

Enrichment of Germanium-73 with the Magnetic Isotope Effect on the Hydrogen Abstraction Reaction of Triplet Benzophenone with Triethylgermane in an SDS Micellar Solution

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Abstract: Using the hydrogen abstraction reaction of triplet benzophenone with triethylgermane in an SDS micellar solution, we succeeded in enriching ⁷³Ge with the magnetic isotope effect. At zero magnetic field, 0.5% enrichment of ⁷³Ge was observed for the cage product (diphenyl(triethylgermyl)methanol). With increasing magnetic field strength (**B**), the enrichment of ⁷³Ge increased initially, attaining the maximum value of 5.3% at 500 G. At higher fields (500 G < **B** ≤ 10 kG), it decreased gradually, becoming 1.0% at 10 kG. The magnetic field dependence of the enrichment of ⁷³Ge can be explained by the relaxation mechanism.

Introduction

Magnetic field effects (MFEs) on chemical reactions of 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 “spin chemistry”.³ The magnetic isotope effect (MIE) is one of the most interesting applications of spin chemistry.^{4–6} 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. It is, therefore, possible to enrich magnetic isotopes in the reactions which occur through radical pairs.

Large MFEs and MIEs have been observed during reactions of light-atom-centered radicals such as carbon-, nitrogen-, and oxygen-centered ones.^{1,2,4,5} MFEs and MIEs, however, decrease drastically with increasing atomic number. This is because the spin–orbit interaction of heavy atoms, which enhances the spin conversion of radical pairs, is insensitive to external magnetic fields. In 1993, we found that the photolysis of methyltriphenylgermane (Ph₃MeGe) in a Brij35 micellar solution gave 4% enrichment of ⁷³Ge.⁷ At that stage, ⁷³Ge was the heaviest magnetic isotope enriched via the MIE from samples of natural abundance. After our report, Khudyakov and Buchachenko reported on the enrichment of ²³⁵U by the MIE from samples of natural abundance.⁵ To the best of our knowledge, only three magnetic isotopes (³³S,⁸ ⁷³Ge,⁷ and ²³⁵U^{5,9}) have ever been found to be

enriched by the MIEs on the reactions involving heavy-atom-centered radicals, although a small degree of the enrichment of ²⁹Si was reported with a Si-substituted carbon-centered radical.¹⁰ There was a report of an MIE of an Sn-centered radical,¹¹ but this was subsequently withdrawn.¹²

It is important, therefore, to find general reaction systems which can be extended to the enrichment of other heavy atoms. In the present study, we have found that ⁷³Ge can be much more efficiently enriched by the MIE on the hydrogen abstraction reaction of triplet benzophenone with triethylgermane in an SDS micellar solution than by the MIE on our previous reaction.⁷ Since the hydrogen abstraction by excited carbonyl compounds is one of the best-known photochemical reactions, one can expect that many other heavy isotopes will be enriched by the MIE on the reactions of this type.

Experimental Section

Materials. Triethylgermane (Et₃GeH) was synthesized as described in the literature.¹³ Diphenyl(triethylgermyl)methanol was synthesized from (triethylgermyl)lithium with benzophenone in hexane.¹⁴ Hexaethyldigermoxane was synthesized by the treatment of triethylchlorogermane with H₂O.¹⁵ Benzopinacol and benzophenone (BP) were

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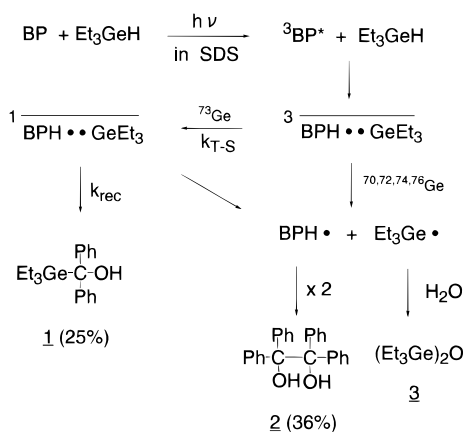
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Scheme 1



obtained commercially and recrystallized from ethanol. Sodium dodecyl sulfate (SDS) was recrystallized from a 1:1 (v/v) mixture of methanol and ethanol. Water was distilled and deionized.

Photochemical Reaction. The concentrations of Et_3GeH , BP, and SDS in the employed micellar solution were 1.0×10^{-2} , 3.0×10^{-3} , and $8.0 \times 10^{-2} \text{ mol dm}^{-3}$, respectively. The irradiation of the sample was carried out with a 500 W Xe lamp at room temperature under nitrogen atmosphere.

