

## Unusual Long Distances of Germanium-Carbon Bond of Organogermyl-alkali Metals Probed by EXAFS

Tsuyoshi KUGITA, Kunio MOCHIDA,\* Kazuyuki TOHJI,<sup>†</sup> and Yasuo UDAGAWA\*<sup>†</sup>  
Department of Chemistry, Faculty of Science, Gakushuin University,  
1-5-1 Mejiro, Tokyo 171

<sup>†</sup>Institute for Molecular Science (IMS), Okazaki, Aichi 444

Extended X-ray absorption fine structure (EXAFS) spectra were analyzed for a series of organogermylalkali metals in solutions. The germanium-carbon bond lengths of the germylalkali metals were found to be longer as much as 10% than those of the corresponding neutral species.

Carbanions,  $R_3C^-$ , play an important role as reaction intermediates in organic chemistry. Similarly, the chemistry of the heavy carbanion analogues, silyl anions  $R_3Si^-$ , germyl anions  $R_3Ge^-$ , and stannyl anions  $R_3Sn^-$ , has received much attention in organic synthesis as reaction intermediate in recent years.<sup>1)</sup> However, structural data of the heavy carbanion analogues have little been determined because of their instability.<sup>2)</sup> Only a few spectroscopic studies (NMR and UV) of these anions have been reported.<sup>3)</sup> To determine the structures of these anions is essential for the understanding of the nature of the bonding and physical and chemical behavior of these systems. In this report we describe structural features of organogermylalkali metals in solution determined by EXAFS spectroscopy for the first time. These results prove that EXAFS is a very useful tool to determine the structure of organogermanium compounds which are stable in solution.

EXAFS measurements were performed by using the laboratory EXAFS spectrometer reported elsewhere.<sup>4)</sup> The alkyl- or aryl-substituted germylalkali metal in hexamethylphosphoric triamide (HMPA)-ether solvents<sup>5,6)</sup> was transferred from a reacting vessel to a Pyrex flat cell (path length  $\approx$  2 mm) in an argon atmosphere in order to avoid decomposition by moisture, and the cell was sealed after the sample was degassed.

The EXAFS spectra of two aryl-substituted germanium compounds ( $Ph_4Ge$  and  $Ph_3GeH$ ) and two alkyl-substituted germanium compounds ( $Et_4Ge$  and  $Et_3GeH$ ) were measured as reference materials. The EXAFS spectra and the associated  $k^1$  weighed Fourier transforms of these germanium compounds are shown in Figs. 1 A-D.

The peak a, b, and c in Fig. 1 correspond to the interatomic distances of germanium and the first, second, and third nearest carbon of the aryl ring in Figs. 1 A-B and the alkyl group in Figs. 1 C-D, respectively. Indeed, a calculation including phase factors show the peaks a represent interatomic distance of 1.96 Å.

