Time-resolved gas-phase kinetic study of the reaction of germylene with propene over the temperature range 293–415 K: the thermal stabilities of germiranes

Rosa Becerra [a], Robin Walsh [b],*

[a] *Instituto de Quimica-Fisica "Rocasolano", C.S.I.C., C/Serrano 119, 28006 Madrid, Spain*
[b] *Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading RG6 6AD, UK*

Dedicated to Professor Oleg Nefedov on the occasion of his 70th birthday

Abstract

Absolute rate constants have been obtained for the title reaction over the pressure range 1–100 Torr (in SF_6 bath gas) and the temperature range 293–415 K, by means of laser flash photolysis to generate and monitor germylene, GeH_2. The reaction showed the characteristic pressure dependence of a third-body assisted association reaction. The high pressure rate constants, obtained by extrapolation, gave the Arrhenius equation:

$$\log(k^\infty/cm^3 \text{ molecule}^{-1} \text{ s}^{-1}) = (-10.86 \pm 0.19) + (7.16 \pm 1.23 \text{ kJ mol}^{-1})/RT \ln 10$$

The parameters correspond to a fast reaction occurring at ca. 59% of the collision rate at room temperature. Collision efficiencies for GeH_2 π-additions are not much less than those of SiH_2. RRKM (Rice, Ramsperger, Kassel, Marcus) modelling, based on a variational transition state consistent with the kinetics, gave a good fit to the data, with the value of $E_o = 105$ kJ mol^{-1} corresponding to $\Delta H° = 122 \pm 12$ kJ mol^{-1} for 2-methylgermirane decomposition. This result in conjunction with other work shows that C-methyl substitution lowers the thermal stability of germirane, and that germiranes are ca. 50–60 kJ mol^{-1} less stable to decomposition than their silirane counterparts. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Germylene; Thermal stabilities; Germiranes; Rate constants

1. Introduction

The reactions of germylene, GeH_2, are of interest both because of their involvement in the breakdown mechanisms of germanes leading to solid germanium (chemical vapour deposition) [1,2] and also because of their involvement in germane [3] and organogermane decompositions [4]. In collaboration with the group of O.M. Nefedov, we have recently begun a series of gas-phase studies of the kinetics of GeH_2 reactions by time-resolved means leading to the first directly measured rate constants for GeH_2 [5–10]. The group of King and Lawrance has also recently begun similar studies [11,12]. Up to now these have mainly focussed on the investigation of insertion reactions of GeH_2 into Ge–H [6,7,12] and Si–H bonds [8,10,12] which have been shown to proceed via association complexes rather similar to those implicated in the insertion reactions of SiH_2 [13–19]. The results confirm that under the conditions of study, GeH_2 reactions, although quite fast, seem to occur more slowly than their SiH_2 counterparts, but also show more selectivity. Moreover, we have also found [6–8,10] that GeH_2 insertion reactions have greater (i.e. more negative) activation energies than the analogous SiH_2 reactions. This indicates that reactions of GeH_2 slow down more than those of SiH_2 at higher temperatures.

In order to increase our understanding of the reactivity of GeH_2, we have investigated its addition reaction with propene. Until now the only reports of kinetic studies of GeH_2 with π-bonded systems are room tem-

---

* Corresponding author. Fax: + 44-118-931-6331.
E-mail address: r.walsh@reading.ac.uk (R. Walsh).

perature studies of the reactions of $GeH_2 + C_2H_2$, i-C_4H_8 and $1,3$-C_4H_6 by us [5] and $GeH_2 + C_2H_2$ over the temperature range 295–436 K by Alexander et al. [12]. These studies indicate, inter alia, that these reactions are also very fast, occurring at only ca. a factor of 3 slower than their SiH_2 counterparts. We have also carried out a study of the reaction of $GeH_2 + C_2H_4$, as yet only presented at conferences [20]. This last system indicated that the rate of the addition process was not only temperature dependent, but also highly pressure dependent. The current study was undertaken to obtain the temperature and pressure dependence of the $GeH_2 + C_3H_6$ system, in order to compare more fully the π-type additions of SiH_2 and GeH_2.

An additional incentive for this study was to gain information about the stability of 2-methylgermirane, the probable product of the addition reaction.