Isotope Analysis. For analysis of the germanium isotope after photolysis, the reaction products and starting compounds (Et_3GeH and BP) had to be isolated from the micellar solution, but this isolation was very difficult. We isolated them by using a JAI-LC908 recycle HPLC with a Hitachi Kasei GL-W252 gel permeation chromatography (GPC) column. The isotope ratios were measured using a VG-ELEMENT PQ- Ω inductively coupled plasma mass spectrometer (ICP-MS).⁷

Results and Discussion

First, product analysis for the photochemical reaction of benzophenone (BP) with triethylgermane (Et_3GeH) in the SDS micellar solution was carried out. Results are described in Scheme 1. Irradiation of the micellar solution for 20 min gave diphenyl(triethylgermyl) methanol (**1**, 25%¹⁶), benzopinacol (**2**, 36%¹⁶), and hexaethyldigermoxane (**3**) under 95% conversion of BP. These products were separated by preparative GLC and identified in comparison with authentic samples by MS and NMR. As a minor product, a coupling product of benzophenone ketyl radical and alkyl radical from SDS was also obtained. Here, it is considered that product **1** is a cage product and products **2** and **3** are escaped ones. As shown in Scheme 1, upon photolysis of the SDS micellar solution containing Et_3GeH and BP, the benzophenone triplet state (${}^3\text{BP}^*$) is produced, followed by the hydrogen abstraction reaction to produce a triplet radical pair of the triethylgermyl radical ($\text{Et}_3\text{Ge}\bullet$) and benzophenone ketyl radical ($\text{BPH}\bullet$) in the micellar supercage. The triplet radical pair in the cage converts to the singlet radical pair, and the radicals in the radical pairs partially escape from the cage, forming escaped radicals. Since triethylgermyl radical is unstable in H_2O , the escaped radical immediately reacts with H_2O , resulting in product **3**. On the other hand, two escaped ketyl radicals are coupled with each other, forming product **2**. From the singlet radical pair, cage recombination resulting in product **1** can occur. Here, the triplet-singlet (T-S) spin conversion of the radical pair involving magnetic ${}^{73}\text{Ge}$ ($I = 9/2$) is much faster than that involving nonmagnetic ${}^{70}\text{Ge}$, ${}^{72}\text{Ge}$, ${}^{74}\text{Ge}$, and ${}^{76}\text{Ge}$. Consequently, the ${}^{73}\text{Ge}$ isotope can be enriched in product **1**.

(16) The product yield was determined by GLC on the basis of consumed benzophenone.

Table 1. Relative Isotope Enrichment, $\delta({}^{72}\text{Ge})$ and $\delta({}^{73}\text{Ge})$, Observed upon Photolysis of Benzophenone with Triethylgermane in SDS Micellar Solution at Room Temperature in the Absence of an External Magnetic Field

entry ^a	$\delta({}^{72}\text{Ge})/\%$ ^b	$\delta({}^{73}\text{Ge})/\%$ ^b
1	0.0 ± 0.5	0.5 ± 0.3
2	0.1 ± 0.5	0.4 ± 0.6
3	0.0 ± 0.5	0.5 ± 0.5

^a In each entry, the δ values were measured 10 times, the error being the relative standard deviation (RSD) of such measurements. ^b $\delta({}^{Z}\text{Ge}) = (({}^Z\text{Ge}/{}^{74}\text{Ge})/({}^Z\text{Ge}/{}^{74}\text{Ge})_0) - 1$.

Thus, we investigated the magnetic isotope effects (MIEs) on product **1**. After photolysis of the SDS micellar solution containing Et_3GeH and BP under 95% conversion in the absence of an external magnetic field, the ratios of ${}^{72}\text{Ge}/{}^{74}\text{Ge}$ and ${}^{73}\text{Ge}/{}^{74}\text{Ge}$ in product **1** were measured by the ICP-MS. The relative enrichment of ${}^Z\text{Ge}$ ($\delta({}^Z\text{Ge})$) can be represented as follows:

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

Here, $({}^Z\text{Ge}/{}^{74}\text{Ge})_0$ and $({}^Z\text{Ge}/{}^{74}\text{Ge})$ represent the isotope ratios of ${}^Z\text{Ge}/{}^{74}\text{Ge}$ observed before (on starting compound Et_3GeH) and after (on product **1**) reactions, respectively. Typical results observed for the $\delta({}^Z\text{Ge})$ values at zero field are listed in Table 1. This table shows that the $\delta({}^{73}\text{Ge})$ values are slightly larger than the experimental errors, but the $\delta({}^{72}\text{Ge})$ ones are almost zero. This means that enrichment of magnetic ${}^{73}\text{Ge}$ was observed slightly in the absence of an external magnetic field, but that no appreciable enrichment of nonmagnetic ${}^{72}\text{Ge}$ was observed at zero field.

