

24 March 2000

Chemical Physics Letters 319 (2000) 529-534

CHEMICAL PHYSICS LETTERS

www.elsevier.nl/locate/cplett

Temperature dependence of germylene reactions with acetylene, trimethylsilane, and phenylgermane

Ula N. Alexander ^a, Keith D. King ^b, Warren D. Lawrance ^{a,*}

^a Department of Chemistry, Flinders University, GPO Box 2100, Adelaide, S.A. 5001, Australia ^b Department of Chemical Engineering, Adelaide University, Adelaide, S.A. 5005, Australia

Received 3 December 1999; in final form 2 February 2000

Abstract

Gas-phase reaction rate constants have been determined over the temperature range 295–436 K for the reactions of germylene, GeH₂, with acetylene (GeH₂ addition across a triple bond), trimethylsilane (GeH₂ insertion into a Si–H bond), and phenylgermane. The room-temperature rate constant for germylene reacting with benzene has been measured and is found to be a factor of ~ 300 smaller than that for phenylgermane, indicating that the latter reacts by GeH₂ insertion into the Ge–H bonds. A negative temperature dependence is observed in all cases. The activation energies, obtained from weighted linear fits to the data over the experimental temperature range, are -3.5 ± 0.3 , -11.0 ± 0.4 , and -3.6 ± 0.3 kJ mol⁻¹ for acetylene, trimethylsilane, and phenylgermane, respectively, while the respective frequency factors, log(A/cm^3 molecule⁻¹ s⁻¹), are -10.5 ± 0.1 , -11.8 ± 0.1 , -10.1 ± 0.1 . © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The first direct kinetic measurements of germylene, GeH₂, have recently been reported by Walsh's group [1] using the technique of laser flash photolysis combined with time-resolved laser resonant absorption. This species is of considerable interest due to its relevance to chemical vapour deposition [2–4]. Becerra et al. [5] have also determined the temperature dependence of the insertion of GeH₂ into the Ge–H bond of triethylgermane (Et₃GeH), reporting the first activation energy for a germylene reaction. Most recently, Becerra et al. have completed a study of the temperature dependence of the reaction of GeH₂ with germane (GeH₄) [6].

We have recently become interested in the kinetics of germylene as an extension of our work on the other group-IV hydride radicals singlet methylene $({}^{1}CH_{2})$ and silvlene (SiH₂) and have reported rate constants for GeH₂ with *i*-butylene, trimethylsilane, acetylene, and phenylgermane [7]. Here we report the results of studies of the temperature dependence of GeH₂ with acetylene, trimethylsilane, and phenylgermane. The reaction with acetylene provides insight into the activation energy for GeH₂ addition across a triple bond; the reaction with trimethylsilane gives information concerning GeH₂ insertion into an Si-H bond; and the reaction with phenylgermane provides further information on GeH₂ insertion into Ge-H bonds. The activation energy for the latter reaction may be compared with that obtained by Becerra et al. for GeH₂ insertion into the Ge-H bonds in Et₃GeH and GeH₄.

^{*} Corresponding author. Fax: +61-8-8201-3035; e-mail: warren.lawrance@flinders.edu.au

^{0009-2614/00/\$ -} see front matter © 2000 Elsevier Science B.V. All rights reserved. PII: \$0009-2614(00)00189-5

2. Experimental details

The experimental system is based on that used in our extensive studies of methylene kinetics [8-10] and the features salient to the germylene situation have been described in our earlier paper concerning GeH₂ kinetics [7]. Briefly, an excimer laser operating at 193 nm photolyses phenylgermane to produce GeH₂. Our previous study [7] has shown that under our experimental conditions phenylgermane is a suitable precursor for GeH₂ kinetics, in contrast to earlier observations by Walsh's group [1]. The GeH₂ concentration is followed by time-resolved laser absorption using a single-mode cw ring dye laser tuned to the ⁷⁴GeH₂ band at 17111.31 cm⁻¹. The experiment is performed under conditions such that the reactions are pseudo-first order. To minimise nongermylene contributions to the signal, two sets of decay traces are recorded, one with the laser tuned to a GeH₂ absorption (signal) and one with the laser detuned from GeH₂ (background). The background is subtracted from the signal to provide the GeH₂ decay signal. The precursor, reactant, and a buffer gas flow continuously through the reaction cell.

