

Enrichment of Germanium-73 with the Magnetic Isotope Effect

Masanobu Wakasa and Hisaharu Hayashi*

Molecular Photochemistry Laboratory, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan

Tomoaki Kobayashi and Takeo Takada

Department of Chemistry, Faculty of Science, Rikkyo University, Nishiikebukuro, Toshima, Tokyo 171, Japan

Received: October 25, 1993*

The enrichment of germanium-73 with the magnetic isotope effect (MIE) succeeded, for the first time, in the presence and absence of magnetic fields. At 200 G, the photolysis of methyltriphenylgermane in a Brij35 micellar solution under 92.8% conversion gave the 4% enrichment of germanium-73 ($\alpha = 0.015$). Germanium-73 is the heaviest magnetic isotope to have so far been enriched with MIE from samples of natural abundance.

Introduction

Magnetic field effects (MFEs) on energy-transfer processes and chemical reactions of spin systems, such as excited molecules and radical pairs, have been studied extensively and constitute a rapidly developing field encompassing chemistry, physics, and biology.^{1,2} This is a new branch which may be called "(dynamic) spin chemistry". A radical pair is one of the most important short-lived reaction intermediates and consists of two radicals, each of which has an unpaired electron. MFEs on chemical reactions of radical pairs in solution can be interpreted in terms of the radical-pair model according to which weak magnetic interactions, such as the Zeeman interaction of unpaired electrons and the hyperfine interaction between electron and nuclear spins, can exert great influence on the spin conversion rate between the singlet and triplet states of radical pairs.^{1,2} It is, therefore, possible to enrich magnetic isotopes in the reactions which occur through radical pairs. Thus, the magnetic isotope effect (MIE)^{1,2} is one of the most interesting applications of MFEs of radical pairs. Here, reaction rates of radical pairs can be changed, not by the mass of isotopes but by the hyperfine interaction between electron and nuclear spins.

Large MFEs and MIEs have been observed during reactions of light-atom-centered radicals such as C and O.^{1,2} MFEs and MIEs, however, decrease drastically with increasing atomic number. This is due to the magnetic-insensitive spin-orbit interaction of heavy atoms, which enhances the spin conversion of radical pairs. Until now, a very small MIE of ²⁹Si has been reported for an Si-substituted carbon-centered radical.³ The heaviest magnetic isotope which have so far been enriched with MIE from samples of natural abundance is ³³S.⁴ There was a report of an MIE of an Sn-centered radical,⁵ but this was subsequently withdrawn.⁶ At present there is, therefore, no report of the MIE of Si-, Ge-, and Sn-centered radicals. Since we recently observed MFEs in the reactions of Ge-centered radicals,⁷ a study on the enrichment of ⁷³Ge with the MIE of Ge-centered radicals was undertaken. This Letter reports on the enrichment of ⁷³Ge with the MIE for the first time.

Experimental Section

Methyltriphenylgermane (Ph₃MeGe) was synthesized as described in the literature.⁸ Polyoxyethylene dodecyl ether (Brij35) was used as received. MIEs were studied by the photolysis of Ph₃MeGe in a Brij35 micellar solution. The concentrations of Ph₃MeGe and Brij35 in the employed micellar solution were (1–

TABLE I: Relative Isotope Enrichment, $\delta(^{72}\text{Ge})$ and $\delta(^{73}\text{Ge})$, Observed upon Photolysis of Ph₃MeGe in the Brij35 Micellar Solution at Room Temperature in the Absence of an External Magnetic Field

conversion/%	$\delta(^{72}\text{Ge})/\%$ ^a	$\delta(^{73}\text{Ge})/\%$ ^a
94	+ (0.7 ± 1.0)	+ (20.0 ± 2.0)
88	- (0.1 ± 1.0)	+ (12.3 ± 2.0)

$$^a \delta(^Z\text{Ge}) = ((^Z\text{Ge}/^{74}\text{Ge}) / (^Z\text{Ge}/^{74}\text{Ge})_0) - 1.$$

2) × 10⁻³ and 8.0 × 10⁻² mol dm⁻³, respectively. The irradiation of the sample was carried out with a 500-W deep UV lamp. The details of the sample preparation and photolysis are described in the previous paper.⁷ For germanium isotope analysis after photolysis, the reaction products and starting compound (Ph₃MeGe) should be isolated from the micellar solution, but this isolation was very difficult. We isolated the products and starting compound by using a JAI-LC908 recycle high-performance liquid chromatograph (HPLC) with a gel permeation chromatography (GPC) column. The isotope ratios were measured using a VG-ELEMENT PQ- Ω inductively coupled plasma mass spectrometer (ICP-MS). Although the relative standard deviation (RSD) of the observed isotope ratio was <0.3% in the specifications of the commercially available ICP-MS, it was not so easy to realize this RSD value.