In the absence of an external magnetic field, the enrichment of magnetic ${}^{73}\text{Ge}$ is somewhat small. This may be due to the slow recombination reaction of the singlet radical pair. According to the irreversible reaction system shown by Scheme 1, the isotope enrichment, S , in the cage product can be represented as follows:⁴

$$S = \delta({}^Z\text{Ge}) + 1 = \gamma(k_1 + k_2)/(k_1 + k_2^*) \quad (2)$$

$$\gamma = k_2^*/k_2 \quad (3)$$

where k_1 represents the rate constant of escape the process and k_2 , and k_2^* represent those of the recombination of nonmagnetic and magnetic radical pairs, respectively. The γ value characterizes the efficiency of isotope selection. In such reactions as the present one where reactions occur from T-precursors, the recombination process (k_2 and k_2^*) includes the T-S spin conversion process ($k_{\text{T-S}}$) and the reaction of the singlet radical pair (k_{rec}) as shown in Scheme 1. In the case of a fast reaction ($k_{\text{rec}} > k_{\text{T-S}}$), the isotope enrichment (S) only depends on $k_{\text{T-S}}$. Since the T-S spin conversion of the radical pair involving magnetic ${}^{73}\text{Ge}$ is much faster than that involving nonmagnetic ${}^{72}\text{Ge}$, a large enrichment of magnetic ${}^{73}\text{Ge}$ is expected to occur. However, when the reaction of the singlet radical pair is comparable to or slower than the spin conversion process ($k_{\text{rec}} \leq k_{\text{T-S}}$), the enrichment may be depressed by this slow process. This is due to the fact that the rate-determining process is not the spin conversion but the reaction of the singlet radical pair which is independent of nuclear spins. The small enrichment of the present reaction at a zero field can be explained by the latter case.

Next, the magnetic field dependence of $\delta({}^{72}\text{Ge})$ and $\delta({}^{73}\text{Ge})$ was also measured in the magnetic field range of 0–10 kG.

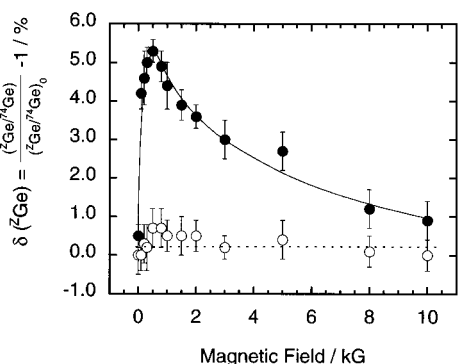


Figure 1. Magnetic field dependence of the relative isotope enrichment $\delta(^{73}\text{Ge})$: open circles, $\delta(^{72}\text{Ge})$; filled circles, $\delta(^{73}\text{Ge})$. After photolysis of SDS micellar solutions containing benzophenone (BP) and triethylgermane (Et_3GeH) under 95% conversion in the magnetic field range of 0–10 kG.

The observed $\delta(^{73,72}\text{Ge})$ values are plotted against the magnetic field strength (\mathbf{B}) in Figure 1. Here, the $\delta(^{72}\text{Ge})$ value shows no appreciable change beyond the experimental error. With increasing \mathbf{B} from 0 to 500 G, however, the $\delta(^{73}\text{Ge})$ value increases initially, attaining the maximum value of $(5.3 \pm 0.3)\%$ at 500 G. With increasing \mathbf{B} from 500 G to 10 kG, the $\delta(^{73}\text{Ge})$ value decreases gradually, becoming $(1.0 \pm 0.3)\%$ at 10 kG. The magnetic field dependence of the isotope enrichment of ^{73}Ge shown in this figure is strong evidence for the enrichment by the MIE.

