

11 January 1999

Chemical Physics Letters 299 (1999) 291-295

CHEMICAL PHYSICS LETTERS

Phenylgermane as a suitable precursor for laser flash photolysis measurements of germylene kinetics

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Received 25 September 1998; in final form 21 October 1998

Abstract

R. Becerra, S.E. Boganov, M.P. Egorov, O.M. Nefedov and R. Walsh [Chem. Phys. Lett. 260 (1996) 433] reported the first direct kinetic measurements of germylene, GeH_2 , using two precursors, 3,4-dimethylgermacyclopentene and phenylgermane. They report that phenylgermane produces anomalously low reaction rate constants. We have re-examined this issue and measure rate constants using phenylgermane that agree with the values reported by Becerra et al. using the precursor 3,4-dimethylgermacyclopentene. The first direct rate constant measurement for GeH_2 + phenylgermane is reported. All rate constants are found to be independent of the total pressure (measured to 50 Torr). Photolysis of phenylgermane at 248 and 193 nm yields the same values for the rate constants within the experimental uncertainty, suggesting that relaxation of vibrationally excited germylene is not altering the measured reaction rate constants. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The kinetics of GeH_n (n = 1-3) radicals are of considerable interest due to their relevance to chemical vapour deposition [1–3]. Becerra et al. [4] (hereafter referred to as BBENW) have recently reported the first absolute kinetic measurements of germylene, GeH₂, using two precursors, 3,4-dimethylgermacyclopentene (DMGCP) and phenylgermane (PhGeH₃). They report that the use of PhGeH₃ leads in all the cases studied to the measured reaction rate constants being anomalously low. For example, the reaction rate constant found for GeH₂ reaction with

trimethylsilane is 2.8×10^{-11} cm³ molecule⁻¹ s⁻¹ with PhGeH₃ precursor, but is almost 3-fold higher $(8.2 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹) with DMGCP as the precursor at 10 Torr total pressure. The larger scatter in their data and an increased dust problem with PhGeH₃ led these authors to believe that the DMGCP data were providing the more reliable rate constants. Despite investigation using modelling of possible mechanisms, they were unable to account for the discrepancy in rate constants for these different precursors.

When different rate constants are obtained for the same species prepared by different photolysis schemes there is a degree of uncertainty as to the validity of the reported rate constants. Consequently we have undertaken a series of experiments to mea-

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sure the reaction rate constants for GeH_2 prepared by photolysis of PhGeH₃ with the aim of identifying the mechanism responsible for the anomalous rate constants found for this precursor. Identification of the mechanism that leads to anomalous rate constants for PhGeH₃ would add confidence that the values reported for DMGCP are indeed accurate. While the experimental technique used in our study is similar in most respects to that used by BBENW, our method incorporates two features, a flow cell and background subtraction, that have the potential to eliminate possible sources of error that might account for the discrepancy reported in BBENW's work.

Using PhGeH₃ we have reproduced the reaction rate constants reported by BBENW for GeH₂ using DMGCP as a precursor, indicating: (1) that PhGeH₃ is a suitable GeH₂ precursor for kinetic measurements under appropriate experimental conditions; and (2) that BBENW's assertion that their DMGCP data provide the more reliable set of rate constants is correct. We find that photolysis of PhGeH₃ at wavelengths of 193 and 248 nm leads to the same values for the GeH₂ rate constants, indicating that vibrational relaxation is not affecting the measured values. We here report the details of this investigation.

2. Experimental details

The experimental system is based on that used in our extensive studies of methylene kinetics [5-7]. An excimer laser, in this case operating at 193 or 248 nm, photolyses a precursor to produce GeH₂. The GeH₂ concentration is followed by time-resolved laser absorption using a single-mode cw ring dye laser tuned to a band in the GeH₂ absorption spectrum. We have used the ⁷⁴GeH₂ band at 17111.31 cm⁻¹, the same band used by BBENW, which provides a monitor of the population in the ground vibrational state (designated (0,0,0)). The probe laser is multipassed through the cell to achieve a path length of 4 m, thereby increasing the absorption signal. To further increase the signal to noise ratio, a portion of the probe laser is split off prior to the reaction cell and used as a reference. The signal and reference dye laser beams are imaged onto separate photodiodes whose outputs are processed by a differential amplifier, largely removing dye laser intensity fluctuations. The differential amplifier output is recorded using a digital oscilloscope (Hewlett Packard 54510A). Typically between 64 and 128 traces are averaged at each reactant pressure, and a minimum of three such averaged traces are recorded and analysed. The experiment is repeated at a number of reactant pressures. To minimise non-germylene 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 method of analysis of the GeH₂ decay signal is discussed when presenting the results.

