# Germane Decomposition: Kinetic and Thermochemical Data

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Abstract—Rate constants for the two stages of germane dissociation (GeH<sub>4</sub>  $\longrightarrow$  GeH<sub>2</sub> + H<sub>2</sub>(I) and GeH<sub>2</sub>  $\longrightarrow$  Ge + H<sub>2</sub>(II)) have been derived from the studies of the chemiluminescence kinetics during germane dissociation in the presence of nitrous oxide behind shock waves at 1060–1300 K and the full density equal to ~10<sup>-5</sup> mol/cm<sup>3</sup>. Analysis in terms of the RRKM model gave the following expressions for the rate constants of these reactions in the high and low pressure limits:  $k_{1,\infty} = 2.0 \times 10^{14} \exp(-208.0/RT) \text{ s}^{-1}$ ;  $k_{1,0} = 1.7 \times 10^{18} (1000/T)^{3.85} \exp(-208.0/RT) \text{ cm}^3/(\text{mol s})$ ; and  $k_{2,0} = 2.8 \times 10^{15} (1000/T)^{1.32} \exp(-135.0/RT) \text{ cm}^3/(\text{mol s})$ . The results, in combination with the available enthalpies of formation of radical GeH<sub>2</sub>, show that the back reaction for stage (I) has an energy barrier of about 66 kJ/mol.

**DOI:** 10.1134/S0023158407050023

The thermal dissociation of germane GeH<sub>4</sub> attracts the attention of researchers for its use in the production of high-purity germanium and  $Si_{1-x}G_x$  films for highspeed electronic devices (see [1] and references cited) and for its potential for use as a germanium atom source in kinetic studies.

GeH<sub>4</sub> thermolysis was studied in the batch mode [2, 3], with a pressure increment being recorded, and on a onepulse shock tube [4], with the chromatographic detection of decomposition products. Germane decomposition was also studied [5] in a shock tube with the atomic-absorption detection of germanium atoms at low starting germane concentrations ([GeH<sub>4</sub>]  $\approx$  (3–5) × 10<sup>13</sup> cm<sup>-3</sup>) at temperatures in the range of 1200–1500 K.

Newman et al. [4] and Votintsev et al. [5] showed that germanium decomposition in the gas occurs in two stages:

 $GeH_4 \longrightarrow GeH_2 + H_2,$  (I)

$$GeH_2 \longrightarrow Ge + H_2,$$
 (II)

the rate constant of reaction (I) was determined as a function of temperature and (in [5]) as a function of pressure.

Although the mechanism of germane dissociation is a full analogue of silane dissociation [6–8], a quantitative difference between the respective kinetic parameters of these processes was noted even in [4, 5]. Moreover, it was suggested that qualitative distinctions exist, in particular, significant barriers to the back reactions (–I) and (–II) of germane dissociation, which are not observed for silane decomposition [6, 7]. In later works [1, 9], it was shown on the basis of experimental data that, indeed, back reaction (–I) has a barrier of 40–70 kJ/mol. However, the rate constant and the barrier height for reaction (II) and the

barrier height for back reaction (–II) remained an open question. Inasmuch as thermochemical and kinetic data for reaction (I) are also limited, it is also pertinent to refine analogous parameters for the first stage.

In this work, kinetic data for germane decomposition are obtained by measuring chemiluminescence profiles during germane decomposition in the presence of nitrous oxide. Similar measurements in the course of silane decomposition gave rate constants for both stages of the process [10]. Hager et al. [11, 12] observed chemiluminescence in the reaction of germanium atoms with nitrous oxide and identified the relevant electron transitions in the GeO molecule.