The observed magnetic field dependence of the isotope enrichment of ^{73}Ge can be explained by the blocking of the $\text{T}_{\pm 1}\text{--S}$ conversion by external magnetic fields. Such MFEs on the $\text{T}_{\pm 1}\text{--S}$ conversion occur through the hyperfine coupling mechanism (HFCM)^{1,2,4,5} and the relaxation mechanism (RM).¹⁷ Figure 2 schematically shows the energy diagram of singlet and triplet radical pairs and the magnetic field dependence of the isotope enrichment (δ) expected for the $\text{T}_{\pm 1}\text{--S}$ conversion through the HFCM and RM. Here, RP_n represents a radical pair involving a nonmagnetic ^{70}Ge , ^{72}Ge , ^{74}Ge , or ^{76}Ge and RP_m that involving a magnetic ^{73}Ge .

According to the HFCM, the half-saturation field ($\mathbf{B}_{1/2}$) of the MFE is given as follows:¹⁸

$$\mathbf{B}_{1/2} = 2(A_1^2 + A_2^2)/(A_1 + A_2) \quad (4)$$

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

$$A_i = \left(\sum_j I_{ij}(I_{ij} + 1)a_{ij}^2 \right)^{1/2} \quad (5)$$

Here, a_{ij} is the isotropic hyperfine coupling constant of the j th nuclei in radical i . In Figure 2a, the half-saturation fields of the MFEs of RP_n and RP_m are represented by $\mathbf{B}_{1/2}$ and $\mathbf{B}_{1/2}^*$, respectively. At zero field, since the triplet and singlet radical pairs are degenerate, the T--S conversions of both RP_n and RP_m occur. Because the T--S conversion of RP_m is much faster than that of RP_n as mentioned above, the enrichment of ^{73}Ge is observed for the cage product. An increase of \mathbf{B} from 0 G to \mathbf{B}_1 ($\approx 2\mathbf{B}_{1/2}$) primarily affects RP_n , in which its $\text{T}_{\pm 1}\text{--S}$ conversion is induced by small a_{ij} values of protons. Therefore, the $\text{T}_{\pm 1}\text{--S}$ conversion of RP_n is almost blocked at $\mathbf{B} = \mathbf{B}_1 \approx 2\mathbf{B}_{1/2}$ as shown by case A of Figure 2. In RP_m , however, the $\mathbf{B}_{1/2}^*$ value is much larger than the $\mathbf{B}_{1/2}$ value, because RP_m

involves a ^{73}Ge -centered radical. Thus, the $\text{T}_{\pm 1}\text{--S}$ conversion of RP_m is not blocked at $\mathbf{B} = \mathbf{B}_1$ as shown by case B of Figure 2. The $\delta(^{73}\text{Ge})$ value at $\mathbf{B} = \mathbf{B}_1$, therefore, becomes larger than that at $\mathbf{B} = 0$ G. With increasing \mathbf{B} from \mathbf{B}_1 , a gradual blocking of the $\text{T}_{\pm 1}\text{--S}$ conversion starts to occur for RP_m . Thus, $\delta(^{73}\text{Ge})$ value starts to decrease with increasing \mathbf{B} from \mathbf{B}_1 . Finally, the decrease in the δ value is saturated at $\mathbf{B} = \mathbf{B}_2 \approx 2\mathbf{B}_{1/2}^*$ as shown by case C of Figure 2. The magnetic field dependence of the $\delta(^{73}\text{Ge})$ value due to the HFCM, therefore, can be summarized as follows: The δ value increases with increasing \mathbf{B} ($0 \text{ G} \leq \mathbf{B} \leq \mathbf{B}_1$), attaining the maximum value at $\mathbf{B} = \mathbf{B}_1$ ($\approx 2\mathbf{B}_{1/2}$). With increasing \mathbf{B} from \mathbf{B}_1 , the δ value decreases, becoming saturated at $\mathbf{B} = \mathbf{B}_2$ ($\approx 2\mathbf{B}_{1/2}^*$) as shown in Figure 2a.