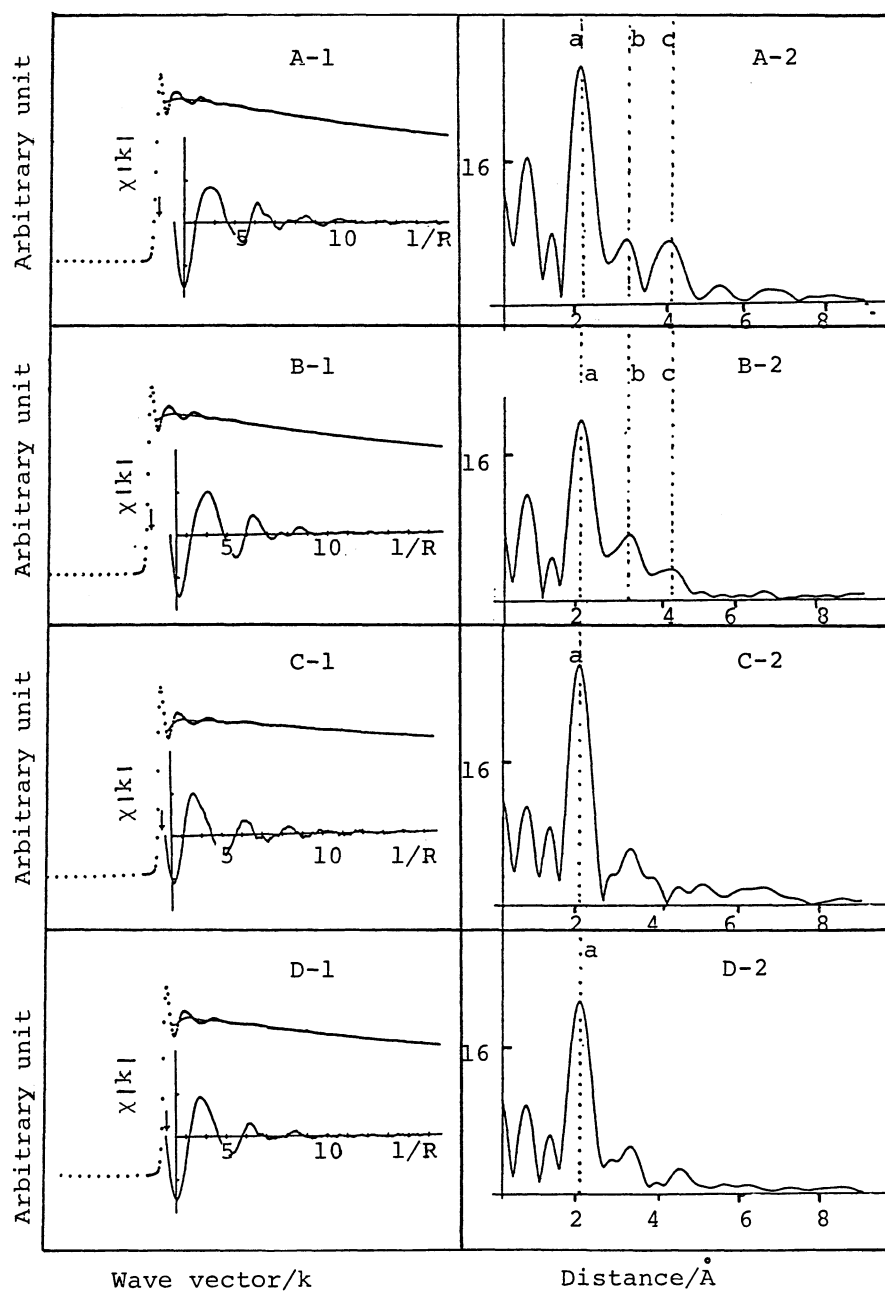


Fig. 1. EXAFS spectra and associated Fourier transforms of  $\text{Ph}_4\text{Ge}$  (A),  $\text{Ph}_3\text{GeH}$  (B),  $\text{Et}_4\text{Ge}$  (C), and  $\text{Et}_3\text{GeH}$  (D).

This is in very good agreement with the known germanium-carbon bond distances.<sup>7)</sup>

Extracted oscillations used to Fourier transform were taken over the same wavevector range of  $3.0 < k < 9.0 \text{ \AA}^{-1}$ . Therefore, the comparison of the coordination number can be made directly from the peak height of radial structure functions.

