

Chlorinative Cleavage of Digermoxanes Initiated by Photo-induced Electron Transfer

Kunio Mochida,* Kakumasa Takekuma, Hideaki Watanabe, and Shigeo Murata[†]

Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171

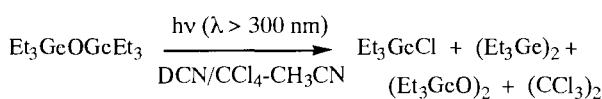
[†]National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305

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Irradiation of digermoxanes ($R_3GeOGer_3$) in CCl_4 - CH_3CN in the presence of 1,2-dicyanonaphthalene (DCN) afforded chlorogermandes, digermyperoxides, and hexachloroethane. Fluorescence of DCN was quenched by $R_3GeOGer_3$ with a rate of $10^9 M^{-1}s^{-1}$ order. A mechanism of free-radical chlorination involving $R_3GeOGer_3$ cation radicals is proposed.

Organometallic compounds containing group 14 element-group 14 element and group 14 element-carbon bonds, which have rather low ionization potentials, are excellent electron donors.¹ An electron-transfer reaction of the group 14 element catenates and tetraalkyl group 14 element compounds in the presence of an electron acceptor has been amply investigated.²⁻¹³ During the course of our study on an electron-transfer reaction of organogermanium compounds,^{14,15} we have found that an electron of digermoxanes ($R_3GeOGer_3$) can be donated to certain π acceptors. For example, $R_3GeOGer_3$ forms charge-transfer complexes with tetracyanoethylene in dichloromethane, followed by formation of organogermyl cyanides.¹⁶ In this paper, we describe the first chlorinative cleavage of the germanium-oxygen bonds of $R_3GeOGer_3$ initiated by photo-induced electron transfer.

Irradiation of hexaethyldigermoxane ($Et_3GeOGerEt_3$, $\lambda_{max} < 200$ nm) in a mixed solvent of carbon tetrachloride (CCl_4) and acetonitrile (CH_3CN) in the presence of 1,2-dicyanonaphthalene (DCN) for 2 h with a high-pressure Hg arc lamp resulted in the formation of triethylchlorogermande (Et_3GeCl), hexaethyldigermyperoxide ($Et_3GeOOGeEt_3$), hexaethylgermane ($Et_3Ge-GerEt_3$), and hexachloroethane. All photoproducts were characterized by NMR and MS spectra in comparison with those of authentic samples.



The reaction did not occur without DCN under the conditions and it is clear that DCN should be excited first by light of wavelength longer than 300 nm. The results of photo-induced reactions of several $R_3GeOGer_3$ are summarized in Table 1.

As shown in Table 1, hexa-n-propyl- and hexa-n-butyl-digermoxanes ($R_3GeOGer_3$, $R_3 = n-Pr_3$ and $n-Bu_3$) also underwent photo-induced chlorinative cleavage to give mainly the corresponding R_3GeCl on irradiation in CCl_4 - CH_3CN in the presence of DCN. Reaction of hexamethyl- and 1,2-dimethyl-1,1,2,2-tetraphenyl-digermoxanes ($R_3GeOGer_3$, $R_3 = Me_3$ and Ph_2Me) did not occur. Among the above digermoxanes, the reactivity decreased in the order: $R_3 = Et_3 > n-Pr_3 > n-Bu_3 > Me_3, Ph_2Me$.

To elucidate the mechanism of the photo-induced electron transfer of $R_3GeOGer_3$ in the presence of DCN, we carried out a

Table 1. Electron-transfer Induced Chlorinative Ge-O Bond Cleavage of Digermoxanes in CCl_4 / CH_3CN ^a

Digermoxane	Conv./%	Products, Yield/%			
		R_3GeCl	$(R_3Ge)_2$	$(R_3GeO)_2$	$(CCl_3)_2$
$(Me_3Ge)_2O$	0				
$(Et_3Ge)_2O$	96	52	4	5	26
$(n-Pr_3Ge)_2O$	53	44	0	5	19
$(n-Bu_3Ge)_2O$	30	47	11	7	21
$(Ph_2MeGe)_2O$	0				

^a The Photochemical reaction was carried out using a mixture of $(R_3Ge)_2O$ (60 mmol) and DCN (6 mmol) in a mixed solvent of CCl_4 (600 mmol)- CH_3CN (2 cm³) at room temperature for 2 h with a high-pressure Hg arc lamp and the yield based on the starting $(R_3Ge)_2O$ was determined by GC using internal calibration standards.

quenching experiment of the fluorescence of DCN and laser flash photolysis.