### **EXPERIMENTAL**

The experiments were carried out in a shock tube at temperatures of 1060–1300 K and the total density equal to ~10<sup>-5</sup> mol/cm<sup>3</sup>. Test blends contained  $1.0 \times 10^{-3}\%$  $GeH_4$  and 1.0 or 3.0%  $N_2O$  in argon. Chemiluminescence was recorded in the region of the  $a^{3}\Sigma^{+} \longrightarrow X^{1}\Sigma^{+}$ transition in the GeO molecule [11, 12]. The required spectral range was separated with an SS-8 glass light filter ( $\lambda = 410 \pm 60$  nm). The light signal was converted to an electric signal by an FEU-39A photomultiplier and recorded by an S9-8 digital oscillograph. The lower bound of the temperature range was determined from the provision of obtaining an acceptable signal-to-noise ratio; the upper boundary was determined from the constraint that the interaction rate of monooxygen formed upon N<sub>2</sub>O decomposition is low compared to the germane dissociation rate.



Fig. 1. Chemiluminescence oscillograms for germane dissociation in the presence of nitrous oxide under the following conditions: 1250 K,  $[Ar] = 1.0 \times 10^{-5} \text{ mol/cm}^3$ ,  $[GeH_4] = 1.0 \times 10^{-10} \text{ mol/cm}^3$ ,  $[N_2O] = 1.0 \times 10^{-7} \text{ mol/cm}^3$ , and  $\lambda = 410 \pm 60 \text{ nm}$ .

Blanks carried out with blends containing  $GeH_4$  or  $N_2O$  alone did not show luminescence in the range of the temperatures studied.

# **RESULTS AND DISCUSSION**

By analogy with the scheme suggested for the description of chemiluminescence profiles during silane dissociation [10], we describe the temporal behavior of chemiluminescence by the following scheme (asterisks mark molecules in the electron-excited state):

$$GeH_2 + N_2O \longrightarrow H_2GeO^* + N_2, \qquad (III)$$

$$Ge + N_2O \longrightarrow GeO^* + N_2,$$
 (IV)

$$GeO^* + M \longrightarrow GeO + M,$$
 (V)

$$H_2GeO^* + M \longrightarrow H_2GeO + M,$$
 (VI)

$$GeO^* \longrightarrow GeO + hv,$$
 (VII)

$$H_2GeO^* \longrightarrow H_2GeO + hv.$$
 (VIII)

The quantum-chemical calculations of the enthalpies of formation for  $H_2$ GeO [13] show that reaction (III) is sufficiently exothermic to yield excited H<sub>2</sub>GeO\* molecules, which luminesce in the separated spectral range. However, we have no data whether the H<sub>2</sub>GeO molecule has proper electron levels. In addition, we did not observe, as it was in the reaction  $SiH_2 + N_2O \longrightarrow$  $H_2SiO^* + N_2$ , that the chemiluminescence profile depended on the N<sub>2</sub>O concentration. This means that the rate of reaction (III) is low, at least, far lower than the rate of the analogous reaction of SiH<sub>2</sub>, which is also relatively low [10, 14]. Another piece of evidence in favor of the assumption that H<sub>2</sub>GeO\* contributes only insignificantly to the observed chemiluminescence is that Hager et al. [12] did not observe chemiluminescence from H<sub>2</sub>GeO\* for the reaction between the products of  $\text{GeH}_4$  decomposition in a glow discharge and  $N_2O$ .

Thus, GeO\* is likely the main source of chemiluminescence in the system under consideration. For the task at hand (for the derivation of the rate constants of reactions (I) and (II) from the chemiluminescence profiles), however, the percentage contribution of GeO\* and H<sub>2</sub>GeO\* is immaterial. The only requirement is that the characteristic yield time of germanium atoms and the characteristic quenching times for GeO\* and H<sub>2</sub>GeO\* be far shorter than the characteristic times of reactions (I) and (II). According to Fontijn et al. [15], the characteristic time of the reaction between germanium and N<sub>2</sub>O for the N<sub>2</sub>O concentrations and temperatures used in this work are less than 1 µs. The sufficiently short lifetime of GeO\* and, probably, H<sub>2</sub>GeO\* (if this molecule is formed) also follows from the blanks, which were carried out at ~1700 K and in which the characteristic luminescence decomposition time was  $\sim 3-4 \mu s$ . In view of the high rates of GeO\* and H<sub>2</sub>GeO\* deactivation and the reaction between germanium and  $N_2O$ , we can demonstrate that quasi-steadystate requirements are fulfilled for these species (Ge, GeO\*, and  $H_2$ GeO\*); the chemiluminescence intensity is proportional to the GeH<sub>2</sub> concentration. Recall that a three-fold change in the N<sub>2</sub>O concentration did not effect the shape of the chemiluminescence profile in the germane system, unlike in the silane system. We inferred from this fact that the rate of the reaction of N<sub>2</sub>O with GeH<sub>2</sub> radicals is lower than their dissociation rate. The solution of rate equations for these conditions leads to the following expression for the radiation intensity:

$$I(t) = C[k_1/(k_2 - k_1)][\exp(-k_1 t) - \exp(-k_2 t)].$$
(1)

Here, *C* is a factor which depends on the kinetic and radiation parameters of the reacting blend and the parameters of the recording system but does not depend on time. The absolute value of *C* is immaterial for the method used. Processing the chemiluminescence versus time profiles (Fig. 1) in terms of Eq. (1), we can obtain  $k_1$  and  $k_2$ . Each profile can be described by two sets of rate constants, with  $k_1 > k_2$  or  $k_1 < k_2$ ; however, we proceeded from the inference made in [5] that  $k_1 < k_2$ .

The derived rate constant versus temperature plots for reactions (I) and (II) are shown in Figs. 2 and 3. For comparison, Fig. 2 displays the data for reaction (I) at close pressures obtained using the atomic-absorption measurements of the temporal evolution of the germanium atom concentration [5]. A good match is observed.

The RRKM model was used to calculate the rate constants for reaction (I) on the basis of the numerical solution of the microkinetic equation in the same way as for silane dissociation [7]. The required parameters are listed in the table. The variable parameter was the reaction-barrier height. The best fit was obtained for the

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**Fig. 2.** Rate constant of the first stage of GeH<sub>4</sub> dissociation (reaction (I)) versus temperature, derived from the chemiluminescence versus time curves in the presence of (1) 1.0 and (2) 3.0% N<sub>2</sub>O, (3) data derived from atomic-absorption measurements at similar pressure values [5], and (4, 5) calculations for  $E_1 = (4)$  208.0, (5') 200, and (5'') 220 kJ/mol.

reaction barrier equal to  $E_1 = 208.0$  kJ/mol. This value is slightly lower that the value derived by Votintsev et al. ( $E_1 = 218.8$  kJ/mol [5]), because in our model, the frequency factor for the rate constant in the high pressure limit ( $A_1 = 2.0 \times 10^{14}$  s<sup>-1</sup>; derived by Simka et al. from quantum-chemical calculations [1]) was substantially lower than the value derived by Votintsev et al. ( $A_1 = 3.0 \times 10^{15}$  s<sup>-1</sup>, an estimate). The value of  $E_1 =$ 208.0 kJ/mol is noticeably lower than the respective value for silane dissociation (245 kJ/mol [7]).

The rate constants for the first stage of germane decomposition in the high and low pressure limits in a temperature range of 1000–1500 K can be represented as follows (with argon as the diluent gas, and the activation energy expressed in kJ/mol):

$$k_{1,\infty} = 2.0 \times 10^{14} \exp(-208.0/RT), \text{ s}^{-1},$$
  
 $k_{1,0} = 1.7 \times 10^{18} (1000/T)^{3.85}$   
 $\times \exp(-208.0/RT), \text{ cm}^3/(\text{mol s}).$ 

Because at pressures up to several tens of atmospheres the decomposition of three-atom molecules occurs in the low-pressure limit, we need not numerically solve the microkinetic equation in calculating the rate constant for reaction (II). For germylene (GeH<sub>2</sub>) dissociation, the rate constant was calculated in the