2. Experimental

Germylene kinetic studies have been carried out by the laser flash photolysis technique, details of which have been published previously [5,7]. Only essential and brief details are therefore included here. GeH_2 was produced by the 193 nm flash photolysis of 3,4-dimethyl-1-germacyclopent-3-ene (DMGCP) by use of a Coherent Compex 100 excimer laser. This source reaction is known [5] to proceed as follows:
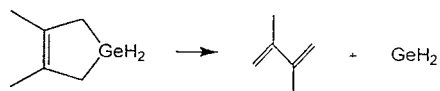
GeH_2 concentrations were monitored in real time by means of a Coherent 699-21 single-mode dye laser pumped by an Innova 90-5 Argon ion laser and operating with Rhodamine 6G. Experiments were carried out
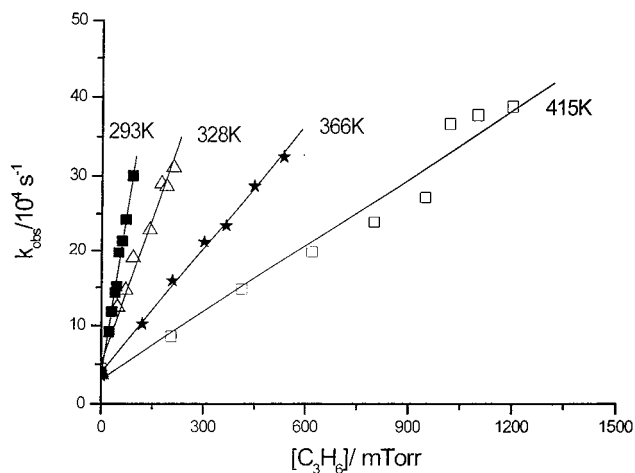
in a variable temperature spectrosil quartz vessel with demountable windows which were regularly cleaned. Photolysis laser pulse energies were typically 50–70 mJ with a variation of $\pm 5\%$. The monitoring laser beam was multipassed up to 36 times through the reaction zone to give an effective path length of up to 1.2 m. The laser wavelength was set by the combined use of a wavemeter (Burleigh WA-20) and referenced to a known coincident transition in the visible spectrum of I_2 vapour and was checked at frequent intervals during the experiments.

The monitoring laser was tuned to 17 111.31 cm^{-1} corresponding to a known strong vibration–rotation transition $(A^1B_1(0,1,0) \leftarrow X^1A_1(0,0,0))$ band) discovered by us previously [5], and recently assigned as the $^PQ_1(6)$ line by intra-cavity laser absorption spectroscopy by Campargue and Escribano [21]. Light signals were measured by a dual photodiode/differential amplifier combination and signal decays were stored in a transient recorder (Datalab DL 910) interfaced to a BBC microcomputer. This was used to average the decays of typically five laser shots (at a repetition rate of 1 or 2 Hz). Signals decays were found to be exponential up to 90% and were fitted by a least-square procedure to provide values for the first-order rate coefficients, k_{obs}, for removal of GeH_2 in the presence of known partial pressures of C_3H_6.

The gas mixtures for photolysis were made up consisting of 3–6 mTorr of DMGCP, variable pressures of C_3H_6 between 30 and 1200 mTorr, and inert diluent bath gas, SF_6, up to total pressures between 1 and 100 Torr. Pressures were measured with capacitance manometers (MKS Baratron).

DMGCP was prepared as previously described [5]. C_3H_6 was obtained from Matheson (99.9%, chemical pure (CP) grade) and SF_6 was obtained from ICI and contained no GC detectable impurities.

3. Results

Checks showed that values for the decay constants, k_{obs}, were not dependent on the exciplex laser energy or the number of photolysis shots. For most experiments five shots of 60 mJ pulse^{-1} were used. A series of experiments was carried out at each of four temperatures in the range 293–416 K. Experiments at the higher temperature of 476 K gave results which were scattered and irreproducible and so the upper limit of measurement was set at 415 K. At each temperature and at 10 Torr total pressure, at least six runs at different partial pressures of C_3H_6 were carried out. The results of these experiments are shown in Fig. 1, which demonstrates the linear dependence of k_{obs} on $[C_3H_6]$, as expected for second-order kinetics. The second-order rate constants, obtained by least-squares

Fig. 1. Second-order plots for reaction of $GeH_2 + C_3H_6$ at 10 Torr (SF_6): ■, 293; △, 328; ★, 366; and □, 415 K.