Results and Discussion

After photolysis of the Brij35 micellar solution of Ph₃MeGe under 55–94% conversions in the absence of an external magnetic field, the ratios of ⁷²Ge/⁷⁴Ge and ⁷³Ge/⁷⁴Ge in the starting compound (Ph₃MeGe) were measured by the ICP-MS. The relative enrichment of ^ZGe (= $\delta(^Z\text{Ge})$) can safely be taken as follows:

$$\delta(^Z\text{Ge}) = ((^Z\text{Ge}/^{74}\text{Ge}) / (^Z\text{Ge}/^{74}\text{Ge})_0) - 1 \quad (1)$$

Here, (^ZGe/⁷⁴Ge)₀ and (^ZGe/⁷⁴Ge) represent the isotope ratios of ^ZGe/⁷⁴Ge observed before and after photolysis, respectively. Typical results of the observed $\delta(^Z\text{Ge})$ values are listed in Table I. This table shows a significant enrichment of magnetic ⁷³Ge in contrast to no appreciable change of nonmagnetic ⁷²Ge.

The reaction scheme can be described by Figure 1. Upon photolysis of the Brij35 micellar solution containing Ph₃MeGe, its triplet state (³Ph₃MeGe*) is produced, and then ³Ph₃MeGe* decomposes to a triplet radical pair (³X··Y) of the diphenylmethylgermyl (Ph₂MeGe*) and phenyl (Ph*) radicals in the micellar supercage. The triplet-singlet (T-S) conversion of the radical pair involving magnetic ⁷³Ge ($I = 9/2$) is much faster than

* Abstract published in *Advance ACS Abstracts*, December 1, 1993.

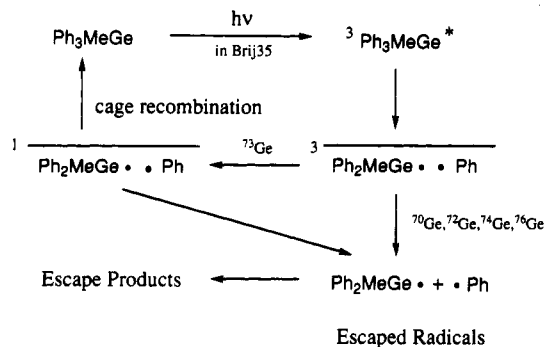


Figure 1. Reaction scheme of methyltriphenylgermane (Ph_3MeGe) in the Brij35 micellar solution.

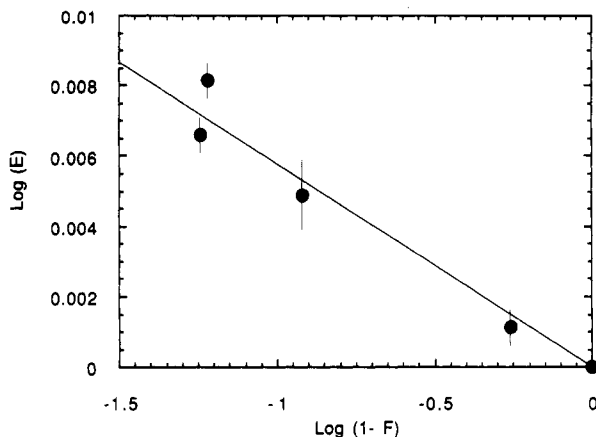


Figure 2. Dependence of the isotope enrichment (E) on the conversion yield (F) observed for Ph_3MeGe in the Brij35 micellar solution.

those involving nonmagnetic Ge. From the singlet radical pair ($^1\text{X}\cdot\text{Y}$), the cage recombination to the starting compound can occur. Thus, the ^{73}Ge isotope can be enriched in the starting compound.

In a partially reversible reaction, the isotope enrichment in the starting compound depends on the conversion yield (F). The higher the conversion yield, the larger the isotope selection and isotope enrichment. Concerning the isotope enrichment (E) of molecule A, the following simple equation can be easily derived:⁹

$$E = (A^*/A)/(A_0^*/A_0) = (1-F)^{-\alpha} \quad (2)$$

Here, A_0^*/A_0 and A^*/A represent the magnetic isotope abundance obtained before and after photolysis. The isotope selection coefficient, α , is a very important parameter governing the isotope enrichment of starting compound. The isotope enrichment, E , can be estimated from the $\delta(^Z\text{Ge})$ value. In Figure 2, the logarithms of E observed at room temperature in the absence of an external magnetic field are plotted against the logarithms of $1-F$. This figure shows that $\log(E)$ and $\log(1-F)$ have a good linear relationship. Using the slope of this figure, we obtained the selection coefficient (α) to be 0.006 ± 0.0007 . This α value is much smaller than those obtained for usual C-centered radicals.⁹ This decrease in the MIE of ^{73}Ge may be due to the spin-orbit interaction of Ge which enhances the spin-independent T-S conversion of the radical pair. The α value observed for the MIE on the reaction of Ph_3MeGe considerably exceeded that expected from the mass isotope effect ($\alpha = 0.0015$). It is noteworthy that the present system certainly brought about an MIE-induced isotope enrichment of ^{73}Ge .