The rate constants reported here were obtained with a total cell pressure of 10 Torr. The PhGeH₂ pressure was typically 10 mTorr. The reactant pressure was typically varied in the range 0.02–1.0 Torr. SF_6 (99.9%, BOC) was used as the buffer gas as it is an efficient collision partner that does not react with GeH₂. At 10 Torr of SF₆, impurities at the 0.1%level correspond to 10 mTorr, comparable to both the lowest reactant pressure used and the precursor pressure. BOC advise us that the impurities in the SF₆ are air and carbon tetrafluoride. Based on the behaviour of methylene and silylene, and on a comparison of the relative rate constants for reaction by these species and germylene, germylene is not expected to react with any of these impurities at a rate that would be detectable in the experiments [11,12]. Likewise, the reactants used will not be affected by the presence of these impurities. We have established previously that the reactions studied are in the highpressure limit under these conditions [7].

Phenylgermane was synthesised as described by Durig et al. [13]. Trimethylsilane (Fluka, $\geq 97\%$) was used as supplied. Acetylene was synthesised by the addition of water to calcium carbide and purified

by several trap-to-trap distillations to remove the water impurity. Infrared spectra of the resultant sample showed no evidence of impurity.

3. Results and discussion

The experimental observable is the GeH_2 relative concentration as a function of time following the photolysis laser pulse. A typical decay curve is shown in Fig. 1. These decay curves are generally analysed by fitting to a double-exponential function to account for both the rise and fall behaviour. For data with very rapid rise times a single exponential is sufficient. The decay rate constant extracted from the fits is the pseudo-first-order rate constant, k_1 , for the reaction:

 $GeH_2 + R \rightarrow products$.

Since the bimolecular rate constant is related to k_1 by $k_1 = k_2[R]$, a plot of k_1 vs. [R] yields k_2 as the slope.

Fig. 2 shows a plot of pseudo-first-order rate constants vs. Me₃SiH pressure over the range of temperatures studied. This figure is typical of the quality of the data obtained for all reactants. The



Fig. 1. A typical experimental decay trace (in this case for Me_3SiH) showing the variation in relative GeH_2 concentration with time. The points are the experimental data; the solid line shows the least-squares fit to these data. The residuals from the fit are shown below the decay trace.



Fig. 2. Plots of reactant pressure vs. pseudo-first-order rate constant, k_1 , for GeH₂ reaction with Me₃SiH at various temperatures in the range, 295–436 K. The slopes give the second-order rate constant, k_2 . Note that the k_2 values decrease with increasing temperature.

error bars in the figure correspond to one standard deviation, determined by the uncertainty in the fits to each decay trace and by the variation in k_1 values extracted from different decay traces. They do not include other experimental uncertainties which, based on the reproducibility of the rate constants from different runs, are expected to be ~ 10%. A linear least-squares fit to the second-order plot yields the bimolecular rate constant, k_2 , at each temperature. A feature of the data shown in Fig. 2 is that the slopes of the k_1 vs. [R] plots decrease with increasing temperature, in contrast with the usual Arrhenius behaviour. This so-called negative temperature dependence is, however, typical of the behaviour found for similar systems [5,6,12,14]. It arises as a conse-

quence of the reaction mechanism involving the formation of an intermediate complex [15].

The k_2 values extracted from the second-order plots are listed in Table 1. It is interesting at this point to compare the reaction efficiencies for each of the reactants at a particular temperature. We define reaction efficiency as the ratio of the observed k_2 value to the calculated Lennard-Jones collision rate for the two species involved. A value of one indicates reaction on every encounter. The values at 293 K are 0.20 for Me_3SiH , 0.30 for C_2H_2 , and 0.64 for PhGeH₃. This indicates broadly comparable efficiencies for GeH₂ insertion into Si-H bonds and addition across the C-C triple bond but significantly higher efficiency for insertion into Ge-H bonds. The k_2 value for the reaction of GeH₂ with the alkene $i-C_4H_8$ reported in Ref. [7] corresponds to a reaction efficiency of 0.31. It appears that GeH₂ reaction with a C-C double bond is of comparable efficiency to reaction with a C–C triple bond.