Table 1
Experimental second-order rate constants for $GeH_2 + C_3H_6$ at 10 Torr (SF_6) and infinite pressure

T (K)	k (SF_6, 10 Torr) [a]	k^{∞} [a,b]
293	0.892 ± 0.031	2.7 ± 0.6
328	0.439 ± 0.021	2.0 ± 0.5
366	0.208 ± 0.003	1.3 ± 0.3
415	0.126 ± 0.008	1.2 ± 0.3

[a] Units: 10^{-10} cm^3 molecule^{-1} s^{-1}.
[b] Obtained by extrapolation (see text).
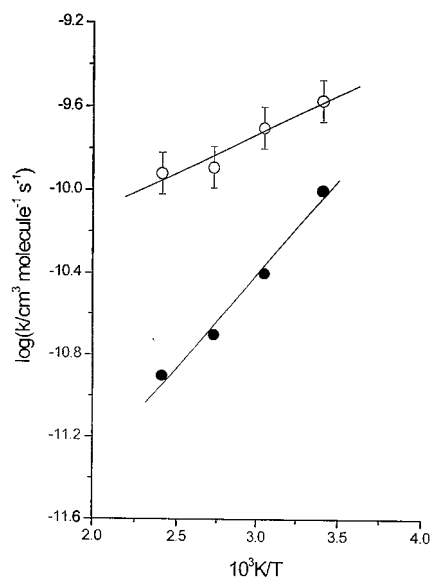
Fig. 2. Arrhenius plots of rate constants for $GeH_2 + C_3H_6$: ○, k^{∞}; and ●, k (10 Torr).
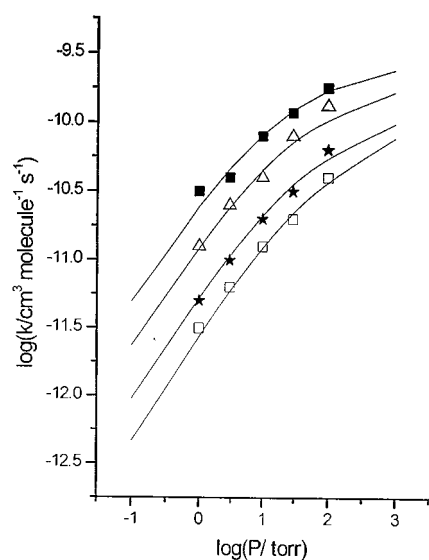

Fig. 3. Pressure dependence of second-order rate constants for $GeH_2 + C_3H_6$ at different temperatures: ■, 293; △, 328; ★, 366; and □, 415 K.

fitting to these plots, are shown in Table 1. The error limits are single standard deviations and are clearly quite small. Table 1 also includes the values of k^{∞}, the rate constants at infinite pressure, obtained by extrapolation with RRKM (Rice, Ramsperger, Kassel, Marcus) theory (see below). These have somewhat larger error limits, because of the uncertainties of the extrapolation. It is clear that the rate constants decrease with temperature (just as has been found for similar SiH_2 addition reactions [22–26]). Arrhenius plots of these rate constants are shown in Fig. 2. Despite some scatter the data give a reasonably linear fit. The following Arrhenius equation for k^{∞} is derived:

$$\log(k^{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$$
$$= (-10.86 \pm 0.19) + (7.16 \pm 1.23 \text{ kJ mol}^{-1})/RT \ln 10$$

In addition to these experiments, another set of runs was carried out at each temperature. In these, the total pressure (SF_6) was varied in the range 1–100 Torr, in order to test the pressure dependence of the second-order rate constants. The data were obtained in the same way as those at 10 Torr, although since second-order behaviour had been established at 10 Torr, only three or four C_3H_6 substrate partial pressures were tried at each total pressure. The rate constant for reaction of GeH_2 with precursor (intercept point on the second-order plots) was found to be pressure independent. The pressure range was limited by practical considerations. Above ca. 100 Torr transient signals became too small and below 1 Torr, pressure measurement uncertainties became significant. The results from these experiments are plotted in Fig. 3, which clearly demonstrates the pressure dependence of the rate constants at each temperature. For convenience, log–log plots are used. The uncertainties are not shown in the figures but they are estimated at ca. $\pm 10\%$.