The magnetic field dependence on the isotope enrichment was also measured in a magnetic field range of 0–1000 G. In Figure 3, the $\delta(^Z\text{Ge})$ values obtained under 92–93% conversion are plotted against the magnetic field strength (B). Here, the $\delta(^{72}\text{Ge})$ value shows no appreciable change beyond the experimental error. With increasing B , the $\delta(^{73}\text{Ge})$ value increases initially,

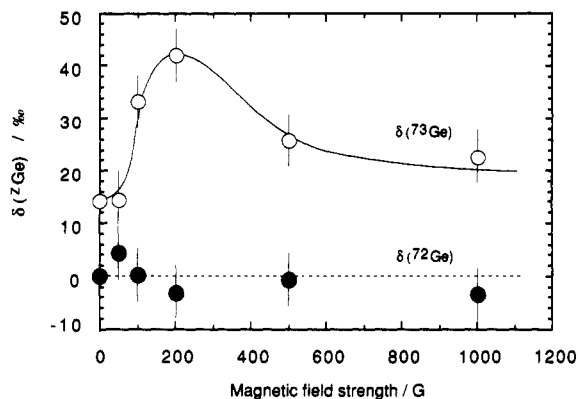


Figure 3. Magnetic field dependence of the relative isotope enrichment $\delta(^Z\text{Ge})$: filled circles, $\delta(^{72}\text{Ge})$; open circles, $\delta(^{73}\text{Ge})$. After photolysis of the Brij35 micellar solutions of Ph_3MeGe under 92–93% conversion in the magnetic field range 0–1000 G, the ratios of $^{72}\text{Ge}/^{74}\text{Ge}$ and $^{73}\text{Ge}/^{74}\text{Ge}$ in the starting compound (Ph_3MeGe) were measured by ICP-MS. The $\delta(^Z\text{Ge})$ value was obtained by eq 1.

attaining a maximum at 200 G, and then decreases slightly in higher fields ($200 \text{ G} < B \leq 1000 \text{ G}$). At 200 G, the photolysis of Ph_3MeGe under 92.8% conversion gives a $\delta(^{73}\text{Ge})$ value of $40 \pm 5\%$ ($\alpha = 0.015$) in the starting compound. The magnitude of the enrichment of ^{73}Ge in the presence of magnetic field at 200 G seems to be considerably large, and the obtained α value is similar to that reported on the enrichment of ^{29}Si ($\alpha = 0.023$) in which the generated radical is not a silyl radical but an Si-substituted carbon-centered radical.³

The magnetic field dependence of the isotope enrichment of ^{73}Ge shown in Figure 3 is strong evidence for the enrichment of ^{73}Ge due to the MIE. Such magnetic field dependence has not yet been obtained for the enrichments of ^{29}Si and ^{33}S . The observed magnetic field dependence of the isotope enrichment of ^{73}Ge can be explained by the blocking of the $T_{\pm 1}$ -S conversion by external magnetic fields.⁹ The half-field ($B_{1/2}$) of the saturation of the MFE due to the hyperfine coupling mechanism is given as follows:¹⁰