A CH_3CN solution of DCN was excited at 440 nm and the emission band (330-500 nm, $\lambda_{max} = 380$ nm) was quenched with $Et_3GeOGerEt_3$ ((0.95-10.13) $\times 10^{-3}$ M) to yield a good linear Stern-Volmer plot with $k_q\tau = 1.82 \times 10^2 M^{-1}$ ($r = 0.985$). From the value of τ (8.40 ns) for DCN, k_q is calculated to be $2.17 \times 10^9 M^{-1}s^{-1}$. Quenching rate constants of DCN fluorescence with $R_3GeOGer_3$ depend on the substituent on the germanium as shown in Table 2. Thus, the quenching rate decreased in the

Table 2. Ionization Potentials and DCN Fluorescence Quenching of Digermoxanes

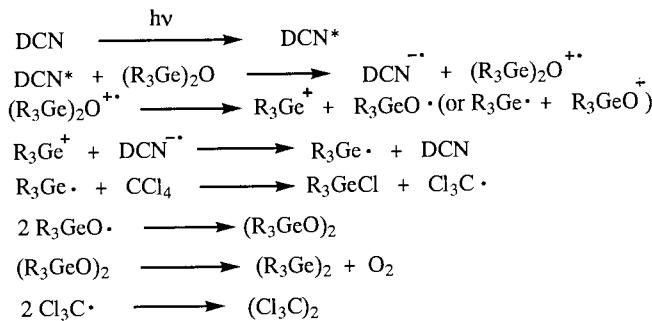
Digermoxane	IP/eV ^a	$k_q/M^{-1}s^{-1}$
$(Me_3Ge)_2O$	9.15	3.91×10^7
$(Et_3Ge)_2O$	8.50	2.17×10^9
$(n-Pr_3Ge)_2O$	-	1.46×10^9
$(Ph_2MeGe)_2O$	9.10	9.53×10^7

^a He I UPS

order: $R_3 = Et_3 > n-Pr_3 > Me_3 > Ph_2Me$. Similar trends are roughly observed in the ionization potentials (IP's).¹⁷ These results accord with the reaction sequence shown in Table 1.

The DCN anion radical¹⁸ was also detected by means of laser flash photolysis ($\lambda = 355$ nm), but failure to detect $R_3GeOGer_3$ cation radicals is attributed to their instability.

From these results, we propose the following scheme as a possible reaction pathway.



Scheme 1.

At first, electron transfer from $\text{R}_3\text{GeOGeR}_3$ to the singlet excited state of DCN (DCN^*) generates the geminate radical ions composed of the DCN anion radical (DCN^-) and the $\text{R}_3\text{GeOGeR}_3$ cation radical ($\text{R}_3\text{GeOGeR}_3^+$). The $\text{R}_3\text{GeOGeR}_3^+$ undergoes spontaneous scission to $\text{R}_3\text{GeO} \cdot$ and R_3Ge^+ . This scission is supported by MS spectra of $\text{R}_3\text{GeOGeR}_3$. The R_3Ge^+ is reduced by DCN^- to afford $\text{R}_3\text{Ge} \cdot$ together with DCN. The $\text{R}_3\text{Ge} \cdot$ thus formed abstracts a chlorine atom from CCl_4 to give R_3GeCl and CCl_3 .¹⁹ It has been reported that the $\text{R}_3\text{GeO} \cdot$ does not abstract a chlorine atom from CCl_4 , but dimerizes to give $(\text{R}_3\text{GeO})_2$.²⁰ The $(\text{R}_3\text{GeO})_2$ cleaves to give $(\text{R}_3\text{Ge})_2$ with extrusion of oxygen.²⁰ Electron transfer from R_3GeGeR_3 formed to DCN^* also generates the radical ion of the DCN^- and the $\text{R}_3\text{GeGeR}_3^+$.²¹ The $\text{R}_3\text{GeGeR}_3^+$ undergoes scission to $\text{R}_3\text{Ge} \cdot$ and R_3Ge^+ . Finally, CCl_3 either adds to DCN or dimerizes.

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