From the examination of Fig. 3 several points are evident. Rate constants decrease with increasing temperature at all pressures. At a given temperature the rate constants increase with increasing pressure, the extent of the variation being greatest at the highest temperature. These effects are characteristic of a third-body mediated association reaction. In order to try to fit this pressure dependence and also to be able to extrapolate the data to the high pressure limit, k^{∞}, we have carried out RRKM modelling calculations [27], as described in the next section.

4. RRKM calculations

The pressure dependence of an association reaction corresponds exactly to that of the reverse unimolecular dissociation process, providing there are no other per-

Table 2
Estimated thermodynamic and kinetic quantities for 2-methylgermirane decomposition reaction (-1)

| T (K)	$\Delta S°$ (J K^{-1} mol^{-1})	T (K)	$\log(A_{-1})$ (s^{-1})
300	165.2	293	16.73
400	164.9	328	16.68
500	163.2	366	16.62
		415	16.54

Table 3
Molecular and transition-state parameters for RRKM calculations for 2-methylgermirane decomposition at 293 K

	2-Methylgermirane	2-Methylgermirane‡
v (cm^{-1})	2960(6)	2960(6)
	2100(2)	2100(2)
	1450(3)	1450(3)
	1410(1)	1410(1)
	1150(1)	1150(1)
	1120(2)	1120(2)
	1000(2)	1000(2)
	955(1)	1500(1)
	935(1)	935(1)
	825(1)	825(1)
	740(2)	740(2)
	637(1)	60(1)
	500(2)	51(1)
	446(1)	45(1)
	370(1)	35(1)
	420(2)	420(2)
	174(1)	174(1)
Reaction coordinate (cm^{-1})	500	
I^+/I	1	
Path degeneracy	1	
E_o (critical energy)	104.6 kJ mol^{-1} (25.0 kcal mol^{-1})	
Collision number, Z_{LJ} (cm^3 molecule^{-1} s^{-1})	4.06×10^{-10} (SF$_6$)	

Table 4
Temperature dependent parameters used in RRKM calculations for 2-methylgermirane decomposition

	T (K)			
	293	328	366	415
Transition state wavenumbers (cm^{-1})	60	65	70	73
	51	60	60	64
	45	47	50	55
	35	35	40	44
E_o (kJ mol^{-1})	104.6	104.6	104.6	104.6
$\Delta H°$ (kJ mol^{-1})	122.2	122.8	123.4	124.1
Z_{LJ} (10^{-10} cm^3 molecule^{-1} s^{-1})	4.06	4.12	4.19	4.27

turbing reaction channels. Therefore we have carried out RRKM calculations of the pressure dependence of the unimolecular decomposition of the probable reaction product, 2-methylgermirane, viz.

$$H_2Ge\!\!\left\langle\!\!\begin{array}{c} CHMe \\ | \\ CH_2 \end{array}\right. \rightleftharpoons GeH_2 + CH_3\text{-}CH=CH_2 \qquad (-1,1)$$
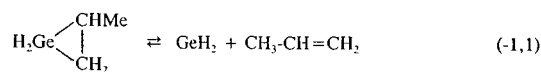
Just as for the parent germirane [20], 2-methylgermirane has never been isolated and therefore its decomposition kinetics are unknown. We are therefore forced to make estimates of the necessary parameters prior to carrying out calculations. Fortunately there is sufficient information of reliable quality to be able to do this. The approach adopted was based on that used earlier for 2-methylsilirane decomposition [26]. First $\Delta S°$ values for reaction ($-1,1$) were assumed the same as those for the silicon analogue [26]. This structural analogy is known to work well for many reaction systems [28]. The $\Delta S°$ values were then combined with the experimental value for A_1 (at infinite pressure) to obtain A_{-1} via the microscopic reversibility relationship, $\ln(A_{-1}/A_1) = \Delta S°/R$. The $\Delta S°$ values and resulting A_{-1} values at the temperatures of interest are shown in Table 2. Because of the temperature dependence of both $\Delta S°$, and the conversion from 1 bar to 1 molecule cm^{-3} standard states, the A_{-1} values show a slight decrease with increasing temperature. Although this behaviour cannot be independently verified, we believe it reflects the variational character of the transition states for many of the decomposition reactions which result in either silylene or germylene formation. In particular it seems to be evident in silirane ring decompositions [25,26].

