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Free radicals formed by reaction of germane with hydrogen atoms in xenon matrix at very low temperatures

K. Nakamura, N. Masaki, M. Okamoto, and S. Sato
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

K. Shimokoshi
Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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The radicals formed by the reaction of GeH_4 with H in the Xe matrix were investigated by electron spin resonance (ESR) spectroscopy at very low temperatures. The radicals observed were identified as GeH_3 and GeH_5. The newly observed radical GeH_5 is considered as the intermediate of the reaction $H + GeH_4 \rightarrow H_2 + GeH_3$. The ESR parameters of these radicals were determined by numerical deconvolution of the observed spectra.

I. INTRODUCTION

The properties of silane (SiH_4) and germane (GeH_4) have been extensively studied because of their importance in the semiconductor industry. Reactions of hydrogen atoms with silane and germane in the gas phase have also been studied.[1–3] The results indicated that the rates of the reactions were even faster than the addition reaction of hydrogen atom to ethylene. It has also been suggested that the reactions: $H + SiH_4 \rightarrow H_2 + SiH_3$ and $H + GeH_4 \rightarrow H_2 + GeH_3$, involve intermediate adducts SiH_5 and GeH_5, respectively.[1,4] A spectroscopic observation of SiH_5 and GeH_5, therefore, would be of great importance to determine the electronic and geometric structures of the radicals and their roles in the chemical processes.

Matrix isolation spectroscopy is an invaluable method for investigating the structure and chemistry of reactive intermediates such as free radicals. The reactions of hydrogen atoms with some organic compounds in low temperature matrices were studied extensively by electron spin resonance (ESR) spectroscopy.[5,6] Recently, we have studied the reaction of SiH_4 with H formed by the photolysis of HI in the matrices of Xe and Kr at the temperatures between 4.2 and 100 K and found that SiH_5 is formed as an intermediate of the reaction: $SiH_4 + H \rightarrow SiH_3 + H_2$.[7]

In the present paper, we report the results of the ESR studies on the reaction of GeH_4 with H atoms in a Xe matrix at low temperatures. The analysis of the spectrum of the newly observed radical GeH_5 will be described.

II. EXPERIMENT

The matrix substance Xe and H_2 obtained from Takachiho Co., GeH_4 from Tori Chemical Co., and I_2 from Koso Chemical Co. were used without further purification. The hydrogen iodide was synthesized from H_2 and I_2 by catalytic reaction on platinized asbestos. Gaseous mixtures of Xe, GeH_4, and HI were condensed in an ESR quartz tube at 77 K. The ESR measurements at low temperatures were made by use of a cryostat, whose bottom was connected to quartz tube which could be inserted into the *X*-band ESR cavity. The concentrations of GeH_4 and HI were varied from 0.001 to 0.1 mol %.

Photolysis was carried out with a high pressure mercury lamp with a filter (I_2–KI solution) to cut off the light with wavelengths shorter than 250 nm. The spectrometer used for the ESR measurement was a JES-FE2XG. The resonance frequency and magnetic field were monitored by a TR-5211C frequency counter and PMR field meter. The thermal annealing at 77 K was performed by transferring the sample tube into the liquid-nitrogen Dewar flask.

III. RESULTS

A typical example of an ESR spectrum obtained for a Xe/GeH_4(0.1 mol %)/HI(0.1 mol %) mixture photolyzed at 4.2 K for 5 min is shown in Fig. 1. The spectrum consists of two components: intense outer signals and a weak central signal. The outer signals are from H atoms and exhibit characteristic superhyperfine structures[8,9] due to the coupling with the magnetic nuclei of ^{129}Xe and ^{131}Xe. H atoms produced by photolysis of HI in Xe matrix are known to be efficiently trapped at 4.2 K.[5,9] The central part of the spectrum, expanded at slow sweep, is shown in Fig. 2(a). The

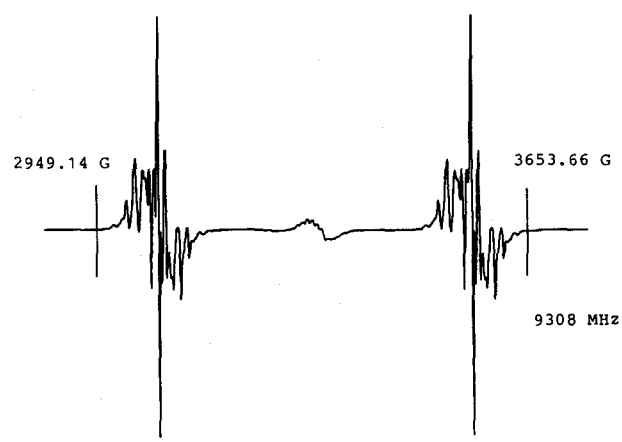

FIG. 1. The ESR spectrum obtained from the Xe/GeH_4(0.1 mol %)/HI(0.1 mol %) mixture after photolysis at 4.2 K.

