COMMUNICATION

PHOTOCHEMISTRY OF PHENYL-SUBSTITUTED DIGERMANOXANE. FIRST DIRECT OBSERVATION OF GERMOXY RADICALS PROBED BY LASER FLASH PHOTOLYSIS

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Abstract—Laser flash photolysis of the phenyl-substituted digermanoxanes $(Ph_nMe_{3-n}Ge)_2O$ ($n = 1$–3) results in Ge—O bond homolysis to give germyl radicals and germoxy radicals.

The chemistry of polysiloxanes and polygermanoxanes has recently become of interest because of their importance as electric conductors, photoresistors, liquid crystals and new materials.[1,2] However, the study of polygermanoxanes is very much limited compared with that of polysiloxanes. Herein we describe the first laser flash photolysis studies on aryl-substituted digermanoxanes, $(Ph_nMe_{3-n}Ge)_2O$ (1–3, $n = 1$–3, respectively). The photolysis of phenylated digermanoxanes causes germanium–oxygen bond homolysis to give germyl radicals and germoxy radicals.

Laser flash photolysis ($\lambda = 266$ nm, pulse width 5 ns, power 10 mJ pulse^{-1})[3] of 1–3 (10^{-3} M) in cyclohexane at 293 K gave a transient absorption around 360 nm for 1, and two separated absorptions at both *ca* 320–330 nm and 360 nm for 2 and 3, as shown in Fig. 1.[4,5] Careful examination of the transient peak of 1 shows that this is composed of two components ($\lambda_{max} = ca$ 320 and 360 nm). The transient peak at *ca* 320 nm arising from 1 cannot be observed apparently because of its much smaller molar coefficient than that of the other transient peak at $\lambda_{max} = 360$ nm.[6]

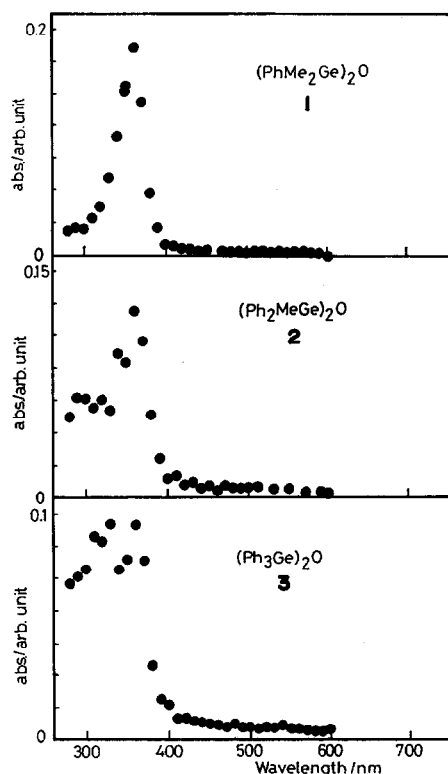Fig. 1. Transient absorption at 200 ns after photo-excitation of $(Ph_nMe_{3-n}Ge)_2O$ (1–3, $n = 1$–3, respectively) in the degassed cyclohexane solution at 293 K.

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Table 1. Rate constants for the disappearance of the transients produced by photolysis of the
germanoxanes in cyclohexane at 293 K

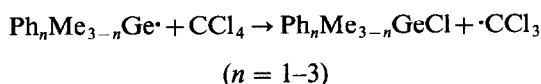|			Rate constant $(M^{-1}\,s^{-1})$		
Compound	λ_{max} (nm)	k/ε $(s^{-1}\,cm)^a$	O_2	CCl_4	Diene
$(PhMe_2Ge)_2O$	360 nm	6.5×10^{6b}	2.3×10^9	Not quenched	2.0×10^9
(1)	320 nm (s)	9.1×10^{6c}	2.0×10^9	1.1×10^8	—^{d}
$(Ph_2MeGe)_2O$	360 nm	1.3×10^{7b}	2.2×10^9	Not quenched	1.4×10^9
(2)	320 nm (s)	8.2×10^{6c}	1.2×10^9	2.0×10^8	—^{d}
$(Ph_3Ge)_2O$	360 nm	2.5×10^{7b}	2.6×10^9	Not quenched	2.0×10^9
(3)	330 nm	7.3×10^{6c}	1.1×10^9	1.2×10^8	—^{d}

$^a k$ is the rate constant of second-order decay and ε is the corresponding molar extinction
coefficient.

^{b} At 370 nm.

^{c} At 330 nm.

^{d} The absorption is too weak to determine the rate constant.