In the present reaction, the $\mathbf{B}_{1/2}$ value of RP_n is calculated to be 18.3 G with the reported hyperfine coupling constants ($a_{\text{CH}_3} = 0.56$ G and $a_{\text{CH}_2} = 4.75$ G for $\text{Et}_3\text{Ge}^\bullet$ ¹⁹ and $a_o = 3.21$ G, $a_m = 1.23$ G, $a_p = 3.64$ G, and $a_{\text{OH}} = 2.91$ G for BPH^\bullet ²⁰). On the other hand, the hyperfine coupling constant of ^{73}Ge of $\text{Et}_3\text{Ge}^\bullet$ has not yet been reported, but it seems to be similar to that of the trimethylgermyl radical which has been reported to be 84.7 G.²¹ Using this value, we estimate the $\mathbf{B}_{1/2}^*$ value of RP_m to be 828 G. Therefore, if the blocking of the $\text{T}_{\pm 1}\text{--S}$ conversion occurs through the HFCM, the $\delta(^{73}\text{Ge})$ value is expected to attain the maximum value around 40 G ($\approx \mathbf{B}_1$), but the decrease of the $\delta(^{73}\text{Ge})$ value is expected to be saturated around 1.7 kG ($\approx \mathbf{B}_2$). In the present study, however, the maximum $\delta(^{73}\text{Ge})$ value was obtained at 500 G and the decrease of the δ value was not saturated even at 10 kG as shown in Figure 1. Thus, the magnetic field dependence observed for the δ value in the present reaction cannot be explained by the HFCM.

On the other hand, according to the RM, the $\text{T}_{\pm 1}\text{--S}$ conversion through the RM occurs by the anisotropic HFCs. In this mechanism, the $\text{T}_{\pm 1}\text{--S}$ conversion rates of RP_n and RP_m decrease gradually with increasing \mathbf{B} from 0 G, but their conversion should not be blocked at \mathbf{B}_1 and \mathbf{B}_2 , respectively. However, with increasing \mathbf{B} from \mathbf{B}_1 , the $\text{T}_{\pm 1}\text{--S}$ conversion of RP_n should be almost blocked at $\mathbf{B} = \mathbf{B}_1' > \mathbf{B}_1$ as shown by case D of Figure 2, because the $\text{T}_{\pm 1}\text{--S}$ conversion rate of RP_n becomes negligible at $\mathbf{B} = \mathbf{B}_1'$. At this stage, the $\text{T}_{\pm 1}\text{--S}$ conversion of RP_m is not blocked as shown by case E of Figure 2. Thus, the δ value increases with increasing \mathbf{B} from 0 G to \mathbf{B}_1' as shown in Figure 2b. At higher fields ($\mathbf{B} > \mathbf{B}_1'$), a gradual blocking of the $\text{T}_{\pm 1}\text{--S}$ conversion also starts to occur for RP_m . Thus, the δ value starts to decrease with increasing \mathbf{B} from \mathbf{B}_1' as shown in Figure 2b. Finally, the $\text{T}_{\pm 1}\text{--S}$ conversion of RP_m is almost blocked at $\mathbf{B} = \mathbf{B}_2' > \mathbf{B}_2$ as shown by case F of Figure 2.

In the present study, the magnetic fields of \mathbf{B}_1' and \mathbf{B}_2' cannot be calculated exactly, because the anisotropic HFCs of $\text{Et}_3\text{Ge}^\bullet$ and BPH^\bullet have never been observed. However, the magnetic field dependence of the isotope enrichment observed for the present reaction can qualitatively be explained by the RM for the following reasons: (1) Since the radical pair generated in the present reaction involves the triethylgermyl radical, the anisotropic HFC of ^{73}Ge seems to be fairly large. (2) The maximum $\delta(^{73}\text{Ge})$ value was obtained at 500 G which is much larger than that (40 G) expected from the HFCM. (3) The decrease of the δ value was not saturated even at 10 kG. Thus,