To obtain the high pressure Arrhenius parameters in the first place, we proceeded as usual [25,26] by making an initial (eyeball) guess at the k^∞ values and then carried out preliminary RRKM calculations (see below), using the curvatures of the derived pressure dependence plots to refine our extrapolations of the data to k^∞. We then repeated the exercise. Nevertheless, we estimate that the final values of k^∞ may still be uncertain by up to $\pm 25\%$, as indicated in Table 1.

The next stage was to assign the vibrational wavenumbers for the 2-methylgermirane molecule and its activated complex at each temperature of decomposition. This was done, for the molecule by judicious adjustment of the wavenumber values for 2-methylsilirane [26] and for the activated complex by alteration of wavenumber values for the transitional modes. This meant increasing the value for the C–C stretching mode but reducing those for the Ge–C stretching and GeH$_2$ wagging, rocking and twisting modes until the entropy of activation and A factor were matched at each temperature. The details of this are shown in Tables 3 and 4. We have assumed, as previously [26], that geometry changes in the decomposing germirane molecule do not

Table 5
Arrhenius parameters for elementary GeH$_2$ and SiH$_2$ addition reactions [a]

Reaction	log A (cm^3 molecule^{-1} s^{-1})	E_a (kJ mol^{-1})	Ref.
GeH$_2$+C$_3$H$_6$	-10.86 ± 0.19	-7.2 ± 1.2	This work
GeH$_2$+C$_2$H$_4$	-10.87 ± 0.14	-6.8 ± 1.0	[20]
GeH$_2$+C$_2$H$_2$	-10.6 ± 0.2	-4.4 ± 1.0	[12]
SiH$_2$+C$_3$H$_6$	-9.79 ± 0.05	-1.9 ± 0.3	[26]
SiH$_2$+C$_2$H$_4$	-9.97 ± 0.03	-2.9 ± 0.2	[25]
SiH$_2$+C$_2$H$_2$	-9.99 ± 0.03	-3.3 ± 0.2	[24]

[a] High pressure limiting values (where known).

lead to significant complications. In modelling the collisional deactivation process, we have used a weak collisional (stepladder) model [27], because there is considerable evidence against the strong collision assumption [29]. The average energy removal parameter, $\langle \Delta E \rangle_{\text{down}}$, which determines the collision efficiency, was taken as 9.6 kJ mol^{-1} (800 cm^{-1}), by analogy with silirane [25] and 2-methylsilirane [26], although variation within the range 8.4–12.0 kJ mol^{-1} had little effect on the fitting.

The key unknown parameter in this calculation was the critical energy, E_o, which was varied in order to obtain the best match with the data. The resulting value (105 kJ mol^{-1}) was treated as fixed for all temperatures, although in variational transition state theory small changes usually occur. This E_o value was used to generate E_a values at each temperature (by addition of thermal energy differences) and finally to obtain $\Delta H°$ values via $\Delta H° = E_{-a} - E_a + RT$. The resulting values of $\Delta H°$ are included in Table 4.

5. Discussion

5.1. Kinetic comparisons and the nature of the addition process

The main experimental purpose of this study was to measure the rate constants and their temperature and pressure dependencies for the reaction of GeH$_2$ + propene for the first time. This has been accomplished and the reaction has been found to have a fairly high A factor and small negative activation energy. Although there is no previous study of this reaction, several illuminating comparisons can nevertheless be made. Table 5 shows the Arrhenius parameters for other GeH$_2$ addition reactions and their SiH$_2$ analogues. The most obviously striking thing about these data are the significantly lower A factors for the GeH$_2$ addition processes compared with their SiH$_2$ counterparts. The GeH$_2$ reactions also have slightly more negative E_a values. This is a very similar situation to that found in the comparison of GeH$_2$ with SiH$_2$ insertion reactions [10]. Because these are nevertheless fast reactions it is also instructive to compare their rate constants with collision numbers. This is done in Table 6 where the comparison is made in terms of Lennard-Jones collision efficiencies. The parameters needed for these estimates were either taken from known sources [30] or earlier papers [19]. It is clear that both the rate constants and the efficiencies of GeH$_2$ addition reactions are almost as high as those of SiH$_2$, with the possible exception of GeH$_2$ + C$_2$H$_2$ (for which, surprisingly, no pressure dependence was reported [12]). Given the uncertainties of extrapolation of the pressure dependence required to obtain these rate constants, they may in fact be close to equal. Certainly, because of the larger negative E_a values, GeH$_2$ reaction rates will approach closer to those of SiH$_2$ at sub-ambient temperatures. Indeed under these conditions both sets of reactions will become encounter controlled.