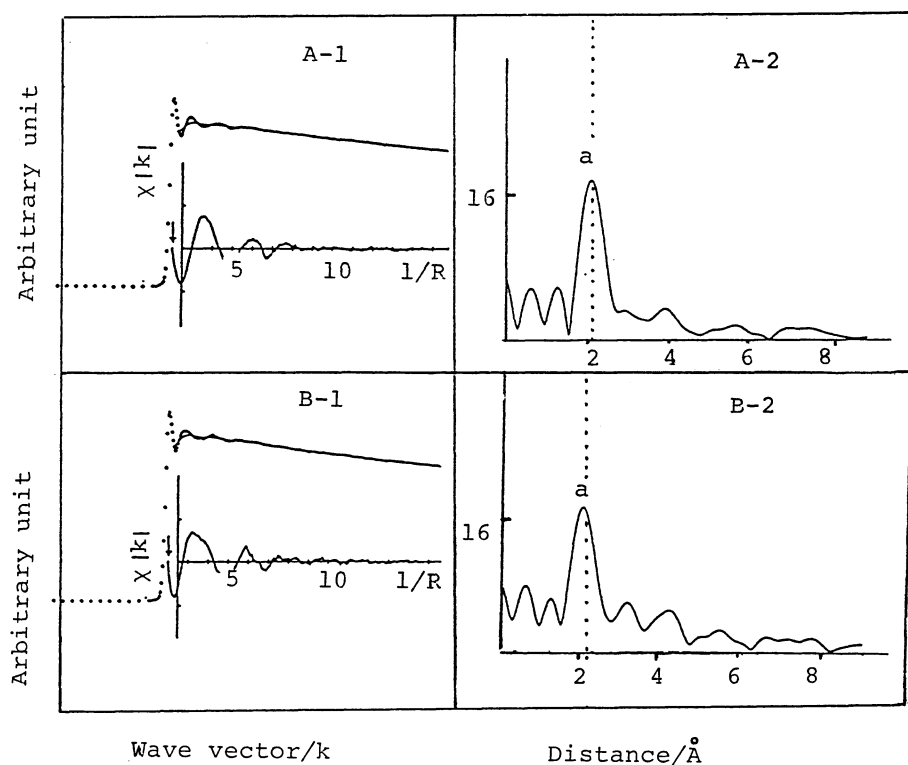


Fig. 2. EXAFS spectra and associated Fourier transforms of  $\text{Me}_3\text{GeNa}$  (A) and  $\text{Ph}_3\text{GeLi}$  (B).

Table 1. The Distance of Germanium-Carbon Bond of Aryl- and Alkyl-Substituted Germylalaki Metals and Related Compounds

No.	Compound	Ge-C bond/Å
1	$\text{Et}_4\text{Ge}$	1.96
2	$\text{Et}_3\text{GeH}$	1.96
3	$\text{Ph}_4\text{Ge}$	1.97
4	$\text{Ph}_3\text{GeH}$	1.96
5	$\text{Me}_3\text{GeLi}$	2.07
6	$\text{Me}_3\text{GeNa}$	2.17
7	$\text{Me}_3\text{GeK}$	2.10
8	$\text{Et}_3\text{GeLi}$	2.06
9	$\text{Ph}_3\text{GeLi}$	2.04

As is expected, the peak height increases with the increase of the substituent. Therefore, it is evident that peak heights can serve as a substituent number marker for unknown compounds. The interatomic distances obtained for the reference com-

pounds are summarized in Table 1.

The EXAFS spectra of aryl- and alkyl-substituted germylalkali metals were measured. As typical examples, EXAFS spectra and the associated Fourier transforms of trimethylgermylsodium ( $\text{Me}_3\text{GeNa}$ ) and triphenylgermyllithium ( $\text{Ph}_3\text{GeLi}$ ) are shown in Figs. 2 A-B. From a comparison of the amplitude of the extracted oscillations and the peak heights with those of the reference compounds it is immediately clear that the three substituents remain around Ge in these solutions. However, peak positions of radial structure functions are appreciably different, suggesting the Ge-C bond lengths are longer in the anions. The values obtained from the calculated including phase factors are also summarized in Table 1.

The most reasonable explanation for the long distance of Ge-C bond of the anions would seem to be that a large negative charge on a germanium atom causes re-hybridization at germanium, placing more s character in the unpaired electron-bearing hybrid. As a result, p character in bond orbitals of the germanium atom is increased, and Ge-C bond lengths of the anions are increased.

We have no information on the degree of association of the anions in this EXAFS study.

This work was supported by the Joint Studies Program (1987/1988) of IMS.

#### References

- 1) For example; D. D. Davies, *Organomet. Chem. Rev. Sect. A*, 6, 283 (1970); M. Fujita and T. Hiyama, *Yuki Gosei Kagaku Kyokai Shi*, 42, 293 (1984) and references cited therein; M. Lesbre, P. Mazerolles, and J. Satge, "The Organic Compounds of Germanium," Wiley, New York (1971), pp. 646-655.
- 2) For example; W. H. Ilskey, T. F. Schaaf, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, 102, 3769 (1980); H. Sakurai, "Free Radicals," ed by J. K. Kochi, Wiley, New York (1973), Vol. II, Chap. 25.
- 3) K. Mochida, M. Wakasa, Y. Sakaguchi, and H. Hayashi, *J. Am. Chem. Soc.*, 109, 7942 (1987).
- 4) K. Tohji, Y. Udagawa, T. Kawasaki, and K. Masuda, *Rev. Sci. Instrum.*, 54, 1482 (1983).
- 5) E. J. Bulten and J. G. Noltes, *Tetrahedron Lett.*, 1966, 5121.
- 6) H. Sakurai, "Shin Jikken Kagaku Koza," ed by Nippon Kagaku Kai, Maruzen, 1482 (1983).
- 7) "Kagaku Binran," ed by Nippon Kagaku Kai, Maruzen, Tokyo (1984), Vol. 2, p. II-667.

(Received December 27, 1988)