

signment of geometrical proximity of spins in polycrystalline or glassy solids.

Acknowledgment. The authors give special thanks to Deborah Ehler and to the Stable Isotope program at Los Alamos including

the NIH Stable Isotope Resource (RR02231) for the ^{13}C -labeled acetates. This work was performed under the auspices of the U.S. Department of Energy.

Registry No. Zinc acetate, 557-34-6.

Laser Photolysis and CIDEP Studies of the Formation of Phenyl-Substituted Group 4B Element (Silicon, Germanium, and Tin)-Centered Radicals in Direct Photoejection of the Group 4B Element-Centered Anions

Kunio Mochida,*† Masanobu Wakasa,† Yoshio Sakaguchi,‡ and Hisaharu Hayashi*†

Contribution from the Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Tokyo 171, Japan, and The Institute of Physical and Chemical Research, Wako, Saitama 351-01, Japan. Received October 14, 1986

Abstract: Phenyl-substituted group 4B element-centered radicals generated by the direct photoejection from the group 4B element-centered anions were observed by laser photolysis at room temperature. In order to clarify the mechanism of this process, CIDEP study of the photolysis of the group 4B element-centered anions was carried out at 77 and 4.2 K. From the emissive patterns observed for the germyl and stannyl anions after the excitation by a pulse laser, the photoejection reactions were most probably considered to occur from triplet anions.

Organic anions, especially of the group 4B elements (silicon, germanium, and tin) have received considerable interest in synthetic chemistry and reaction mechanisms.¹⁻⁷ Although extensive thermal reactions of the group 4B element-centered anions have been made, there are few reports on photochemical studies of these anions.⁸⁻¹⁰ By near-UV photolysis at 93 K of rigid glasses of triphenylstannyl anions, the triphenylstannyl radical was confirmed to be generated from a stationary ESR measurement.⁸ Upon steady-light illumination of aromatic compounds at room temperature in the presence of the triphenylsilyl and triphenylstannyl anions in tetrahydrofuran (THF), anion radicals of the aromatic compounds were found to be produced.^{9,10} Although it was suggested that one-electron transfer would occur from the silyl and stannyl anions to the aromatic compounds, the resulting silyl and stannyl radicals have not yet been observed directly.

On the other hand, the photoejection process from the organic anions, including the group 4B element-centered anions, has received much attention recently in relation to the intermediates of photostimulated $\text{S}_{\text{RN}}1$ reactions¹¹⁻¹⁵ and ion-pair phenomena.^{16,17} Among them, the key problem in this process is the identification of labile intermediates formed during reaction. The laser-photolysis technique is a good method for direct observation of transient species generated immediately after excitation of the anions. Furthermore, chemically induced dynamic electron polarization (CIDEP) has recently become a powerful tool for investigating fast radical reactions. CIDEP is expected to give us unique information about short-lived radicals and their precursors.

In this paper, we describe the direct observation of phenyl-substituted group 4B element (silicon, germanium, and tin)-centered radicals generated by photoejection of the corresponding anions with the aid of a laser-photolysis measurement at room temperature.¹⁸ Furthermore, CIDEP spectra obtained by the photolysis of these anions at 77 and 4.2 K are discussed.

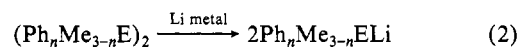
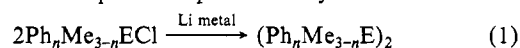
Results and Discussion

Absorption Spectra of Phenyl-Substituted Group 4B Element-Centered Anions. The phenyl-substituted group 4B element-centered anions ($\text{Ph}_n\text{Me}_{3-n}\text{ELi}$: 1-3 for E = Si and $n = 1-3$, 4-6

Table I. Absorption Data of UV Spectra for Phenyl-Substituted Group 4B Element-Centered Anions in THF

compound	λ_{max} (nm) for E =		
	Si	Ge	Sn
PhMe_2ELi	335	290	
Ph_2MeELi	335	310	
Ph_3ELi	335	310	310

for E = Ge and $n = 1-3$, and 7 for E = Sn and $n = 3$, respectively) were prepared from the corresponding chlorides and lithium metal in THF at room temperature quantitatively.



E = Si, Ge, and Sn; $n = 1-3$

The formation of the anions (1-7) from the chlorides and lithium

- (1) Davies, D. D. *Organomet. Chem. Rev., Sect. A* 1970, 6, 283.
- (2) Neuman, W. P. *The Organic Chemistry of Tin*; Wiley: New York, 1970; pp 881-930.
- (3) Lijjten, J. G. A.; van der Kerk, J. M. *The Bond to Carbon*; MacDiamid, A. G., Ed.; Marcel-Dekker: New York, 1968; Chapter 4.
- (4) Coates, A. G.; Green, M. L. H.; Wade, K. *Organometallic Compounds*; Methuen: London, 1967; Vol. 1.
- (5) Fujita, M.; Hiyama, T. *Yuki Gosei Kagaku Kyokaiishi* 1984, 42, 293.
- (6) Lesbre, M.; Mazerolles, P.; Satge, J. *The Organic Compounds of Germanium*; Wiley: New York, 1971; Chapter 10.
- (7) Mochida, K.; Kugita, T. *Nippon Kagaku Kaishi* 1985, 334 and reference cited therein.
- (8) King, B. A.; Bramwell, F. B. *J. Inorg. Nucl. Chem.* 1981, 43, 1479.
- (9) Aruga, T.; Ito, O.; Matsuda, M. *J. Phys. Chem.* 1982, 86, 2950.
- (10) Ito, O.; Aruga, T.; Matsuda, M. *J. Chem. Soc., Faraday Trans.* 1982, 78, 1.
- (11) Ayscough, P. B.; Sargent, F. P.; Wilson, R. *J. Chem. Soc.* 1963, 5418.
- (12) Winkler, H. J. S.; Winkler, H. J. *J. Org. Chem.* 1967, 32, 1695.
- (13) van Tamelen, E. E.; Brauman, J. I.; Ellis, L. E. *J. Am. Chem. Soc.* 1971, 93, 6141.
- (14) Pierini, A. B.; Rossi, R. A. *J. Organomet. Chem.* 1978, 144, C12.
- (15) Fox, H. A. *Chem. Rev.* 1979, 79, 253.
- (16) Wang, H. C.; Lillie, E. D.; Slomkowski, S.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* 1977, 99, 4612.
- (17) Wang, H. C.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* 1978, 100, 6137.
- (18) Preliminary results of this study were reported in: *Chem. Lett.* 1985, 1709.