Table 6
Lennard-Jones collision efficiencies at 298 K for the addition reactions of GeH$_2$ and SiH$_2$

Substrate	GeH$_2$			SiH$_2$		
	k [a]	Z_{LJ} [a,b]	Efficiencies (%)	k [a]	Z_{LJ} [a,b]	Efficiencies (%)
C$_3$H$_6$	2.7 [c]	4.55	59	3.4 [d]	5.31	64
C$_2$H$_4$	2.1 [e]	4.40	48	3.5 [f]	4.92	71
C$_2$H$_2$	1.4 [g]	4.42	32	4.0 [h]	4.90	82

[a] High pressure limiting values, units: 10^{-10} cm^3 molecule^{-1} s^{-1}.
[b] Parameters for evaluating Z_{LJ} given in Ref. [19] (Table 5) and Ref. [30].
[c] This work.
[d] Ref. [26].
[e] Ref. [20].
[f] Ref. [25].
[g] Ref. [24].
[h] Ref. [12] ($P = 10$ Torr).

Table 7
Comparison of decomposition energetics (kJ mol^{-1}) for some germiranes and siliranes

Reaction	E_o (RRKM)	$\Delta H°$	Ref.
2-Methylgermirane → GeH$_2$ + C$_3$H$_6$	105	122	This work
Germirane → GeH$_2$ + C$_2$H$_4$	121	138	[20]
2-Methylsilirane → SiH$_2$ + C$_3$H$_6$	163	176	[26]
Silirane → SiH$_2$ + C$_2$H$_4$	187	201	[25]

The rates of GeH$_2$ addition to C$_3$H$_6$ and C$_2$H$_4$ are virtually identical. Methyl substituents on the alkene are normally expected to enhance the rates of electrophilic processes by making easier the transfer of C=C π-electrons. However, since the reaction rates are so close to their collisional limits this lack of a methyl effect is hardly surprising. The same is true for the analogous SiH$_2$ additions [26].

Theoretical calculations of germylene addition reactions [20,31,32] support the view that they are like those of SiH$_2$ [25,26,33] involving two distinct stages, an initial π-attack or 'electrophilic phase' (donation of C=C π-electrons into the Ge empty 4p orbital), followed by σ-attack or 'nucleophilic phase' (donation of the Ge lone pair electrons into the C=C π*-orbital). The small negative activation energies are nevertheless slightly higher (i.e. more negative) than those normally expected for an association reaction [27,34]. This suggests the possible involvement of an intermediate complex as found for Si–H and Ge–H insertion reactions of GeH$_2$ [6–8,10]. It is still not clear whether such complexes are involved in silylene π-type additions (SiMe$_2$ addition reactions do have similar high negative E_a values [26]). However, the quantum-chemical calculations (MP4/6-31G(d,p) level) of Sakai [31] and (B3LYP/6-31G* level) of Su and Chu [32] on the energy surface of the GeH$_2$ + C$_2$H$_4$ reaction show the involvement of a bound π-complex with a low barrier to rearrangement to germirane. It is not possible on the kinetic evidence alone to distinguish between the intermediate complex mechanism and the alternative entropy bottleneck idea of Houk and colleagues [35].

5.2. RRKM calculations and thermochemistry

The reasonable fit of the RRKM calculations to the pressure dependence of the experimental rate constants lends weight to the conclusion that reaction (1) is a straightforward third-body assisted association process. GC analysis of product mixtures revealed the presence of no product peaks, but this is not surprising since the expected germirane product is even less stable than the undetectable silirane products of silylene addition reactions [25,36].