Arrhenius plots of the k_2 values are shown in Fig. 3. It can be seen from the Arrhenius plots that the data suggest a slight curvature compared to the linear fit. Given the limited temperature range of the data and the small changes in the magnitude of the rate constants it is premature to conclude that this is definitely the case. Nevertheless, we note that the Arrhenius expression for the temperature dependence of the reaction rate constants is an empirically determined relation that successfully describes the temperature dependence of the rate constants of many simple reactions [16]. The negative temperature dependence shows that these reactions are more complex and so the Arrhenius equation is not necessarily applicable to the description of their temperature dependence. Systems comparable to those studied

Table 1

Pressure-independent bimolecular rate constants, k_2 (cm³ molecule⁻¹ s⁻¹) measured for germylene reacting with acetylene, trimethylsilane, and phenylgermane in SF₆ bath gas at a total pressure of 10 Torr, from 295 to 436 K

Temperature (K)	$k_2 (\times 10^{-10})$ for reactant			
	Me ₃ SiH	C_2H_2	PhGeH ₃	
295	1.03 ± 0.05	1.38 ± 0.04	3.00 ± 0.10	
337	0.85 ± 0.02	1.34 ± 0.06	3.06 ± 0.09	
373	0.57 ± 0.014	1.14 ± 0.02	2.76 ± 0.04	
417	0.35 ± 0.006	0.92 ± 0.02	2.30 ± 0.07	
436	0.29 ± 0.028	0.77 ± 0.05	2.05 ± 0.04	
337 373 417 436	$\begin{array}{c} 0.05 \pm 0.02 \\ 0.85 \pm 0.02 \\ 0.57 \pm 0.014 \\ 0.35 \pm 0.006 \\ 0.29 \pm 0.028 \end{array}$	$\begin{array}{c} 1.38 \pm 0.04 \\ 1.34 \pm 0.06 \\ 1.14 \pm 0.02 \\ 0.92 \pm 0.02 \\ 0.77 \pm 0.05 \end{array}$	$3.06 \pm 0.09 \\ 3.06 \pm 0.09 \\ 2.76 \pm 0.04 \\ 2.30 \pm 0.07 \\ 2.05 \pm 0.04$	



Fig. 3. Arrhenius plots of the temperature dependence of the rate constants for GeH_2 reaction with C_2H_2 (open squares), Me_3SiH (open circles), and PhGeH₃ (filled circles). The lines are weighted least-squares linear fits to the data.

here also show curved Arrhenius plots. Examples include the reaction of SiH_2 with SiH_4 [17], GeH_2 with Et_3GeH [5], and SiH_2 with Me_3SiH [5].

Beyond the Arrhenius equation there are a variety of temperature-dependent forms for the rate constant that can be used to fit the data. Laidler discusses these various forms in detail [16]. The recommended form when data do not conform to the Arrhenius equation is

$$k = AT^{m} \exp(-E_0/RT), \qquad (1)$$

where E_0 is the activation energy at 0 K, *m* is a variable parameter, and the remaining parameters have their usual meaning. We have fitted our data to Eq. (1) but find that, in comparison to the Arrhenius

fits where *m* is zero, the presence of an extra parameter leads to the fitting parameters being poorly constrained. There is large uncertainty in the values determined and they are of dubious worth. This arises since the fits are of three parameters to only five data points, each with an associated uncertainty, which span a limited temperature range. The only feature of note from these fits is that in all cases the values of *m* must be large and negative (in the range -10 to -2, depending on the reactant) in order to match the trends in the data.