*Gakushuin University.

†Institute of Physical and Chemical Research.

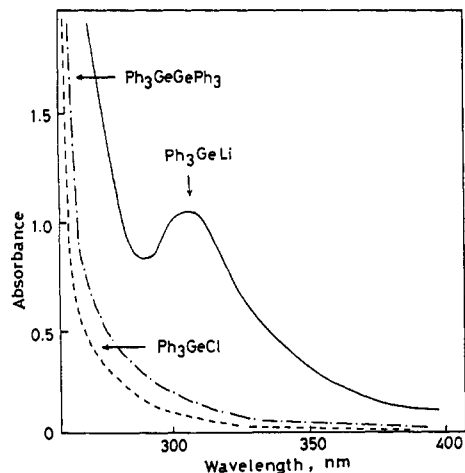


Figure 1. Absorption spectra of Ph_3GeCl (1.8×10^{-3} M), $\text{Ph}_3\text{GeGePh}_3$ (3.3×10^{-4} M), and Ph_3GeLi (4.8×10^{-5} M) in THF at 23 °C. Optical path length is 1 cm.

Table II. Photochemical Reactions of the Anions (1, 5, and 7) at 300 K^a

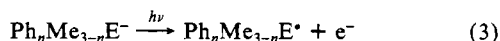
substrate (mmol)	products (mmol) ^b	
	E-H	E-E
PhMe_2SiLi (1) (0.78)	0.54	0.13
Ph_2MeGeLi (5) (0.90)	0.30	0.30
Ph_3SnLi (7) (1.21)	0.52	0.41

^a Reaction carried out for 1 h. ^b Hydrolysis products. Estimated accuracy $\pm 5\%$.

metal can be rationalized by the dissociative electron transfer attachment processes.

All phenyl-substituted group 4B element-centered anions (1–7) were colored reddish brown. As a typical example, the absorption spectrum of Ph_3GeLi (6) is shown in Figure 1 together with those of Ph_3GeCl and $\text{Ph}_3\text{GeGePh}_3$. Each of the anions (1–7) has an absorption peak at 290–335 nm. The wavelengths of the maximum absorption (λ_{max}) observed with the THF solutions containing 1–7 are summarized in Table I. This absorption band can be explained in terms of a transition from a nonbonding orbital of metal (E) to an antibonding orbital of phenyl group which is formed by $p\pi-p\pi$ overlap.¹⁹ As shown in Table I, λ_{max} 's of 1–7 have the following order: $\lambda_{\text{max}}(\text{Si}) > \lambda_{\text{max}}(\text{Ge}) \approx \lambda_{\text{max}}(\text{Sn})$. The decrease of λ_{max} shows the decrease of the conjugation between metal (E) and the phenyl group of the anions. The decrease of the conjugation means an increase of electron localization on E. Thus, the photoejection of the group 4B element-centered anion ($\text{Ph}_n\text{Me}_{3-n}\text{E}^-$) used in this study is considered to occur in the order of $\text{E} = \text{Sn} \approx \text{Ge} > \text{Si}$.

Photochemical Reactions of the Group 4B Element-Centered Anions. The THF solution containing 1, 5, or 7 in a quartz photolysis cell was degassed and then irradiated by a xenon lamp at room temperature for 5–120 min. The reaction products after hydrolysis were analyzed by gas chromatography, liquid chromatography, and GC-mass spectrometry. The main products of this photochemical reaction were found to be the corresponding dimers; disilane for 1, digermane for 5, and distannane for 7, respectively, and hydride. These dimers are considered to be derived from the group 4B element-centered radicals generated by photoejection of 1, 5, and 7, respectively.



Thus, the phenyl-substituted group 4B element-centered radicals are suggested to be generated as shown by reaction 3.

On the other hand, the hydrides are considered to be produced by hydrolysis of unreacted anions. This fact was confirmed by

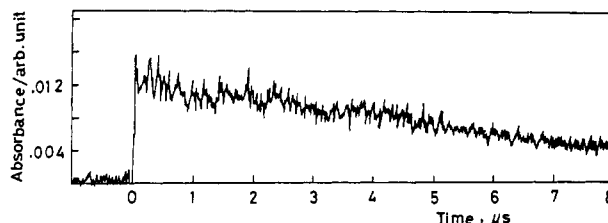


Figure 2. Plots of the absorbance at 330 nm against t observed with the THF solution of Ph_2MeGeLi (5).

