Organometallics **1994,** *13,* 404-406

Laser Flash Photolysis of Polygermanes. Generation of Germylenes and Polygermyl Radicals

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Received June 17, 1993[⊗]

Summary: Laser flash photolysis of polygermanes involves both Ge–Ge bond homolysis to give polygermyl radicals and extrusion of germylenes.

The chemistry of polysilanes has been the subject of considerable interest in recent years because of their unique physical and chemical properties arising from electronic delocalization in the Si–Si σ framework.[1-6] However, there have been few reports on photochemical studies of the germanium analogs.[7,8] We describe herein the first laser flash photolysis studies on the high-molecular-weight germanium compounds $(Et_2Ge)_n$ ($\bar{M}_w = 3.4 \times 10^3$, **1**), $(Bu_2Ge)_n$ ($\bar{M}_w = 4.1 \times 10^3$, **2**), $(Hex_2Ge)_n$ ($\bar{M}_w = 11.5 \times 10^3$, **3**), and $(PhMeGe)_n$ ($\bar{M}_w = 5.0 \times 10^3$, **4**).[9] Photolysis of polygermanes involves both germanium–germanium bond homolysis to give polygermyl radicals and extrusion of germylenes.

Laser flash photolysis[10] ($\lambda = 266$ nm, pulse width 5 ns, power 10 mJ/pulse) of **1**–**4** (ca. 10^{-3} M) in cyclohexane at 293 K gave two well-separated transient absorption bands at 350–370 and 430–460 nm, as shown in Figure 1. The transient peak at longer wavelengths (430–460 nm) may be assigned to that of a germylene from comparison of its spectral characteristics with those of similar germylenes reported.[11-17] These transient peaks from **1**–**4** in cyclohexane decayed with second-order kinetics, suggesting the formation of digermenes.[12] This is substantiated further by quenching experiments with the germylene trapping agents 2,3-dimethylbutadiene[18] and carbon tetrachloride.[17,19] The transients from **1**–**4** in cyclohexane in the presence of a large excess of the diene decayed with pseudo-first-order kinetics ($k = (0.31–2.2) \times 10^8\ s^{-1}\ M^{-1}$). Addition of carbon tetrachloride also quenched the transient absorptions ($k = (0.16–1.3) \times 10^9\ s^{-1}\ M^{-1}$). The quenching rate constants for the germylenes observed in this study are 1 order of magnitude faster than those of reported phenylated trigermanes.[11] The large value for disappearance of germylenes obtained in this study may be explained by the generation of free germylenes.[20,21] Similar phenomena were also observed in the silicon cases.[22,23] The experimentally determined decay constants of these transient species are summarized in Table 1.

On the other hand, the transient peaks at shorter wavelengths (350–370 nm) may be assigned to polygermyl radicals by comparison of their spectral characteristics with those reported for similar germyl radicals.[11,14,15,24] These transients from **1**–**4** in cyclohexane decayed with second-order kinetics, suggesting the dimerization or disproportionation of polygermyl radicals. The assignment as a polygermyl radical was confirmed by quenching experiments using 2,3-dimethylbutadiene and carbon tetrachloride as germyl radical quenchers. The rate constants for quenching of these transient species are shown in Table 1. The values ($k = (4.0–11) \times 10^8\ s^{-1}\ M^{-1}$ for CCl_4 and $(2.5–34) \times 10^7\ s^{-1}\ M^{-1}$ for diene) as shown in Table 1 are consistent with those reported for germyl radicals within error limits (10–20%). There is a possibility that the transient band near 360 nm is due to a digermene

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1993.

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(9) All polygermanes were prepared by the reaction of sodium dispersions with dichlorogermanes: $(Et_2Ge)_n$, $\bar{M}_w = 3.4 \times 10^3$, $\bar{M}_n = 2.8 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.2$, λ_{max} 303 nm; $(Bu_2Ge)_n$, $\bar{M}_w = 4.1 \times 10^3$, $\bar{M}_n = 3.1 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.3$, λ_{max} 320 nm; $(Hex_2Ge)_n$, $\bar{M}_w = 11.5 \times 10^3$, $\bar{M}_n = 7.8 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.5$, λ_{max} 325 nm; $(PhMeGe)_n$, $\bar{M}_w = 5.0 \times 10^3$, $\bar{M}_n = 3.6 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.4$, λ_{max} 327 nm. Molecular weights and distributions were determined by GPC analysis using ASI ultragel columns and are relative to polystyrene. The wavelengths of λ_{max} for polygermanes used in this study are considerably shorter than those reported in the literature for polygermanes.[6-8] This may be a molecular weight effect, since the molecular weights of the materials are relatively low. The relationship between the values of λ_{max} and molecular weights of polygermanes will be discussed elsewhere.