An Arrhenius treatment of each data set in principle indicates the frequency factor, A, from the intercept and the activation energy for the reaction, E_a , from the slope of the plot. The frequency factor yields information on the entropy difference between the reactants and the transition state. This is, of course, only true when the Arrhenius equation is an appropriate description of the behaviour. Fitting the data to the Arrhenius equation using a weighted fit yields the Arrhenius parameters given in Table 2. This table includes values for other similar systems for comparison. We have included in this table values for the GeH₂ + trimethylsilane reaction that Becerra et al. have recently made available to us prior to publication [18].

The Arrhenius parameters determined by Becerra et al. for germylene reacting with trimethylsilane are the only instance where there is another set of data with which ours may be directly compared. A number of important points arise when comparing our results with those of Becerra et al.: (1) Becerra et al. do not see a curvature when their data, which extend to higher temperature than ours, are plotted in the

Table 2

Activation energy, E_a (kJ mol⁻¹), and pre-exponential factor, A (cm³ molecule⁻¹ s⁻¹), from Arrhenius fit to GeH₂ + Me₃SiH, C₂H₂ and PhGeH₃ data and comparison with literature values

Reaction	$\log(A)$	E_{a}	Ref.	
$\overline{\text{GeH}_2 + \text{Me}_3\text{SiH}}$	-11.8 ± 0.1	-11.0 ± 0.4	this work	
	-12.15 ± 0.06	-11.58 ± 0.44	[18]	
$GeH_2 + C_2H_2$	-10.5 ± 0.1	-3.5 ± 0.3	this work	
$GeH_2 + PhGeH_3$	-10.1 ± 0.1	-3.6 ± 0.3	this work	
$\text{GeH}_2 + \text{GeH}_4$	-11.17 ± 0.10	-5.2 ± 0.7	[6]	
$GeH_2 + Et_3GeH$	-11.43 ± 0.15	-10.64 ± 1.11	[5]	
$SiH_2 + Me_3SiH$	-10.11 ± 0.05	-2.93 ± 0.33	[12]	
$\operatorname{SiH}_2 + \operatorname{C}_2\operatorname{H}_2$	-9.99 ± 0.03	-3.3 ± 0.19	[19]	

Arrhenius form; (2) the Arrhenius parameters determined by the two groups are very similar. We find $E_a = -11.0 \pm 0.4 \text{ kJ mol}^{-1}$ while Becerra et al. obtain a value of $-11.58 \pm 0.44 \text{ kJ mol}^{-1}$; and (3) while the frequency factors are similar, $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -11.8 \pm 0.1$ (us) vs. -12.15 ± 0.06 (Becerra et al.), the difference arises from a systematic difference in the magnitudes of the rate constants determined by the two groups. We consistently measure rate constants slightly larger than those found by Becerra et al. While this was noted previously [7], we are unable to account for this trend.

The activation energies, listed in Table 2, show that the trimethylsilane reaction rate is the most strongly dependent on temperature while the phenylgermane reaction rate is the least temperature dependent. The frequency factors suggest that the reactions $GeH_2 + phenylgermane$ and $GeH_2 + acetylene$ have a smaller change in geometry between the reactants and the transition state than does the $GeH_2 +$ trimethylsilane reaction. Both the activation energies for these reactions, which are small and negative, and the frequency factors are of the order seen for analogous silylene reactions (see Table 2).

The magnitude of the activation energy found here for GeH₂ + PhGeH₃ is similar to the value reported by Becerra et al. for GeH₂ + Et₃GeH [5] and is a factor of ~ 2 greater than that measured for GeH₂ + GeH₄ [6]. We have measured the rate constant for GeH₂ with benzene and find it to be $(1 \pm 1) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, a factor of ~ 300 less than the rate for GeH₂ + phenylgermane. Thus, in the latter case reaction proceeds via insertion into the Ge–H bonds, as is the case for GeH₂ + Et₃GeH and GeH₂ + GeH₄.