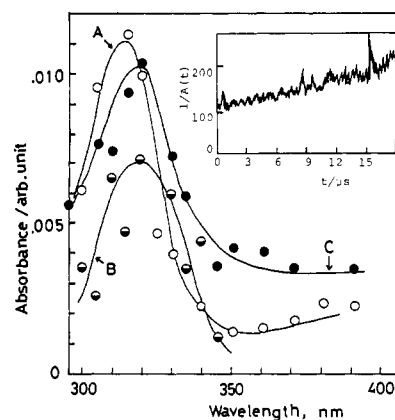


Figure 3. Transient absorption spectra observed 200 ns after excitation of the THF solutions containing (A) 1, (B) 2, and (C) 3, respectively. The concentrations of 1–3 are ca. $1.0\text{--}2.0 \times 10^{-4}$ M. Insert: a second-order plot for decay of the absorption at 320 nm for 1.

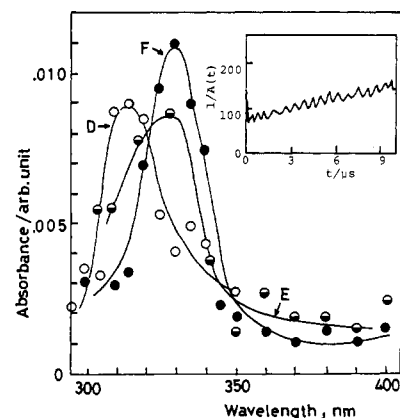


Figure 4. Transient absorption spectra observed 200 ns after excitation of the THF solutions containing (D) 4, (E) 5, and (F) 6, respectively. The concentrations of 4–6 are ca. $1.0\text{--}2.0 \times 10^{-4}$ M. Insert: a second-order plot for decay of the absorption at 330 nm for 5.

the formation of the d_1 hydrides after hydrolysis of the reaction mixture with D_2O . The results of photochemical reactions of 1, 5, and 7 at room temperature for 1 h are listed in Table II. As shown in Table II, the yields of the dimers increased in the order: $\text{Sn} \approx \text{Ge} > \text{Si}$.

Laser-Photolysis Studies of the Group 4B Element-Centered Anions. Nanosecond transient absorption spectra measurements were performed on the degassed solutions containing 1–7 at room temperature using the fourth harmonic pulse of a Nd:YAG laser as an exciting light source.²⁰

The time dependence of absorbance of the transient absorption $A(t)$ was measured with each of the THF solutions containing 1–7. The $A(t)$ curves were measured at the wavelength region of 300–700 nm. Appreciable signals were obtained below 400 nm. The signals show fast rise and following slow decay. The rise time was about 10 ns, which was the time resolution of the

(19) Waack, R.; Doran, M. A. *Chem. Ind. (London)* 1965, 564.

(20) For example: Sakaguchi, Y.; Hayashi, H.; Nagakura, S. *J. Phys. Chem.* 1982, 86, 3177.

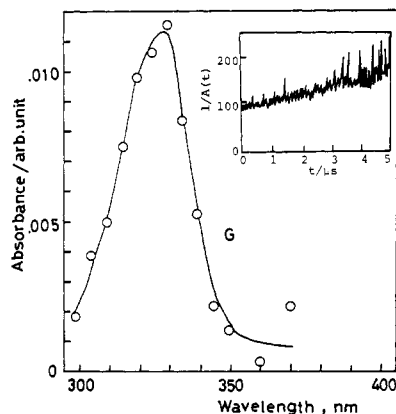


Figure 5. Transient absorption spectrum observed 200 ns after excitation of the THF solution containing (G) **7**. The concentration of **7** is ca. 1.5×10^{-4} M. Insert: a second-order plot for decay of the absorption at 330 nm for **7**.

Table III. Transient Absorption Spectra Data for Phenyl-Substituted Group 4B Element-Centered Anions at 300 K

substrate	λ_{\max} (nm)	k/ϵ (cm s ⁻¹)
PhMe ₂ SiLi (1)	315	1.9×10^6
Ph ₂ MeSiLi (2)	320	1.7×10^6
Ph ₃ SiLi (3)	320	2.1×10^6
PhMe ₂ GeLi (4)	315	1.2×10^7
Ph ₂ MeGeLi (5)	330	9.4×10^6
Ph ₃ GeLi (6)	330	5.2×10^6
Ph ₃ SnLi (7)	330	7.7×10^6

present apparatus. As a typical example, the $A(t)$ curve observed with **5** at 330 nm is shown in Figure 2. In some cases, the signals due to biphenyl anion radical were observed at 400 and 510 nm.²¹

Using the $A(t)$ curves observed at different wavelengths, the time-resolved absorption spectra of **1–7** at the delay time of 200 ns after laser excitation were obtained, and the results are shown by spectra A–G in Figures 3–5. As shown in these figures, we have obtained transient signals below 350 nm for all the THF solutions containing **1–7**. From the plots of $1/A(t)$ against t , the early stages of $A(t)$ curves observed with these anions were proved to decay with second-order kinetics. As typical examples, second-order plots for decay of the absorption band for **1**, **5**, and **7** are inserted in Figures 3–5. The peak positions of spectra A–G and the k/ϵ values at the peak positions were obtained, and the results are shown in Table III. Here k is the rate constant of second-order decay and ϵ is the molar extinction coefficient. Neither the absolute nor the relative value of k can be obtained because no information about ϵ has been given for the group 4B element-centered radicals ($\text{Ph}_n\text{Me}_{3-n}\text{E}^*$).