The precursor, reactant and a buffer gas continuously flow through the reaction cell (1 m long \times 25 mm dia.) at room temperature (295 K). The flow rate and excimer laser repetition rate are adjusted to ensure that reaction product concentrations are negligible. The gas mixture is controlled using mass flow controllers (MKS 1159B and 2159B). The rate constants reported here were obtained with a total cell pressure of 10 Torr. The PhGeH₃ pressure was typically 10 mTorr for experiments using 193 nm photolysis and 25 mTorr using 248 nm photolysis. The reactant pressure was typically varied in the range 20–120 mTorr. N₂ (99.9%, BOC) and SF_6 (99.9%, BOC) were used as buffer gases. Reaction rate constants were found to be independent of the buffer gas used.

BBENW used 193 nm as their PhGeH₃ photolysis wavelength. In order to provide a direct comparison with their experiment we have also used this wavelength. However, for *i*-butylene and trimethylsilane, the two reactants with the largest discrepancy between the reported rate constants using DMGCP vs. PhGeH₃ as precursors, we have used 248 nm as an additional photolysis wavelength. Should vibrationally excited GeH₂ be produced in the photolysis step, its collisional relaxation provides a growth mechanism for the GeH₂ (0,0,0) and might explain the observations of BBENW. Such circumstances can be illuminated using different photolysis wavelengths: a difference in the GeH₂ vibrational populations will be produced using different photolysis photon energies and so different GeH₂ removal rate constants would be observed. This effect has been reported for singlet methylene kinetics [8].

Phenylgermane was synthesised as described by Durig et al. [9]. *i*-Butylene (Matheson, CP grade, \geq 99%) and trimethylsilane (Fluka, \geq 97%) were used as supplied. Because both *i*-butylene and trimethylsilane react efficiently with germylene the presence of impurities at the levels specified will not affect the reaction rate constants determined. 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 synthesised samples showed no evidence of impurities.

3. Results and discussion

BBENW report four reactants with which they have measured rate constants for GeH_2 using both of their precursors. In all cases they found a difference between the PhGeH₃ and DMGCP results, with PhGeH₃ consistently giving lower reaction rate constants. We have measured rate constants for GeH_2 with three of the same four reactants, viz. acetylene, *i*-butylene and trimethylsilane. The largest discrepancy in reaction rate constants reported by BBENW was for *i*-butylene, where the rate constant for DMGCP precursor is 4.7 times larger than the value with PhGeH₃.



Fig. 1. A typical experimental decay trace 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. Plot of the pseudo-first-order rate constants, k_1 , vs. reactant pressure for $i-C_4H_8$ (248 nm photolysis) and C_2H_2 (193 nm photolysis) at 10 Torr total pressure and 295 K. The slope of the linear least-squares fit to the data is the bimolecular reaction rate constant, k_2 .

The experimental data consist of relative GeH₂ concentration vs. time traces at varying reactant (R) pressures. Generally, these traces are least-squares fit to a double-exponential function to account for both the rise and fall behaviour. For data with very rapid rise times a single-exponential fit is sufficient. The decay rate constant extracted from the fits is the pseudo-first-order rate constant, k_1 , for the reaction: GeH₂ + 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. 1 shows a typical fitted decay curve while Fig. 2 shows plots of k_1 vs. reactant pressure for acetylene with 193 nm photolysis and *i*-butylene with 248 nm photolysis. The error bars in this 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 traces. They do not include other experimental uncertainties which, based on the reproducibility of the rate constants from different runs, are expected to be $\sim 10\%$. The k_2 values extracted from the plots are listed in Table 1. This table also includes the values reported by BBENW for both precursors.