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**Fig. 3.** Rate constant of GeH<sub>2</sub> dissociation derived from the chemiluminescence versus time curves in the presence of (1) 1.0 and (2) 3.0% N<sub>2</sub>O: (3, 4) calculated for  $E_2 = (3)$  135.0, (4') 130, and (4'') 140 kJ/mol.

same way as for silylene (SiH<sub>2</sub>) dissociation [6]. The required parameters are displayed in the table. The variable parameter was the reaction-barrier height. The best fit was achieved for the reaction barrier equal to  $E_2 = 135.0 \text{ kJ/mol}$ . This value is substantially lower than the same parameter for SiH<sub>2</sub> dissociation (160 kJ/mol [6]).

The relevant rate constant for germylene dissociation under an argon atmosphere at 1000–1500 K can be represented as follows (with the activation energy expressed in kJ/mol):

$$k_{2,0} = 2.8 \times 10^{15} (1000/T)^{1.32}$$
  
  $\times \exp(-135.0/RT), \text{ cm}^3/(\text{mol s})$ 

The barrier heights for the back reactions (–I) and (–II) were calculated from the enthalpy changes and barrier heights for reactions (I) and (II) (these quantities were known). The overall enthalpy change for reactions (I) and (II), i.e., for GeH<sub>4</sub>  $\longrightarrow$  Ge + 2H<sub>2</sub>, is well known ( $\Delta H_{1,0}^{\circ} + \Delta H_{2,0}^{\circ} = 267.8$  kJ/mol, as  $\Delta H_{f,0}^{\circ}$  (GeH<sub>4</sub>) = 101.2 kJ/mol,  $\Delta H_{f,0}^{\circ}$  (Ge) = 369.0 kJ/mol, and  $\Delta H_{f,0}^{\circ}$  (H<sub>2</sub>) = 0 kJ/mol; see [22] and references cited therein). Therefore, it is sufficient to determine the enthalpy change in reaction (I) from the enthalpies of formation of the GeH<sub>2</sub> radical and the GeH<sub>4</sub> molecule ( $\Delta H_{1,0}^{\circ} = \Delta H_{f,0}^{\circ}$  (GeH<sub>2</sub>) +  $\Delta H_{f,0}^{\circ}$  (H<sub>2</sub>) –  $\Delta H_{f,0}^{\circ}$  (GeH<sub>4</sub>)). The enthalpy of formation of this radical was estimated

#### **SMIRNOV**

Parameters used in the calculations of rate constants for	for GeH <sub>2</sub>	$_1$ and GeH <sub>2</sub>	dissociation
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Parameter	Notes, sources		
GeH <sub>4</sub>			
Vibration frequencies, cm <sup>-1</sup>			
$v_1 = 2106$			
$v_2 = 930.6 (2)$	[16]		
$v_3 = 2111.8 (3)$			
$v_4 = 819.3 (3)$			
Dissociation energy of GeH <sub>2</sub> -H <sub>2</sub> bond, 208.0 kJ/mol	Chosen to fit the measured temperature dependence of $k_1$		
Frequency factor for the rate constant of reaction (I) in the high-pressure limit, $A_{\infty} = 2.0 \times 10^{14} \text{ s}^{-1}$	Calculated by quantum-chemical techniques [1]		
Correction for weak collisions, $\beta_w = 50/T$	Assumed on the basis of analysis of data in [17]		
Rate constant of binary collisions $Z = 2.85 \times 10^{14} \times (1000/T)^{0.3} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Calculated from the molar volume and boiling temperatures of $GeH_4$ and Ar [18, 19]		
GeH <sub>2</sub>			
Vibration frequencies, cm <sup>-1</sup>	Frequencies for the ${}^{1}A_{1}$ state, an experiment [20]; for the ${}^{3}B_{1}$		
$v_1 = 1887 \ (1185)$	state (in parentheses), calculations [21]; the energy difference		
$v_2 = 920 \ (924)$	between the ${}^{*}B_{1}$ and ${}^{*}A_{1}$ states, 79.5 kJ/mol, calculations [21]		
$v_3 = 1864 \ (2063)$			
Activation-barrier energy, 135.0 kJ/mol	Chosen to fit the measured temperature dependence of $k_2$		
$\beta_c = 50/T$	as for GeH <sub>4</sub>		
$Z = 2.5 \times 10^{14} \times (1000/T)^{0.3} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Assumed by analogy with SiH <sub>2</sub> [6]		