Spectra A–G can safely be assigned to the phenyl-substituted group 4B element-centered radicals ($\text{Ph}_n\text{Me}_{3-n}\text{E}^*$) generated by the direct photoejection from the anions, **1–7**.



This assignment can be derived for the following reasons. (1) The spectral shapes and peak positions of **3–7**, respectively, agree well with those generated by abstraction of hydrogen of the phenyl-substituted silane, germane, and stannane with *tert*-butoxyl radical.^{22,23} The spectra of PhMe_2Si^* and Ph_2MeSi^* have not yet been reported. However, the spectral shapes and peak positions of spectra A and B resemble those reported for PhH_2Si^* and Ph_2HSi^* .²³ (2) As mentioned above, the dimers were found to be produced upon irradiation of the THF solutions containing **1**, **5**, and **7**. The formation of the dimers is most probably interpreted by the dimerization of $\text{Ph}_n\text{Me}_{3-n}\text{E}^*$ as shown by reaction 4. (3)

The second-order decays observed in the transient absorptions are also in good agreement with the conclusion that the generated transient species are $\text{Ph}_n\text{Me}_{3-n}\text{E}^*$.

To the best of our knowledge, this is the first obvious observation of phenyl-substituted group 4B element-centered radicals generated by the direct photoejection of the corresponding anions.

Since the rise times of spectra A–G were the same as the time resolution of the employed apparatus, the electron ejection processes could not be studied with the present measurement. Therefore, the reaction precursors and reaction rates of the processes could not be investigated at this stage. Measurement with a transient optical absorption with a picosecond laser or a transient ESR technique with a nanosecond laser may be useful for studying these processes. Some of the results obtained in the transient ESR measurement will be discussed later.

The photoejection of the stannyl and germlyl anions occurred easily compared with that of the corresponding silyl anion. The driving force for such photoejection process may be considered to be dependent on the oxidation potentials of these anions.¹² In fact, the oxidation potentials of triphenylstannyl and triphenylgermyl anions are lower than that of the triphenylsilyl anion.²⁴ This trend of the oxidation potentials of the group 4B element-centered anions is almost consistent with that of the absorption bands of these anions.

As shown in reaction 5, an electron is considered to be ejected from the anions. How does the ejected electron behave? There are three places where the electron is going. (1) The ejected electron is solvated with THF. (2) The electron reduces a lithium cation to give a lithium atom. (3) The electron is trapped by other species. The solvated electron in THF has its absorption band at ca. 2100 nm.²⁵ Our apparatus cannot measure such an infrared region. The absorption spectrum of lithium also is not expected to be observed in the wavelength region of 300–700 nm. As mentioned above, the transient absorption spectrum due to biphenyl anion radical was observed in some cases. However, its signal intensity depended upon the preparation processes of samples. Biphenyl was produced as a by-product while the synthesis of phenyl-substituted group 4B element-centered anions could not be eliminated completely.¹³ However, the concentration of biphenyl was so small in the employed solutions that no biphenyl was detected by gas chromatography. Therefore, the ejected electron is considered to be partly trapped by biphenyl, but the places where most of the electron goes are still unclear.

In order to clarify further the photoejection process and the behavior of the ejected electron, both stationary and transient ESR studies were carried out.

ESR Measurement at Room Temperature. At first, stationary ESR signals were measured at room temperature on a THF solution containing **4** in a sealed ESR tube irradiated by a mercury lamp. In this case, only the signals due to biphenyl anion radical were obtained. The signals due to PhMe_2Ge^* were not observed. This fact can be explained by the fast dimerization reaction of this germlyl radical as observed in the transient optical absorption measurement. The signals due to the solvated electron and lithium atom were not observed. The signal intensity of biphenyl anion radical varied from sample to sample depending on the conditions of sample preparation. This is due to the trapping of the ejected electron by an impurity (biphenyl) as was the case observed in the transient optical absorption measurement.

Next, naphthalene was added to the THF solution of **4** as an electron quencher and the stationary ESR measurement was carried out at room temperature. In this case, the signals due to naphthalene anion radical were observed and their intensities did not depend on the conditions of sample preparation. This means that all of the ejected electrons are trapped by naphthalene at the final stage. With the other phenyl-substituted group 4B element-centered anions, ESR signals due to biphenyl and

(21) Grodzinski, J.; Feld, M.; Yang, S. L.; Szwarc, M. *J. Phys. Chem.* **1965**, *69*, 628.

(22) Hayashi, H.; Mochida, K. *Chem. Phys. Lett.* **1983**, *101*, 307.

(23) Chatilialoglu, C.; Ingold, K. U.; Lusztzyk, J.; Narzen, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332.

(24) Dessey, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121.

(25) Dorfman, L. K. *Techniques of Chemistry*; Weissberger, E., Ed.; Wiley-Interscience: New York, 1974; p 463.