From Table 2 it can be seen that the activation energies for silylene and germylene reacting with acetylene are very similar, as are the log A values. This indicates that the rate constants for individual steps in the reaction mechanism are similar for both reactants, with similar energetics and changes in entropy involved. However, this is not the case for these species reacting with trimethylsilane. For germylene, the activation energy for reaction with trimethylsilane is a factor of ~ 3.7 greater in magnitude than the value for silylene reacting with this species. The log A values are likewise significantly different, with the germylene value being -11.8 compared with a silylene value of -10.1. Becerra et al. have discussed the significance of such changes in the context of the GeH₂ + triethylgermane reaction [5]. Essentially, the probable mechanism is via a H-bonded intermediate Me₃SiH · · · XH₂, leading to the product Me₃SiXH₃, X = Si, Ge. If we denote the rate constant for formation of the complex by k_1 , that for its decomposition to reactants by k_2 , the larger *A* value for silylene indicates that the ratio k_2/k_{-1} is larger for silylene than for germylene. There are no data available for the temperature dependence of the reaction rate for silylene with phenylgermane with which to compare.

Acknowledgements

This work was supported by the Australian Research Council. U.N.A. acknowledges the financial support provided by an Australian Postgraduate Award. The help of the Mechanical and Engineering Workshop staff at Flinders University is gratefully acknowledged. We thank Professor Robin Walsh for fruitful discussions and correspondence, and for providing preprints of his work prior to publication. We also thank Professor John Barker for helpful comments on the manuscript.

References

- R. Becerra, S.E. Boganov, M.P. Egorov, O.M. Nefedov, R. Walsh, Chem. Phys. Lett. 260 (1996) 433.
- [2] W. Du, L.A. Keeling, C.M. Greenlief, J. Vac. Sci. Technol. A 12 (1994) 2284.
- [3] H. Simka, M. Hierlemann, M. Utz, K.S. Jensen, J. Electrochem. Soc. 143 (1996) 2646.
- [4] C. Isobe, H. Cho, J.E. Crowell, Surf. Sci. 295 (1993) 117.
- [5] R. Becerra, S.E. Boganov, M.P. Egorov, O.M. Nefedov, R. Walsh, Mendeleev Commun. 3 (1997) 87.
- [6] R. Becerra, S.E. Boganov, M.P. Egorov, V.I. Faustov, O.M. Nefedov, R. Walsh, J. Am. Chem. Soc. 120 (1998) 12657.
- [7] U.N. Alexander, N.A. Trout, K.D. King, W.D. Lawrance, Chem. Phys. Lett. 299 (1999) 291.
- [8] W.S. Staker, K.D. King, G.J. Gutsche, W.D. Lawrance, J. Chem. Soc., Faraday Trans. 87 (1991) 2421.
- [9] W.S. Staker, K.D. King, G.J. Gutsche, W.D. Lawrance, J. Chem. Soc., Faraday Trans. 88 (1992) 659.

- [10] F.J. Hayes, G.J. Gutsche, W.D. Lawrance, W.S. Staker, K.D. King, Combust. Flame 100 (1995) 653.
- [11] F.J. Hayes, W.D. Lawrance, W.S. Staker, K.D. King, Chem. Phys. Lett. 231 (1994) 530.
- [12] R. Becerra, R. Walsh, in: R.G. Compton, G. Hancock (Eds.), Research in Chemical Kinetics, Vol. 3, Elsevier, Amsterdam, 1995.
- [13] J.R. Durig, C.W. Sink, J.G. Turner, J. Chem. Phys. 49 (1968) 3422.
- [14] F. Hayes, W.D. Lawrance, W.S. Staker, K.D. King, J. Phys. Chem. 100 (1996) 11314.

- [15] J. Troe, J. Chem. Soc., Faraday Trans. 90 (1994) 2303.
- [16] K.J. Laidler, Chemical Kinetics, 3rd edn., Harper and Row, New York, 1987.
- [17] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, M. Gordon, J. Chem. Soc., Faraday Trans. 91 (1995) 2723.
- [18] R. Becerra, R. Walsh, Phys. Chem. Chem. Phys. 1 (1999) 5301.
- [19] R. Becerra, R. Walsh, Int. J. Chem. Kinet. 26 (1994) 45.