The transient peaks at shorter wavelength are reasonably assigned to those of the aryl-substituted germyl radicals, $Ph_nMe_{3-n}Ge\cdot$ ($n = 1$–3), from comparison of spectral characteristics with those of the germyl radicals reported.[4–7] The transient from 1–3 in cyclohexane decayed with second-order kinetics, suggesting the dimerization of germyl radicals to give digermenes. The experimentally determined decay constants of these transients are summarized in Table 1. The assignment of the shorter wavelength transient is futher substantiated by quenching experiments with carbon tetrachloride, oxygen and 2,3-dimethyl-1,3-butadiene. Addition of carbon tetrachloride, an effective radical scavenger,[8] quenched the transient absorption as shown in Table 1.

$$Ph_nMe_{3-n}Ge\cdot + CCl_4 \rightarrow Ph_nMe_{3-n}GeCl + \cdot CCl_3$$

$$(n = 1\text{–}3)$$

The quenching rate constants observed agreed with the values reported for the germyl radicals.[4–7] Similarly, oxygen quenched the shorter wavelength very rapidly, as shown in Table 1. The laser flash photolysis of 1–3 in cyclohexane containing oxygen was also performed. The transients at shorter wavelength disappeared, resulting in the build-up of transient peaks at the longer wavelength.

On the other hand, the transient at the longer wavelength in Table 1 may be assigned to that of a germoxy radical by comparing its spectral properties with that generated by laser flash photolysis of germyl-t-butylperoxide $(R_3GeOOBu^t)$ and 1–3 in cyclohexane containing oxygen. The photolysis of germyl-t-butylperoxides is well known to give germoxy and t-butoxy radicals.[9]

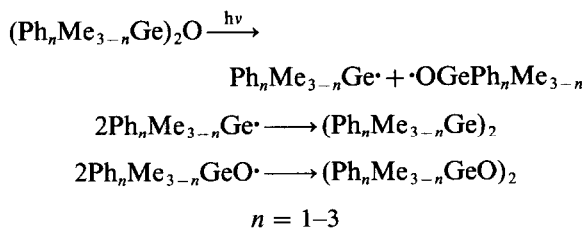$$R_3GeOOBu^t \xrightarrow{hv} R_3GeO\cdot + \cdot OBu^t$$
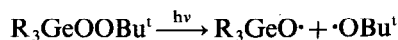
These transients arising from 1–3 in cyclohexane

decayed with second-order kinetics, suggesting the dimerization of germoxy radicals to give digermyl peroxides. The transient from 1–3 in cyclohexane in the presence of a large excess of 2,3-dimethyl-1,3-butadiene and oxygen decayed with pseudo first-order kinetics, and the rate constants obtained are shown in Table 1.

The values of k/ε in Table 1 increase in the order: $Ph_3Ge\cdot < Ph_2MeGe\cdot < PhMe_2Ge\cdot$ for the phenylated germyl radicals, and $PhMe_2GeO\cdot < Ph_2MeGeO\cdot < Ph_3GeO\cdot$ for the phenylated germoxy radicals, respectively. The trend for the germyl radicals may reflect the steric environments around the germanium atom. On the other hand, the trend for the germoxy radicals may be explained by the electronic effect of triorganogermyl groups on the oxygen atom due to the longer Ge—O bond length.

Along with the laser flash photolysis experiments, product studies were carried out by photolysing 1–3 (0.04 M) in cyclohexane with a 110 W low-pressure mercury arc lamp (spiral type) at room temperature for 8–10 h under argon. Unidentified, high molecular weight compounds containing germanium (mol. wt = ca 4000) were formed.[10] The cyclohexane solution of 1–3 containing CCl_4 was similarly irradiated for 1 h to give the corresponding chlorogermanes in unexpectedly high yields (168, 200 and 185% for 1, 2 and 3, respectively).

$$(Ph_nMe_{3-n}Ge)_2O \xrightarrow{hv}$$

$$Ph_nMe_{3-n}Ge\cdot + \cdot OGePh_nMe_{3-n}$$

$$2Ph_nMe_{3-n}Ge\cdot \longrightarrow (Ph_nMe_{3-n}Ge)_2$$

$$2Ph_nMe_{3-n}GeO\cdot \longrightarrow (Ph_nMe_{3-n}GeO)_2$$

$$n = 1\text{–}3$$

Scheme 1.

These results are best rationalized by a homolytic scission of the germanium–oxygen bonds of the digermanoxanes **1–3**, as described in Scheme 1. Judging from the yields of the chlorogermanes produced by the photolysis of digermanoxanes **1–3** in cyclohexane containing CCl_4, germyl radicals, which abstract chlorine atoms from CCl_4, may be effectively formed by the photolysis of digermyl-peroxides.

The bathochromic shift of the observed germoxy radicals relative to that of the corresponding carbon analogue, such as the butoxy radical ($\lambda_{max} = 320$ nm), may be explained by a contribution in part by the Ge=O resonance structure as follows:
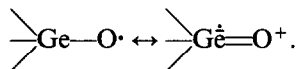
$$\text{>Ge--O}\cdot \leftrightarrow \text{>G}\overset{\cdot}{\text{e}}\text{=O}^+.$$

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