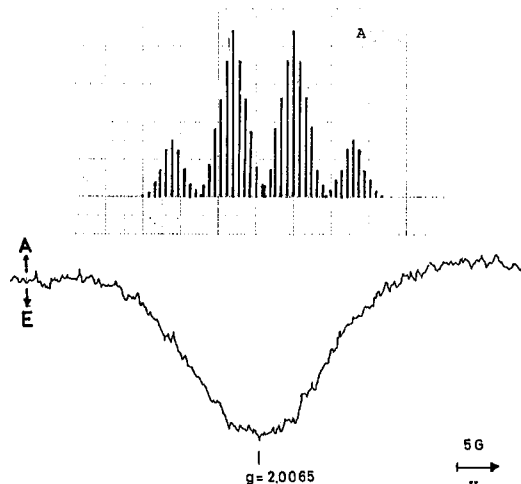


Figure 6. The CIDEP spectrum observed with **5** at a time delay of 1.2 μ s after laser excitation at 77 K.

Table IV. *g* Factors of Signals Generated by the Photoejection of the Germyl Anions (4–6) at 77 K

substrate	<i>g</i> factor ^a	ref
PhMe ₂ GeLi (4)	2.0088 (2.0086)	this work 28
Ph ₂ MeGeLi (5)	2.0065 (2.0070)	this work 28
Ph ₃ GeLi (6)	2.0055 (2.0054)	this work 28

^aThe *g* factors were determined by reference to that of the biphenyl anion radical observed at room temperature.

naphthalene anion radicals were also obtained in similar conditions. The existence of the ESR signals due to biphenyl and naphthalene anion radicals clearly indicates the fact that an electron is photoejected through reaction 5.

A transient ESR technique with a nanosecond laser has recently become very useful for investigating fast radical reactions, because it is expected to give us the unique informations about short-lived radicals and their precursors. However, the transient ESR measurement of **1–7** could not be carried out at room temperature. In fact, it was very difficult to let the sample solutions flow through an ESR cell, because the samples are extremely sensitive to oxygen and moisture. On the other hand, the excitation of each sample solution in a sealed ESR tube with the employed nitrogen laser was found to destroy the sample very quickly. Therefore, we tried to carry out laser flash photolysis (LFP)–ESR measurements at low temperature.²⁶

Transient ESR Measurement at 77 K. At first, transient ESR measurement of the THF solutions of **4–6** was carried out at 77 K, and broad and emissive signals were obtained at the delay time of several microseconds after excitation with a nitrogen laser. As a typical example, the signal observed at 1.2 μ s after excitation of **5** is shown in Figure 6. This signal corresponds to a paramagnetic species which has a *g* value of 2.0065. No signal was observed at any other magnetic field. The *g* values observed with **4** and **6** are listed in Table IV. These *g* values were found to be much larger than those of usual carbon-centered radicals,²⁷ but to agree well with the reported *g* values for the corresponding germyl radicals (Ph_{*n*}Me_{3–*n*}Ge[•]) as shown in table IV.

The observed ESR signals can safely be assigned to the CIDEP ones due to the corresponding germyl radicals from the following reasons. (1) Since the observed ESR signals have emissive phase patterns, they should not be originated from thermal equilibrium spin states but from nonequilibrium ones. Such nonequilibrium states can be generated from molecular triplet states, radical pairs,

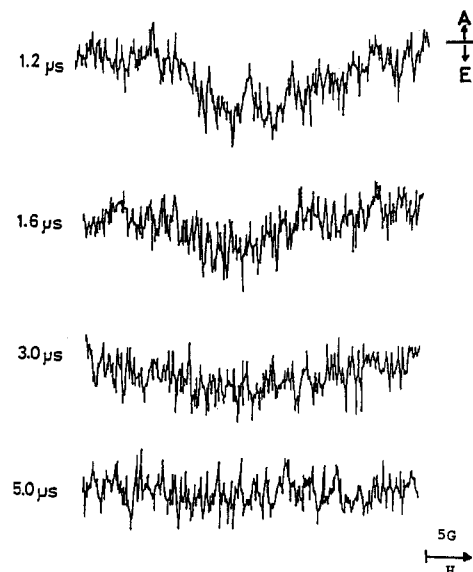


Figure 7. The time dependence of the CIDEP signals observed with **5** at 77 K.

and biradicals. (2) In the present reactions, biradicals are not possible to produce, but triplet states and radical pairs are possible. (3) The widths of the observed signals are about 20 G. These values are too small to be explained by triplet anions because molecular triplet states should have much wider ESR signals corresponding to their zero-field splittings. (4) Thus, the observed signals can safely be explained by the CIDEP signals of radical pairs. Since reaction 5 was confirmed to occur at room temperature with the transient optical absorption measurement described above, similar reactions are possible at 77 K giving the germyl radicals and electron. (5) As shown in Table IV, the observed *g* values are almost the same as those reported for the corresponding germyl radicals. Moreover, the signal widths can also be explained by unresolved hyperfine structures as shown in Figure 6. Thus, the observed signals can safely be assigned to the germyl radicals. (6) No CIDEP signal due to counter radicals of produced radical pairs such as solvated electron, biphenyl anion radical, or lithium atom was observed. Since the relaxation time of solvated electron is not considered to be shorter than 1 μ s, its signal should be observed if it existed. Thus, solvated electron is not considered to exist at 77 K. On the other hand, the relaxation time of the lithium atom is considered to be shorter than 1 μ s because of its fast exchange with lithium cation. Thus, the CIDEP signal of lithium atom may not be observed even if the ejected electron is trapped by lithium cation. It is also difficult to detect the signals of biphenyl anion radical because its concentration is very small.