Examination of Table 1 shows that we obtain different reaction rate constants to those reported by

Table 1

Bimolecular rate constants, k_2 (10⁻¹⁰ cm³ molecule⁻¹ s⁻¹), for GeH₂ reacting with various reactants at 10 Torr total pressure and 295 K

Reactant	This Letter (PhGeH ₃ precursor) ^a		Beccera et al. (Ref. [4])		
	193 nm photolysis	248 nm photolysis	DMGCP precursor	PhGeH ₃ precursor	
C,H,	1.38 ± 0.04	-	1.29 ± 0.04	0.94 ± 0.03	_
$i-\tilde{C}_4\tilde{H}_8$	1.41 ± 0.10	1.21 ± 0.05	1.24 ± 0.08	0.26 ± 0.06	
Me ₃ SiH	1.03 ± 0.05	0.92 ± 0.11	0.82 ± 0.01	0.28 ± 0.03	
PhGeH ₃	3.00 ± 0.10	-	-	_	

^aReported errors correspond to one standard deviation and are determined from the uncertainty in the fits to each decay trace, the variation in k_1 values extracted from different traces, and the uncertainties in determining k_2 from the k_1 vs. reactant concentration plots. They do not include other experimental uncertainties which, based on the reproducibility of the rate constants from different runs, are estimated to be $\pm 10\%$.

BBENW with PhGeH₃ as a precursor. However, the reaction rate constants that we have obtained with PhGeH₃ precursor match quite well those measured by BBENW with DMGCP precursor. There is, perhaps, a tendency for our rate constants to lie above those reported by BBENW, but the differences are within the uncertainties of both groups' measurements. The fact that our results agree with BBENW's DMGCP results confirms the accuracy of the rate constants reported for this precursor. This is the first independent verification of these direct GeH₂ reaction rate constant measurements. Our results show that BBENW were correct in assessing DMGCP to be affording the correct reaction rate constants.

BBENW did not report a rate constant for GeH₂ with PhGeH₃ due to the problems they experienced with this precursor. We find dust generation to be less of a problem than is indicated by BBENW in their paper. This has allowed us to determine that the reaction of GeH₂ with PhGeH₃ follows the expected second-order behaviour with a rate constant of (3.0 \pm 0.1) \times 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹.

It is puzzling why our results with $PhGeH_3$ do not match those obtained by BBENW with this precursor. Two major differences in the conditions of the experiment between the two groups are: (1) our experiment uses a flow cell while a static cell is used by BBENW; and (2) we correct the decay traces for non-germylene contributions while BBENW do not. It may be that with $PhGeH_3$ as the precursor in their experiment a product is formed that is interfering with the kinetic measurement.

Within experimental uncertainty no difference was found between the rate constants for GeH_2 reaction

using 248 vs. 193 nm photolysis. It is probable that GeH_2 is produced vibrationally hot at 193 nm, since this is the case with SiH₂ produced from PhSiH₃ at 193 nm [10]. The good agreement between the rate constants from 248 and 193 nm photolysis shows either that vibrational relaxation is rapid, so that (0,0,0) germylene is not continuously produced by vibrational relaxation while we monitor reaction, or that it is sufficiently slow that it does not influence the reaction rate. Measurements of the pressure dependence of the rate constants shows them to be independent of pressure up to 50 Torr, indicating that the former explanation is the most likely. This observation also shows the reactions to be in the high-pressure limit at these pressures.

In summary, we have demonstrated that the reaction rate constants reported by BBENW for GeH_2 using DMGCP as a precursor are reproduced using PhGeH₃ as a precursor. This indicates that BBENW's assertion that these were the more reliable set of rate constants is correct. It further indicates that PhGeH₃ is a suitable GeH_2 precursor for kinetic measurements under appropriate experimental conditions. Photolysis of PhGeH₃ at 193 and 248 nm leads to the same values for the GeH_2 rate constants, indicating that vibrational relaxation is not affecting the measured values.

Acknowledgements

This work was supported by the Australian Research Council. UNA 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.

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