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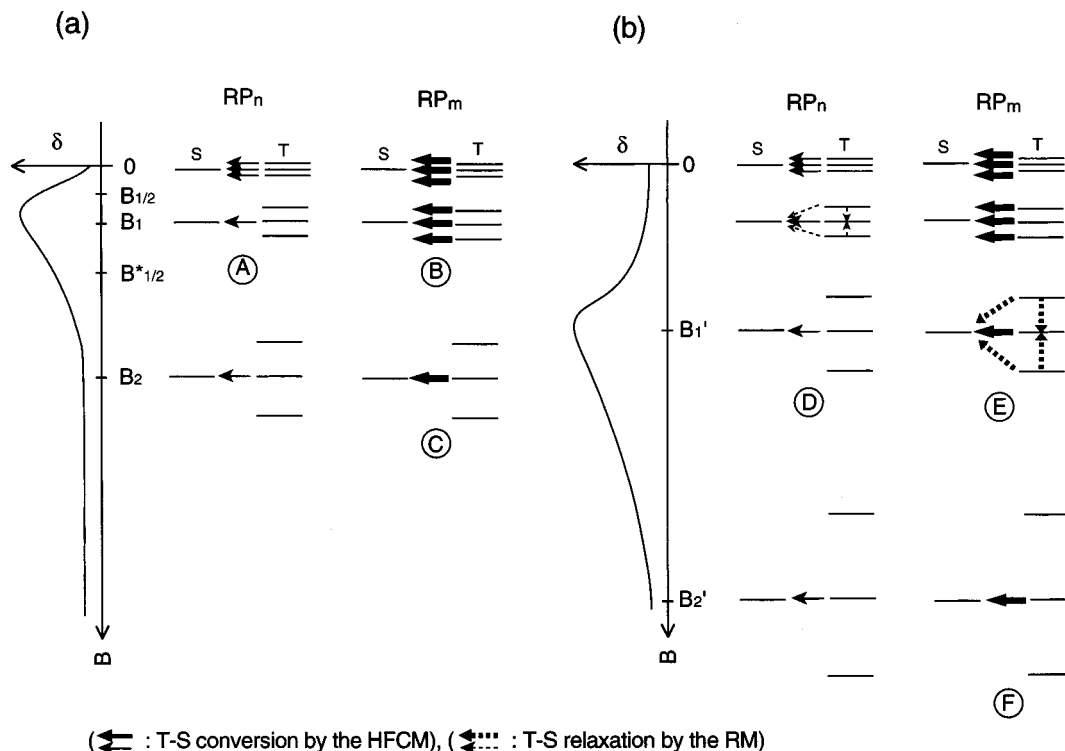


Figure 2. Schematic energy diagram of singlet and triplet radical pairs and the magnetic field dependence of isotope enrichment (δ) by the HFCM and RM: (a) in the case of the HFCM, (b) in the case of the RM. Here, RP_n represents a radical pair involving a nonmagnetic ^{70}Ge , ^{72}Ge , ^{74}Ge , or ^{76}Ge and RP_m that involving a magnetic ^{73}Ge .

the present magnetic field dependence of the δ value was concluded to be due to the RM. Such magnetic isotope enrichment by the RM was theoretically proposed by Salikhov,⁶ but no experimental result has ever been reported until now.²² Therefore, the present study is the first experimental report on the isotope enrichment due to the RM.

In a partially reversible reaction system such as the previous one,⁷ the isotope enrichment depends on the conversion yield. Thus, the larger the isotope enrichment, the higher the conversion yield (and therefore the lower the product yield). Actually, in the previous reaction,⁷ we had to continue the reaction until 93% conversion in order to enrich ^{73}Ge by 4%. This means that the yield of the product involving enriched ^{73}Ge is as small as 7%. On the other hand, in an irreversible reaction system, the isotope enrichment is independent of the product yield but only dependent on the γ value ($= k_2^*/k_2$). We, therefore, can expect to obtain a large isotope enrichment with a high product

yield if we choose a suitable irreversible reaction. In the present study, the isotope enrichment (5.3%) and the yield of the cage product (25%) were certainly larger than those observed in the previous study⁷ for a partially reversible reaction system. In the present study, we have found that the hydrogen abstraction reactions of triplet carbonyls are suitable for the magnetic isotope enrichment of heavy atoms.

Conclusion

In the present study, we have succeeded in enriching ^{73}Ge using a general photochemical reaction system of hydrogen abstraction of triplet benzophenone. The observed magnetic field dependence of the isotope enrichment has the following characteristic features: (1) The magnetic field of the maximum δ (^{73}Ge) value is fairly large. (2) The decrease of the δ (^{73}Ge) value is not saturated even at 10 kG. This magnetic field dependence can be explained by the RM. The irreversible reaction system such as the present one is suitable for the large isotope enrichment with high product yield. The enrichments of many other heavy isotopes are expected to be observed with similar hydrogen abstraction reactions of triplet carbonyls.

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(22) Similar large experimental $B_{1/2}$ values were reported by Turro et al. (Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Weed, G. C.; Kraeutler, B. *J. Am. Chem. Soc.* **1980**, *102*, 4843. Turro, N. J.; Mattay, J. *J. Am. Chem. Soc.* **1981**, *103*, 4200), but they explained their magnetic field dependence only with the HFCM. Although Steiner suggested^{1b} that the experimental $B_{1/2}$ values reported by Turro et al. were significantly larger than those calculated with the HFCM, he did not refer to the RM.