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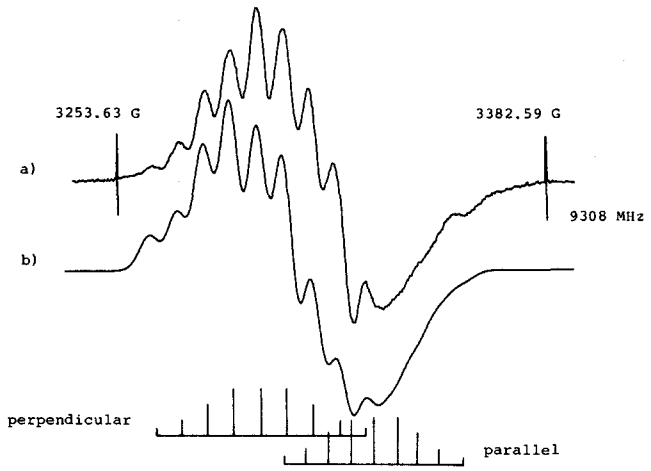

FIG. 2. The expanded ESR spectra of the central part of the spectrum shown in Fig. 1: (a) the observed spectrum; (b) the calculated spectrum using ESR parameters; (I) $g_\perp = 2.0169, g_\parallel = 1.9965, A_\perp$ (quartet) = 15.90 G, $A_\parallel$ (quartet) = 13.50 G, $A_\perp$ (triplet) = 7.85 G, $A_\parallel$ (triplet) = 6.66 G, and (II) $g = 2.0073$, A(triplet) = 14.5 G with mixing ratio of (I):(II) = 10:2 and the Gaussian linewidth of two components: 6.5 and 14.5 G, respectively. The stick diagram indicates the hyperfine line positions of the component (I).

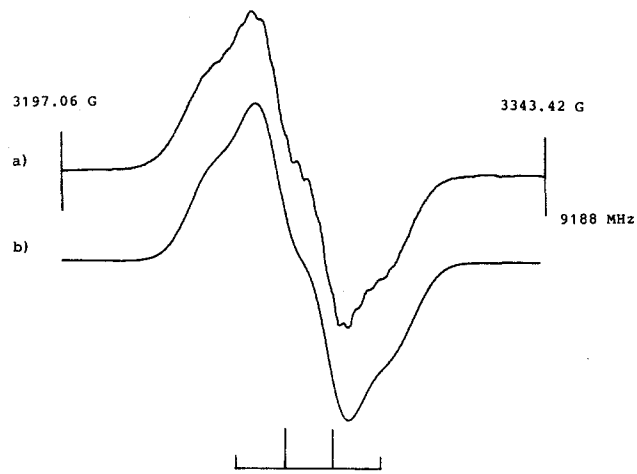

FIG. 3. The ESR spectrum obtained at 4.2 K after thermal annealing at 77 K: (a) the observed spectrum; (b) the calculated spectrum using the ESR parameters: $g = 2.0073$, A(triplet) = 14.5 G and the Gaussian linewidth of 16.0 G.

spectrum consists of a partially resolved multiplet with at least nine lines and exhibits a large g anisotropy. The hyperfine structure of the spectrum could be analyzed as the superposition of two components: (I) a quartet of triplets with $g_\perp > g_\parallel$ (II) a broad symmetric signal which looks like a singlet. The line shape due to these components could be well reproduced by the calculated spectrum as shown in Fig. 2(b) using the ESR parameters for each species: (I) $g_\perp = 2.0169$, $g_\parallel = 1.9965$, $A_\perp$ (quartet) = 15.90 G, $A_\parallel$ (quartet) = 13.50 G, $A_\perp$ (triplet) = 7.85 G, $A_\parallel$ (triplet) = 6.66 G, and (II) $g = 2.0073$, A (triplet) = 14.5 G with the mixing ratio of (I):(II) = 10:2 and the Gaussian linewidth of two components: 6.5 and 14.5 G, respectively. The stick diagram shows the hyperfine lines of the component (I). The perpendicular feature is well resolved, while the parallel one is smeared out. Consequently, it is difficult to determine the coupling constants exactly for parallel component for the hyperfine interaction.

The reactions of detrapped H atoms have been studied by measuring the spectrum at 4.2 K after annealing at 77 K. H atoms are known to be detrapped at 35–50 K[5] and migrate through the Xe matrix to react with germane molecules. By annealing at 77 K, the outer signals of H atoms completely disappeared and the central signal changed to an intense broad singlet centered at $g = \sim 2.0073$. Figure 3(a) shows the spectrum observed after annealing, whose intensity is 30 times larger than that of the signal shown in Fig. 2(a). A poorly resolved structure observed on a broad singlet is different from that of the spectrum shown in Fig. 2(a). Figure 3(b) shows the calculated spectrum using the ESR parameters: $g = 2.0073$, A(triplet) = 14.5 G, and the Gaussian linewidth of 16.0 G.