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(21) Kinetic data as shown in Table 1 are not always explained by the generation of free germylenes. There is a possibility that the transient bands are due to germyl-substituted germylenes, as shown in silicon cases.[6]

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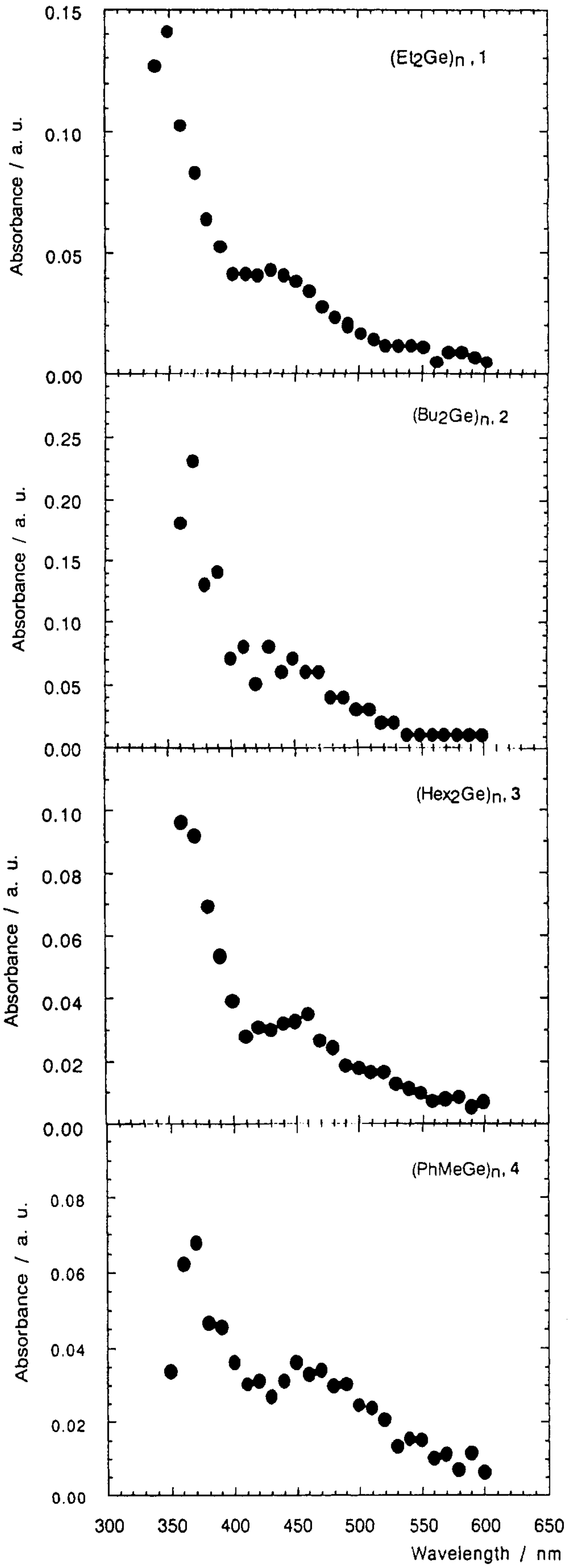


Figure 1. Transient absorption spectra at 200 ns after photoexcitation of 1-4 (10^{-3} M) in degassed cyclohexane solution.

Table 1. Rate Constants for Disappearance of the Transients in the Photolysis of 1-4 in Cyclohexane at 293 K

			rate constant (s^{-1} M^{-1})	
polygermane	λ_{max} (nm)	k/ϵ (cm s^{-1})[a]	CCl_4	diene
$(Et_2Ge)_n$ (**1**)	430	1.1×10^6 (at 460 nm)	1.0×10^9	8.4×10^7
	350	1.8×10^5 (at 370 nm)	7.7×10^8	8.3×10^7
$(Bu_2Ge)_n$ (**2**)	450	2.4×10^5 (at 450 nm)	9.2×10^8	3.1×10^7
	370	5.1×10^5 (at 370 nm)	1.1×10^9	2.5×10^7
$(Hex_2Ge)_n$ (**3**)	460	1.5×10^5 (at 450 nm)	1.3×10^9	4.0×10^7
	360	2.3×10^4 (at 360 nm)	9.5×10^8	3.7×10^7
$(PhMeGe)_n$ (**4**)	440	4.1×10^5 (at 450 nm)	1.6×10^8	2.2×10^8
	360	3.1×10^5 (at 370 nm)	4.0×10^8	3.4×10^8