The main outcome of the modelling exercise is the value for E_o for 2-methylgermirane decomposition leading to $\Delta H°(1, -1) = -122$ kJ mol^{-1}. Uncertainties in this value arise from potential uncertainties in the transition state model (based on the estimated value for A_{-1}) and the collision deactivation model. These problems have been discussed in detail previously [25,26] and generally suggest a maximum uncertainty of ± 12 kJ mol^{-1} in the derived E_o and $\Delta H°$, although the fit to all four temperatures together, and not just one, suggests the probable error is less than this.

Although highly substituted germiranes have been synthesised by Ando and colleagues [37], including even a transient germirane without carbon substituents [38], there are no kinetic studies of germirane decompositions. The modelling studies thus provide the only current means to assess their decomposition rates and thermal stabilities (apart from theoretical calculations). The existing data are shown in Table 7, together with the equivalent figures for silirane analogues. The only other independent information about germirane decomposition comes from theoretical calculations. For germirane decomposition itself, Horner et al. [39] obtained a value of $\Delta H° = 126$ kJ mol^{-1} by a mixture of ab initio calculation and thermochemical reasoning. A figure of 103 kJ mol^{-1} was obtained by Sakai [31] by similar means, although using ab initio means alone (MP4/6-31G(d,p)) a low value of $\Delta E°(+ ZPE$ at 0 K$) = 51.9$ kJ mol^{-1} was found. Su and Chu [32] have most recently obtained a value of 115 kJ mol^{-1} for $\Delta H°$ by ab initio means (B3LYP/6-31G* level). There are no quantum-chemical calculations for 2-methylgermirane. The values for $\Delta H°$ from Table 7 indicate that germiranes are 50–60 kJ mol^{-1} less stable thermally than the equivalent siliranes. The data also show that 2-methyl substitution causes a significant weakening of the germirane ring by ca. 16 kJ mol^{-1}. This points to the probability that the ring strain energy in germirane is increased by C-methyl substitution, just as has been found in the siliranes, but in contrast to the cyclopropanes [26]. This question will be explored in a future publication [40] which will provide full details of our GeH$_2$ + C$_2$H$_4$ studies [20] including quantum-chemical (ab initio) calculations on these systems. It is worth pointing out that the magnitudes of these germirane decomposition (activation) energies are such that, if the right preparative method can be found, they ought to be stable enough to handle and indeed to study their decomposition kinetics. This is a worthy synthetic and mechanistic challenge to fellow organometallic chemists, and is in the spirit that has guided the work of our distinguished colleague, Oleg Nefedov.

Acknowledgements

References

[1] C. Isobe, H. Cho, J.E. Sewell, Surf. Sci. 295 (1993) 117.

[2] W. Du, L.A. Keeling, C.M. Greenlief, J. Vac. Sci. Technol. A 12 (1994) 2281.

[3] C.G. Newman, J. Dzarnoski, M.A. Ring, H.E. O'Neal, Int. J. Chem. Kinet. 12 (1980) 661.

[4] J. Dzarnoski, H.E. O'Neal, M.A. Ring, J. Am. Chem. Soc. 103 (1981) 5740.

[5] R. Becerra, S.E. Boganov, M.P. Egorov, O.M. Nefedov, R. Walsh, Chem. Phys. Lett. 260 (1996) 433.

[6] R. Becerra, S.E. Boganov, M.P. Egorov, O.M. Nefedov, R. Walsh, Mendeleev Commun. (1997) 87.

[7] R. Becerra, S.E. Boganov, M.P. Egorov, V.I. Faustov, O.M. Nefedov, R. Walsh, J. Am. Chem. Soc. 120 (1998) 12657.

[8] R. Becerra, R. Walsh, Phys. Chem. Chem. Phys. 1 (1999) 5301.

[9] R. Becerra, S.E. Boganov, M.P. Egorov, V.I. Faustov, O.M. Nefedov, R. Walsh, Can. J. Chem. 78 (2000) 1428.

[10] R. Becerra, S.E. Boganov, M.P. Egorov, V.I. Faustov, O.M. Nefedov, R. Walsh, Phys. Chem. Chem. Phys. 3 (2001) 184.

[11] U.N. Alexander, N.A. Trout, K.D. King, W.D. Lawrance, Chem. Phys. Lett. 299 (1999) 291.