IV. DISCUSSION

The ESR spectrum of GeH_3 obtained by γ irradiation of GeH_4 at 4.2 K has been reported by Gordy *et al.*[10,11] In the Xe matrix, the spectrum is a very broad but symmetrical singlet centered at $g = 2.0073 \pm 0.0010$. The feature of the spectrum shown in Fig. 3(a) is much the same as that reported for GeH_3, although the present spectrum has a little

TABLE I. ESR parameters of GeH_5 and SiH_5.

Radical	g factors	Hyperfine couplings (G)	Matrix	Reference
$GeH_5(D_{3h})$	$g_\perp = 2.0169$	$A_\perp$ (3H) = 15.90 ± 0.20	Xe	This work
	± 0.0002	$A_\perp$ (2H) = 7.85 ± 0.35		
	$g_\parallel = 1.9965$	$A_\parallel$ (3H) = 13.5 ± 2.0		
	± 0.0005	$A_\parallel$ (2H) = 6.7 ± 2.0		
$SiH_5(D_{3h})$	2.0024	A (3H) = 9.30	Xe	7
		A (3H) = 2.45		
$SiH_5(D_{3h})$	2.0014	A (3H) = 7.98	Kr	7
		A (2H) = 2.45		
$SiH_5(C_{4v})$	2.0016	A (4H) = 8.70	Xe	7
		A (1H) = 24.50		

TABLE II. ESR parameters of GeH_3 and SiH_3.

Radical	g factors	Hyperfine couplings (G)	Matrix	Reference
GeH_3	2.0073 ± 0.0002	14.5 ± 1.5	Xe	This work
GeH_3	2.0073 ± 0.0010		Xe	11
GeH_3	$g_\perp = 2.017$	15 ± 2	Kr	11
	$g_\parallel = 2.003$			
SiH_3	2.0030	8.10	Xe	7
SiH_3	$g_\parallel = 2.0013$	$A_\perp = 7.84$	Kr	7
	$g_\parallel = 2.0012$	$A_\parallel = 8.15$		
SiH_3	$g_\perp = 2.0014$	$A_\perp = 7.4$	Kr	15
	$g_\parallel = 2.0012$	$A_\parallel = 8.1$		

better resolution than that reported previously. The g factor obtained is about 2.0073 which is the same as that reported for GeH_3. The spectrum shown in Fig. 3(a) obtained after annealing, therefore, may be assigned as due to GeH_3. Previously, we observed well resolved lines due to SiH_3 radicals interacting with magnetic nuclei of Xe on the broad spectrum of SiH_3 and estimated the coupling constants of ^{129}Xe and ^{131}Xe.[12] A poorly resolved structure observed on a broad singlet might be due to superhyperfine interaction of GeH_3 with magnetic nuclei of Xe.

The spectrum of quartet of triplets observed immediately after photolysis is reasonably explained by the hyperfine interaction of five protons: $H_a \times 2 + H_b \times 3$ with unpaired electron on Ge. The most plausible candidate for this radical is GeH_5 with D_{3h} symmetry. According to the theoretical calculations of Hartmann *et al.*,[13] GeH_5 is able to take two stable forms, D_{3h} and C_{4v}, in which the radical with D_{3h} has larger stabilization energy. In the case of SiH_5, the spectra due to both symmetries, D_{3h} and C_{4v}, have been observed in the matrix of Xe at 4.2 K,[7] although three forms of D_{3h}, C_{4v}, and C_{3v} were predicted by the theoretical calculations.[3,14] At 40 K in the Xe matrix and at 4.2 K in the Kr matrix was observed the spectrum due only to D_{3h} symmetry. In the case of GeH_5, only D_{3h} symmetry may be stable in the Xe matrix at 4.2 K.

Comparison between the proton hyperfine couplings in SiH_3 and SiH_5 with D_{3h} symmetry shows that the coupling constant of three equivalent protons in SiH_5 is nearly equal to that of SiH_3. A similar relation may be expected between GeH_5 and GeH_3. In fact, the coupling constant of the three equivalent protons obtained from the spectrum shown in Fig. 2(a) is close to that of GeH_3 previously reported in a Kr matrix.[10,11] The ESR parameters obtained for GeH_5 and GeH_3 are listed in Tables I and II, respectively, along with those for SiH_5 and SiH_3 previously reported.[7,11,15]

The observation of the ESR spectrum of GeH_5 radicals suggests that the reaction

$$H + GeH_4 \rightarrow H_2 + GeH_3 \qquad (1)$$

involves the formation of GeH_5 as an unstable intermediate, which easily converts to $GeH_3 + H_2$ at the temperature between 4.2 and 77 K. A broad component comprised in the spectrum shown in Fig. 2 might be due to GeH_3 formed by the conversion of GeH_5 during photolysis at 4.2 K. Choo *et al.*[1] studied the reaction of hydrogen atoms with silane and germane in a discharge flow system and reported that the activated complex for reaction (1) in the gas phase differs from the simple linear structure proposed for the usual hydrogen transfer reaction (H_3Ge–H–H), suggesting the possibility of the formation of an intermediate adduct GeH_5. It is very likely that this intermediate adduct is stabilized in the low temperature Xe matrix.

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