Although many spin-polarized signals have hitherto been obtained for photoexcited triplet molecules in low-temperature matrices (usually at 77 K),²⁸ no CIDEP measurement has yet been performed for photochemical reactions in low-temperature matrices. For the appearance of CIDEP of a radical pair, molecular diffusion plays an important role. In low-temperature matrices, diffusive motions of usual radicals are so suppressed that no CIDEP has been expected to be included for any radical pair. In actuality, however, we have observed some CIDEP signals in the present reactions. This may be due to the high mobility of ejected electrons. To the best of our knowledge, this is the first observation of CIDEP in low-temperature matrices.

The phase patterns of the CIDEP signals observed with **4–6** were totally emissive ones. As typical examples, the dependence of the signals observed with **5** is shown in Figure 7.

Since there has been no precedent for CIDEP at low-temperature matrices, there is no established theory for explaining the

(26) Mochida, K.; Wakasa, M.; Murai, H.; I'Haya, Y. J.; Sakaguchi, Y.; Hayashi, H. *Chem. Lett.* **1986**, 513.

(27) *Chemically Induced Magnetic Polarization*; Muus, L. T., Atkins, P. W., McLachlan, K. A., Eds.; D. Reidel: Dordrecht, Holland, 1977.

(28) Sakurai, H.; Mochida, K.; Kira, M. *J. Am. Chem. Soc.* **1976**, *94*, 929; *J. Organomet. Chem.* **1977**, *124*, 235.

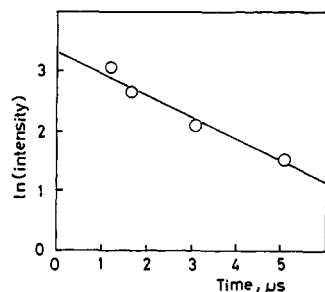
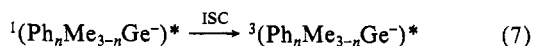


Figure 8. Plots of \ln (intensities) against t observed with THF solution containing **5**.

observed phase patterns of such CIDEP. However, the ordinary mechanisms for CIDEP observed in liquid solutions also seem to be applicable to CIDEP in low-temperature matrices. Therefore, we tentatively use the ordinary CIDEP mechanisms for explaining the CIDEP signals observed for the present reactions.

According to the ordinary CIDEP mechanisms, emission phase patterns can be explained by the triplet mechanism, the $S-T_{-1}$ one (triplet or free-radical precursor), and the $S-T_{+1}$ one (singlet precursor). For the $S-T_{-1}$ (or $S-T_{+1}$) mechanism, the selection rule for a nuclear spin (ΔM_I) should be $\Delta M_I = 1$ (or -1). Thus, asymmetric spectra should be expected from the $S-T_{-1}$ and $S-T_{+1}$ mechanisms. The observed spectra, however, were symmetric with respect to the central positions. Thus, the observed phase patterns are most probably interpreted in terms of the triplet mechanism. Thus, the photoejection of the germynyl anions (**4-6**) at 77 K is most probably considered to proceed through their triplet states as shown below.



ISC = intersystem crossing

The logarithms of the signal intensities observed with **5** are plotted against time in Figure 8. This figure shows that the decay of the signal can be represented by a first-order decay and its rate constant was determined to be $4 \times 10^5 \text{ s}^{-1}$. This value may be the constant of the spin-lattice relaxation of the generated germynyl radicals.

Upon addition of naphthalene to the THF solution of **5** as an electron quencher, the observed ESR spectra showed drastic changes as displayed in Figure 9. Although the spectrum observed at an early stage ($1.2 \mu\text{s}$) of excitation has an almost emissive phase pattern which is quite similar to that shown in Figure 7, the pattern changes to an E(emissive)/A(absorptive) one as time proceeds. The observed change of phase pattern from an emissive one to an E/A one as shown in Figure 9 indicates the existence of a radical pair between the germynyl radical and the naphthalene anion radical. The g value of the germynyl radical (~ 2.0068) is clearly different from that of naphthalene anion radical (~ 2.0028). Thus, the ejected electron is considered to be trapped by nearby naphthalene as is the case at room temperature, forming a radical pair between the germynyl radical and naphthalene anion radical. If the ordinary mechanisms for CIDEP in liquid solution are applicable to CIDEP in low-temperature matrices, the observed E/A phase pattern can be explained by the $S-T_0$ mechanism which is often applied to CIDEP in liquid solution. According to the $S-T_0$ mechanism of ordinary CIDEP in liquid solution, an E/A phase pattern should be produced through a radical pair which has a negative J and which is produced from a triplet or free-radical precursor.

In the present transient ESR measurement at 77 K, the signals due to the germynyl radicals have been obtained. Without an added quencher, the photoejected electron at 77 K is considered to be trapped by lithium cation and/or impurities such as biphenyl. On the other hand, no CIDEP signal was observed at 77 K with THF

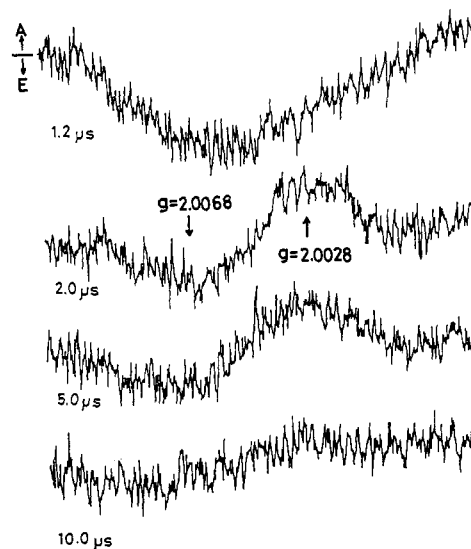


Figure 9. The time dependence of the CIDEP signals observed for **5** in the presence of naphthalene at 77 K.