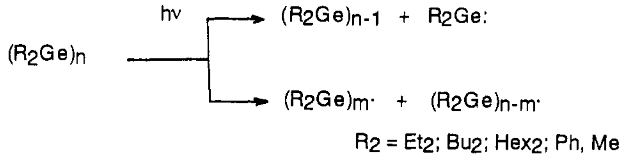
[a] k is the rate coefficient of second-order decay, and ϵ is the molar extinction coefficient.

Table 2. Products and Yields from 254-nm Photolysis of High-Molecular-Weight Polygermanes in the Presence of Carbon Tetrachloride in Cyclohexane[a]

		photoproducts (yield (%))[c]	
polygermane	conversn (%)[b]	$R^1R^2GeCl_2$	$(CCl_3)_2$
$(Et_2Ge)_n$	63.0	23.0	46.0
$(Bu_2Ge)_n$	100	80.0	46.0
$(Hex_2Ge)_n$	100	84.0	37.0
$(PhMeGe)_n$	81.0	46.0	36.0

[a] Photolyses were carried out with a 110-W low-pressure Hg arc lamp for 30 min to 1 h at room temperature. [b] Polygermanes used in this study show a monomodal molecular weight distribution. Conversion yields were estimated by the decrease of initial GPC peak areas after irradiation. [c] Yields of photoproducts were based on 1-4 consumed. Error limits were estimated to be ca. 10%.

Scheme 1



caused by dimerization of germylenes.[12] However, this possibility can be ruled out, because the transients at the shorter wavelengths appear immediately after pulsing 1-4 and do not "grow in" in a diffusive process.

Along with laser flash photolysis, product studies were carried out by photolyzing 1-4 (ca. 5.0×10^{-4} M) in cyclohexane with a 110-W low-pressure Hg arc lamp at room temperature for 0.5-1 h under argon. Upon irradiation of polygermanes 1-4 spectral bleaching is caused by chain scission, which produces lower molecular weight chain fragments. To trap possible reactive intermediates, cyclohexane solutions of 1-4 containing carbon tetrachloride were similarly irradiated. Dichlorogermanes and hexachloroethane were obtained as the main products. The presence of dichlorogermane seems to indicate the intermediacy of germylenes. Thus, the formation of dichlorogermanes may result by stepwise chlorine abstraction from carbon tetrachloride by germylene, as shown in the silicon cases.[25,26] The presence of hexachloroethane is consistent with the intermediacy of polygermyl radicals generated by germanium-germanium bond homolysis as well as germylenes. Photogenerated polygermyl radicals abstract a chlorine atom from carbon tetrachloride to give polygermyl chlorides and trichloromethyl radical. The trichloromethyl radical dimerizes to form hexachloroet-

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(26) The formation of dichlorogermanes may also result from the thermal decomposition of (trichloromethyl)chlorogermanes, which are produced by insertion of germylenes into the C-Cl bond of carbon tetrachloride.[17,19]

hane.[27] The formation of polygermyl chlorides could not be detected. The photochemical results are summarized in Table 2.

Photochemically generated germylenes from **1**–**3** are not trapped effectively by 2,3-dimethylbutadiene, but that from **4** reacts with the diene to give the corresponding germacyclopentene in fair yield (40.5%).[28]

In view of these experimental results, two possible reactions (Ge–Ge bond homolysis and extrusion of germylenes), shown in Scheme 1, are considered most likely to occur in the photolysis of polygermane high polymers.

Acknowledgment. This research was partly supported by the Ministry of Education, Science and Culture (Grant-in-Aid for Scientific Research No. 05236233).

OM930409F

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(27) Photolysis of a cyclohexane solution of carbon tetrachloride gave a small amount of hexachloroethane.

(28) Thermally generated germylenes effectively react with 2,3-dimethylbutadiene to form (2 + 4) π adducts.[18] On the other hand, photochemically generated germylenes are known to react with the butadiene to give the corresponding adducts.[12-15] 1-Germacyclopentenes easily decompose to give polymers under photochemical conditions.