$$B_{1/2} = 2(B_1^2 + B_2^2)/(B_1 + B_2) \quad (3)$$

The individual B_i value characterizing the radical ($i = 1, 2$) is given by

$$B_i = \left(\sum_j I_{ij}(I_{ij} + 1)a_{ij}^2 \right)^{1/2} \quad (4)$$

Here, a_{ij} is the isotropic hyperfine coupling constant of the j th nuclear in radical i . Among the stable isotopes of Ge, ^{73}Ge is only the magnetic one ($I = 9/2$). The other stable Ge isotopes are nonmagnetic. For the generated radical pair ($\text{Ph}_2\text{MeGe}\cdot\text{Ph}$) involving a nonmagnetic Ge atom (RP_n), the $B_{1/2}$ value is calculated to be 38 G from the reported hyperfine coupling constants ($a_{\text{Me}} = 5.36 \text{ G}$, $a_{\text{o,p}} = 0.97 \text{ G}$, and $a_{\text{m}} = 0.49 \text{ G}$ for $\text{Ph}_2\text{MeGe}\cdot$ ¹¹ and $a_{\text{o}} = 17.4 \text{ G}$, $a_{\text{m}} = 5.9 \text{ G}$, and $a_{\text{p}} = 1.9 \text{ G}$ for $\text{Ph}\cdot$ ¹²). On the other hand, the hyperfine coupling constant of ^{73}Ge in $\text{Ph}_2\text{MeGe}\cdot$ has not yet been reported, but it seems to be similar to those of trimethylgermyl and triphenylgermyl radicals which are reported to be ca. 80 G.¹³ Using this $a^{73}\text{Ge}$ value ($=80 \text{ G}$), the $B_{1/2}$ value of the radical pair involving ^{73}Ge (RP_m) is estimated to be 750 G. An increase of B in the low-field region ($0 \text{ G} < B < 200 \text{ G}$) first affects RP_n , in which the T-S conversion is induced by the small hyperfine couplings of protons ($B_{1/2} = 38 \text{ G}$). Therefore, the $T_{\pm 1}$ -S conversion of such pairs is almost blocked at $B \sim 200 \text{ G}$. In RP_m , however, the hyperfine interaction of ^{73}Ge is significantly strong ($B_{1/2} = 750 \text{ G}$), and then the $T_{\pm 1}$ -S conversion is not blocked at $B \sim 200 \text{ G}$. Thus, the $\delta(^{73}\text{Ge})$ value at $B = 200 \text{ G}$ becomes larger than that at $B = 0 \text{ G}$. The $\delta(^{73}\text{Ge})$

value should decrease with increasing B from $B = 200$ G because a gradual blocking of the $T_{\pm 1}$ -S conversion starts to occur for RP_m .

In the present study, we have succeeded in enriching ^{73}Ge using its MIE for the first time. We have extended the heaviest magnetic isotope enriched with MIE from samples of natural abundance to ^{73}Ge from ^{33}S , although the MIE of ^{235}U has already been reported for ^{235}U -enriched samples.¹⁴ With similar reactions to the present one, MIEs of Si- and Sn-centered radicals are expected to be observed. Further studies along this way are now in progress.

Acknowledgment. H.H. thanks a partial support by Grant-in-Aid for Scientific Research on Priority Area of "Molecular Magnetism" (Area No. 228/0424107) from the Ministry of Education, Science and Culture, Japan.

References and Notes

- (1) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.

- (2) Hayashi, H. *Photochemistry and Photophysics*; CRC Press: Boca Raton, FL, 1990; Vol. 1, Chapter 2.
- (3) Step, E. N.; Tarasov, V. F.; Buchachenko, A. L. *Chem. Phys. Lett.* **1988**, *144*, 523.
- (4) Step, E. N.; Buchachenko, A. L.; Turro, N. J. *Chem. Phys.* **1992**, *162*, 189.
- (5) Podoplelov, A. V.; Leshina, T. V.; Sagdeev, R. Z.; Molin, Yu. N.; Gol'danskii, V. I. *JETP Lett.* **1979**, *29*, 380.
- (6) Podoplelov, A. V.; Medvedev, V. I.; Sagdeev, R. Z.; Salikhov, K. M.; Molin, Yu. N.; Moralev, V. M.; Gol'danskii, V. I. In *Proceedings of the International Conference on Chemically Induced Spin Polarization and Magnetic Effects in Chemical Reactions*; Sagdeev, R. Z., Ed.; Novosibirsk: U.S.S.R., 1981; p 81.
- (7) Wakasa, M.; Sakaguchi, Y.; Hayashi, H. *J. Am. Chem. Soc.* **1992**, *114*, 8171.
- (8) Kraus, C. A.; Foster, L. S. *J. Am. Chem. Soc.* **1927**, *49*, 457.
- (9) Buchachenko, A. L. *Prog. React. Kinet.* **1984**, *13*, 163.
- (10) Weller, A.; Nolting, F.; Staerk, H. *Chem. Phys. Lett.* **1983**, *96*, 24.
- (11) Sakurai, H.; Mochida, K.; Kira, M. *J. Am. Chem. Soc.* **1975**, *97*, 929.
- (12) Zemel, H.; Fessenden, R. W. *J. Phys. Chem.* **1975**, *79*, 1419.
- (13) Lloyd, R. V.; Rogers, M. T. *J. Am. Chem. Soc.* **1973**, *95*, 2459.
- (14) Geoffroy, M.; Ginet, L.; Lucken, E. A. C. *Chem. Phys. Lett.* **1976**, *38*, 321.
- (14) Rykov, S. V.; Khudyakov, I. V.; Skakovsky, E. D.; Tychinskaya, L. Yu.; Ogorodnikova, M. M. *J. Photochem. Photobiol. A* **1992**, *66*, 127.