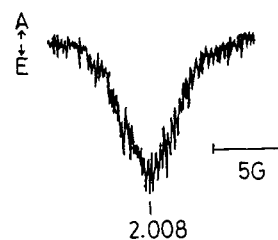


Figure 10. The CIDEP spectrum observed with **7** at a time delay of $3.4 \mu\text{s}$ after laser excitation at 4.2 K.

solutions containing **1-3**. This is considered to be due to the low reactivity of the silyl anions at 77 K or fast recombination process of the generated silyl radicals with ejected electron. Although **7** is expected to be photoejected more easily than **4-6**, no CIDEP was observed at 77 K for **7**. Since the large spin-orbit interaction of the tin atom is considered to bring about a very fast electron-relaxation time of the generated stannyl radical at 77 K, CIDEP studies at 4.2 K were carried out.

Transient ESR Measurement at 4.2 K. An LFP-ESR measurement at 4.2 K was carried out upon irradiation of a THF solution of **7** with a XeCl excimer laser. In this case, a weak signal was obtained at the delay of $2.9 \mu\text{s}$ after the excitation. This signal had a totally emissive phase pattern and corresponds to a paramagnetic species with a g value of 2.008, as shown in Figure 10. On the other hand, the g value of the triphenylstannyl radical was reported to be 2.008.²⁹ From similar reasons as used for the germynyl radicals, the present signal can safely be assigned to the CIDEP one due to the stannyl radical. Particularly, the width of this spectrum is so narrow that this signal cannot be assigned to the triplet state of **7**. Since the spin-lattice relaxation time of the stannyl radical is expected to slow down at 4.2 K compared with the time at 77 K, its signal is considered to appear. From the observed phase pattern, this stannyl radical can tentatively be considered to be produced through the triplet state of **7**. To the best of our knowledge, this is the first observation of CIDEP in photochemical reactions at 4.2 K. No CIDEP signal other than that of the stannyl radical was observed at 4.2 K. Similar results were also obtained at $1.4 \mu\text{s}$ after excitation of **7** at 25 K. No CIDEP signal was obtained with the THF solutions containing **1-3** at 4.2 K.

Conclusion

Laser photolysis of phenyl-substituted silyl, germynyl, and stannyl anions at room temperature leads to the corresponding radicals,

(29) Davies, A. G. *Adv. Chem. Ser.* 1976, No. 157, 26.

respectively. From the emissive phase pattern obtained by means of CIDEP of the anions at 77 and 4.2 K, the germyl and stannyl radicals are tentatively considered to be produced through the triplet state of the germyl and stannyl anions.

Experimental Section

¹H NMR spectra were recorded on a Varian FT 80A, with tetramethylsilane as internal standard. GC-mass spectra were obtained with a JEOL JMS-DX 303 mass spectrometer. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. UV and visible spectra were recorded on a Shimadzu UV-180 and a Hitachi U-3400 spectrometers. Gas chromatography was performed on a Shimadzu GC-6A and -8A with 2-m 20% SE-30 and 2-m 30% Apiezon L columns. Liquid chromatography was performed on a JASCO TWINCLE with Finepak SIL C₁₈ column.

Materials. Ph₃SnCl was commercially available. PhMe₂SiCl, bp 112–115 °C (36 mmHg),³⁰ Ph₂MeSiCl, bp 105–108 °C (0.9 mmHg),³¹ Ph₃SiCl, mp 95 °C,³² PhMe₂GeCl, bp 115–124 °C (24 mmHg),³³ Ph₂MeGeCl, bp 135–140 °C (1 mmHg),²⁸ and Ph₃GeCl, mp 114 °C,³⁴ were prepared as described in the cited references.

Solvent. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen.

Absorption Spectra of the Anions. The phenyl-substituted group 4B element-centered anions are extremely sensitive to oxygen and moisture. A closed absorption cell was used to observe the absorption spectra of these anions.³⁵ The absorption cell apparatus used in these studies consists of a 1-cm quartz absorption cell sealed to a side arm of a round-bottom flask. The apparatus was connected to a high-vacuum system for alternate degassing and flushing with argon. Access to the flask was through a second side arm closed by a rubber syringe cap. The anions were prepared by contact with lithium metal with the corresponding chlorides in highly degassed THF solvent in the round-bottom flask. The concentrations of the anions were determined as follows. The anions were taken out via a Hamilton syringe, protected by an argon atmosphere. A slight positive argon pressure was maintained when piercing the rubber cap. The anion was hydrolyzed with water to produce the corresponding hydrides. The concentrations of hydrides produced were estimated as those of the anion.

Photochemical Reactions of the Anions. The THF solution containing the anion ($0.5\text{--}1.0 \times 10^{-3}$ M) was sealed in vacuum in a quartz tube connected to a Pyrex tube as the upper part. The irradiation of the

sample was carried out using a Xe lamp (1 kW) of USHIO Electric Co., Type UXL-1000 D-0, Pyrex cylinder lens, and a 10-cm water cell filter. After irradiation, the reaction mixture was hydrolyzed with water. The organic layer was dried over anhydrous sodium sulfate. The products were analyzed by gas chromatography, liquid chromatography, and GC-mass spectrometry.

