of activation which must be associated with a highly order transition state is particularly significant. Negative entropies of activation of this magnitude are frequently found for Diels–Alder [7] and [2 + 3]-cycloaddition reactions [8]. For this reason, we are tempted to propose a cyclic six-membered transition state for this reaction as outlined below.



Further work on this reaction and other exchange reactions between silicon and germanium is under active investigation in our laboratories.

Experimental

All reagents and solvents were dried over activated 4 Å molecular sieves prior to use. Five millimeter NMR tubes were dried overnight in an oven at 120° C, purged

Table 1

Rate constants [a] for the reaction of trimethylsilyl azide and hexamethyldigermoxane

Temperature (° C)	k (l/mol min) ($\times 10^{-3}$)
21	4.0 ± 0.8
30	6.3 ± 0.9
38	8.2 ± 1.2
48	14 ± 0.2
53	20 ± 0.3

[a] Rate constant errors are based on an estimate of a ±5% error in the concentration of trimethylsilyl azide.

with Argon, cooled and capped with a rubber septum.

The kinetics were run on an IBM-Bruker FT-WP 270 MHz-SY spectrometer equipped with a variable temperature accessory. The temperature in the probe was controlled by balancing a flow of cold nitrogen gas with a heater. The temperature was measured by a thermocouple. The temperature was calibrated by measuring the proton chemical shift difference between the CH and OH groups of ethylene glycol. Temperatures were reproducible to within ±0.5° C and the accuracy was ±1° C. IR spectra were run on a Perkin-Elmer PE-281 spectrometer. These were taken on neat oils between NaCl plates.

A typical procedure is as follows. A sample of 15.2 μl of hexamethyldigermoxane and 0.58 ml of chloroform-d_1 was thermostated in the NMR probe at the desired temperature for 10 min. At this time, 10 μl of trimethylsilyl azide (trimethylsilyl azide = hexamethyldigermoxane = 0.13 mol/l) was added to the NMR tube as quickly as possible. FIDs were collected every 40 min from this time. Fourier transform of these FIDs permits integration of the concentrations of the starting materials and products for each series of spectra. A linear relationship exists between 1/trimethylsilyl azide and reaction time as well as between 1/hexamethyldigermoxane and reaction time. The rate constants were obtained by a least-squares method (see Table 1). An Arrhenius plot gave the activation parameters reported in the text.

Trimethylsilyl azide was obtained from Petrarch Systems Inc.

Trimethylgermyl azide had properties in complete agreement with literature values [9]. ^{1}H NMR δ: 0.54 (s,9H). ^{13}C NMR δ: 0.21. IR μ: 2100 cm^{-1}.

Triethylgermyl azide had properties in agreement with literature values [10]. ^{1}H NMR δ: 1.10 (br.m,15H). ^{13}C NMR δ: 7.77, 6.95. IR ν: 2100 cm^{-1}.

Hexamethyldigermoxane was prepared from tetramethylgermane. Tetramethylgermane was converted to trimethylchlorogermane by treatment with acetyl chloride and aluminum chloride [11]. Hydrolysis of trimethylchlorogermane gave hexamethyldigermoxane [12,13]. ^{1}H NMR δ: 0.335 (s,18H). ^{13}C NMR δ: 3.47.

Hexaethyldigermoxane was prepared in a similar manner from tetraethylgermane [14]. ^{1}H NMR δ: 1.02 (br.m). ^{13}C NMR δ: 8.91, 8.09.

Trimethyl(trimethylsiloxy)germane had properties identical with literature values [15]. ^{1}H NMR δ: 0.36 (s,9H), 0.03 (s,9H). ^{13}C NMR δ: 3.00, 2.69. ^{29}Si NMR δ: 8.61.

Triethyl(trimethylsiloxy)germane had properties identical with literature values [16,17]. ^{1}H NMR δ: 0.02 (s,9H), 1.00 (m,15H). ^{13}C NMR δ: 8.50, 7.80, 2.76. ^{29}Si NMR δ: 7.06.

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