[12] U.N. Alexander, K.D. King, W.D. Lawrance, Chem. Phys. Lett. 319 (2000) 529.

[13] R. Becerra, R. Walsh, in: R.G. Compton, G. Hancock (Eds.), Research in Chemical Kinetics, vol. 3, Elsevier, Amsterdam, 1995, p. 263.

[14] J.M. Jasinski, R. Becerra, R. Walsh, Chem. Rev. 95 (1995) 1203.

[15] J.E. Baggott, H.M. Frey, P.D. Lightfoot, R. Walsh, I.M. Watts, J. Chem. Soc. Faraday Trans. 86 (1990) 27.

[16] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, M.S. Gordon, J. Am. Chem. Soc. 114 (1992) 2751.

[17] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, M.S. Gordon, J. Chem. Soc. Faraday Trans. 91 (1995) 2723.

[18] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, J. Organomet. Chem. 521 (1996) 343.

[19] R. Becerra, S.E. Boganov, R. Walsh, J. Chem. Soc. Faraday Trans. 94 (1998) 3569.

[20] (a) R. Becerra, S.E. Boganov, M.P. Egorov, O.M. Nefedov, R. Walsh, Paper Presented at the 6th International Conference on the Chemistry of Carbenes and Related Intermediates, St. Petersburg, Russia, May 28–30, 1998;
(b) R. Becerra, S.E. Boganov, M.P. Egorov, O.M. Nefedov, R. Walsh, Paper Presented at the 15th International Symposium on Gas Kinetics, Bilbao, Spain, September 6–10, 1998.

[21] A. Campargue, R. Escribano, Chem. Phys. Lett. 315 (1999) 397.

[22] N. Al-Rubaiey, H.M. Frey, B.P. Mason, C. MacMahon, R. Walsh, Chem. Phys. Lett. 204 (1993) 301.

[23] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, J. Chem. Soc. Chem. Commun. (1993) 1050.

[24] R. Becerra, R. Walsh, Int. J. Chem. Kinet. 26 (1994) 45.

[25] N. Al-Rubaiey, R. Walsh, J. Phys. Chem. 98 (1994) 5303.

[26] N. Al-Rubaiey, I.W. Carpenter, R. Walsh, R. Becerra, M.S. Gordon, J. Phys. Chem. A 102 (1998) 8564.

[27] K.A. Holbrook, M.J. Pilling, S.H. Robertson, Unimolecular Reactions, 2nd ed., Wiley, New York, 1996.

[28] S.W. Benson, Thermochemical Kinetics, 2nd ed., Wiley, New York, 1976.

[29] H. Hippler, J. Troe, in: M.N.R. Ashfold, J.E. Baggott (Eds.), Advances in Gas Phase Photochemistry and Kinetics, vol. 2, Royal Society of Chemistry, London, 1989, p. 209 (Ch. 5).

[30] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York, 1988.

[31] S. Sakai, Int. J. Quantum Chem. 70 (1998) 291.

[32] M.-D. Su, S.-Y. Chu, J. Am. Chem. Soc. 121 (1999) 11478.

[33] F. Anwari, M.S. Gordon, Isr. J. Chem. 23 (1983) 129.

[34] J.W. Davies, M.J. Pilling, in: M.N.R. Ashfold, J.E. Baggott (Eds.), Advances in Gas Phase Photochemistry and Kinetics, vol. 2, Royal Society of Chemistry, London, 1989, p. 105 (Ch. 3).

[35] K.N. Houk, N.G. Rondan, J. Mareda, Tetrahedron 41 (1985) 1555.

[36] J.E. Baggott, M.A. Blitz, H.M. Frey, P.D. Lightfoot, R. Walsh, J. Chem. Soc. Faraday Trans. 2 84 (1988) 515.

[37] W. Ando, H. Ohgaki, Y. Kabe, Angew. Chem. Int. Ed. Engl. 33 (1994) 659.

[38] H. Ohgaki, Y. Kabe, W. Ando, Organometallics 14 (1995) 2139.

[39] D.A. Horner, R.S. Grev, H.F. Schaefer III, J. Am. Chem. Soc. 114 (1992) 2093.

[40] R. Becerra, S.E. Boganov, M.P. Egorov, V.I. Faustov, O.M. Nefedov, R. Walsh, 2001, to be published.