Time-Resolved Optical Absorption. The samples contained in quartz cells with an optical length of 5 mm were degassed by four freeze-pump-thaw cycles. The concentration of the anion was ca. $1.0\text{--}2.0 \times 10^{-4}$ M. Laser-photolysis experiments were performed at room temperature by using the fourth harmonic (266 nm) of a Quanta-Ray DCR-1 Nd:YAG laser as an exciting light source. The laser pulse width was ~5 ns. The details of the laser-photolysis apparatus were published elsewhere.²⁰ The signals were monitored by a Tektronix 485 oscilloscope (350 MHz) and recorded by an Iwatsu DM-901 digital memory (10 ns/point, 8 bit) controlled by a NEC PC 8801 microcomputer.

ESR Measurement at Room Temperature. ESR spectra were taken on a Varian E-109 spectrometer at room temperature. About $2.0\text{--}3.0 \times 10^{-3}$ mol of the anion in THF was sealed in vacuo, in a Pyrex tube (ϕ 10 mm), carrying a quartz side arm (ϕ 4 mm). The irradiation was carried out by using a Xe lamp (1 kW) of USHIO Electric Co., Type UXL-1000D-0, and a Pyrex lens or a Molecron UV 14 nitrogen laser.

ESR Measurements at 77 K. ESR spectra were taken on a Varian E-109 spectrometer with minor modification. Two cavities were employed: a multipurpose E-231 cavity and a bimodal E-236 cavity, the latter having been used to set up the condition in which the microwave magnetic field was parallel to the external field. A Molecron UV 24 nitrogen laser was used for the excitation of the degassed samples with a repetition rate of 20 Hz. An NF BX-531 boxcar integrator was used in a fixed gate mode to record the time-resolved ESR spectra. The details of the apparatus were published elsewhere.³⁶

ESR Measurement at 4.2 K. Transient ESR spectra were taken on a JEOL-FE3X ESR spectrometer. The ESR spectra were taken by feeding the output of the preamplifier of the microwave unit to a PAR 160 boxcar integrator whose gate was open at 1.5 μ s after the laser excitation. A Lumonics TE 861 M excimer laser with XeCl fill was used as the exciting light source. The details of the apparatus were published elsewhere.³⁷

Acknowledgment. We thank Dr. Hisao Murai and Professor Yasumasa J. I'Haya of the University of Electro-Communication for measuring transient CIDEP spectra at 77 K. We also thank Dr. Seigo Yamauchi and Professor Noboru Hirota of Kyoto University for measuring transient CIDEP spectra at 4.2 K.

(30) Daubet, W. H.; Hyde, J. F. *J. Am. Chem. Soc.* **1952**, *74*, 386.

(31) Rosenburg, S. D.; Walburn, J. J.; Ramsden, H. E. *J. Org. Chem.* **1957**, *22*, 1606.

(32) Allen, A. D.; Modena, G. *J. Chem. Soc.* **1957**, 3671.

(33) Kumada, M.; Sakamoto, S.; Ishikawa, M. *J. Organomet. Chem.* **1969**, *17*, 235.

(34) Brooks, E. H.; Glockling, F. *J. Chem. Soc. A* **1966**, 1241.

(35) Waack, R.; Doran, M. A. *J. Am. Chem. Soc.* **1962**, *85*, 1651.

(36) Murai, H.; Hayashi, T.; I'Haya, Y. *J. Chem. Phys. Lett.* **1984**, *106*, 139.

(37) Terazawa, M.; Yamauchi, S.; Hirota, N. *Chem. Phys. Lett.* **1983**, *98*, 145.

Hyperconjugation: Equilibrium Secondary Isotope Effect on the Stability of the *tert*-Butyl Cation. Kinetics of Thermoneutral Hydride Transfer

Michael Meot-Ner (Mautner)

Contribution from the Chemical Kinetics Division, Center for Chemical Physics, National Bureau of Standards, Gaithersburg, Maryland 20899. Received January 30, 1987

Abstract: The thermochemistry of the hydride transfer equilibrium $(\text{CD}_3)_3\text{C}^+ + (\text{CH}_3)_3\text{CH} \rightleftharpoons (\text{CH}_3)_3\text{C}^+ + (\text{CD}_3)_3\text{CH}$ was measured by pulsed high-pressure mass spectrometry. Measurements over a wide temperature range, 145–600 K, allowed an accurate determination of the values: $\Delta H^\circ = -0.57 \pm 0.02$ kcal/mol; $\Delta S^\circ = -0.57 \pm 0.08$ cal/(mol·K); $\Delta G^\circ_{298} = -0.40 \pm 0.07$ kcal/mol; and $K_{298} = 1.97 \pm 0.20$. The direction of the observed isotope effect is consistent with C–H bond weakening in the ion due to hyperconjugation. The kinetics of the reaction show a slow rate and a large negative temperature coefficient, with $k_{300} = 0.36$ and $k_{600} = 0.00625 \times 10^{-10}$ cm³ s⁻¹, i.e., reaction efficiencies of about 0.03 to 0.0005. The observed negative temperature coefficient, $k = AT^{-5.8}$, is larger than those observed for more exothermic hydride transfer reactions. The approach to collision rate is abrupt.

Hyperconjugation interactions between charged centers and alkyl substituents are assumed to occur in alkylated ions. For

example, hyperconjugation in the carbonium ions C_2H_5^+ , $i\text{-C}_3\text{H}_7^+$, and $t\text{-C}_4\text{H}_9^+$ arises as a filled π symmetry orbital on methyl groups