on the basis of quantum-mechanical and experimental data. Unfortunately, both the experimental and calculation data had high scatters. The  $\Delta H_{f,0}^{\circ}$  (GeH<sub>2</sub>) value was derived from Li's data [23] using the following rela-



**Fig. 4.** Enthalpy changes in reaction (I) calculated from data of various researchers: (1) an experiment, (2) quantumchemical calculations, (3) an average, and (4) the lower estimate obtained in this work. The uncertainty bars for the measured values indicate the experimental error; for the calculations, the scatter of the values obtained by different quantum-chemical methods.

tionship:  $\Delta H_{f,0}^{\circ}$  (GeH<sub>2</sub>) =  $\Delta H_{f,0}^{\circ}$  (Ge<sub>2</sub>H<sub>6</sub>) +  $E_0 - \Delta H_{f,0}^{\circ}$  (GeH<sub>4</sub>) = 233.9 ± 12.0 kJ/mol, where  $E_0$  is the barrier height for the reaction Ge<sub>2</sub>H<sub>6</sub>  $\longrightarrow$  GeH<sub>4</sub> + GeH<sub>2</sub> (155 kJ/mol [23]). The value of  $\Delta H_{f,0}^{\circ}$  (Ge<sub>2</sub>H<sub>6</sub>) = 180.2 kJ/mol was taken from [24]. In the same way, the Noble and Walsh data [25] give  $\Delta H_{f,0}^{\circ}$  (GeH<sub>2</sub>) = 238.1 ± 12.0 kJ/mol. The respective enthalpy changes in reaction (I) are shown in Fig. 4; the average  $\Delta H_{1,0}^{\circ}$  value for all data displayed in this figure is 141.8 kJ/mol.

Figure 5 displays the energy diagram for germane dissociation, designed using the results of this work and the literature data. The dissociation of the GeH<sub>2</sub> radical from the ground state  ${}^{1}A_{1}$  to Ge( ${}^{3}P$ ) and H<sub>2</sub>( ${}^{1}\Sigma$ ) being spin-forbidden, this reaction likely involves the transition to the triplet term GeH<sub>2</sub> ( ${}^{3}B_{1}$ ), as in the dissociation of CO<sub>2</sub>, N<sub>2</sub>O, and other three-atom molecules [29].

Our results, in combination with the related literature, indicate the existence of a significant energy barrier to the recombination reaction  $\text{GeH}_2 + \text{H}_2 \longrightarrow$  $\text{GeH}_4$  (~66 kJ/mol). For comparison, the barrier to the similar reaction involving silylene (SiH<sub>2</sub> + H<sub>2</sub>  $\longrightarrow$  SiH<sub>4</sub>) is virtually nonexistent (1.26 kJ/mol [7]).

The significant scatter of the enthalpies of formation keeps us from unambiguously deciding whether an energy barrier to the recombination reaction  $\text{Ge} + \text{H}_2 \longrightarrow \text{GeH}_2$  exists or not.

To summarize, we have obtained kinetic and thermochemical data about the first stage of germane thermolysis. We have measured for the first time the rate

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**Fig. 5.** Energy diagram for germane dissociation (TS1 and TS2 are the transient states for reactions (I) and (II)); the energies are expressed in kJ/mol.

constant for the second thermolysis stage, which is the elimination of a hydrogen molecule from the germylene radical. A more detailed description of this system requires additional studies; in particular, the recombinations of a germanium atom and a germylene radical with dihydrogen should be studied.

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