4 January 2002

ELSEVIER

Chemical Physics Letters 351 (2002) 47–52

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Absolute rate constants for the reactions of germylene and dimethylgermylene with dimethylgermane: the deactivating effect of methyl groups in heavy carbenes

Rosa Becerra [a], Mikhail P. Egorov [b], Irina V. Krylova [b], Oleg M. Nefedov [b], Robin Walsh [c,*]

[a] *Instituto de Quimica-Fisica 'Rocasolano', C.S.I.C., C/ Serrano 119, Madrid 28006, Spain*
[b] *N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospekt 47, Moscow 117913, Russian Federation*
[c] *Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading RG6 6AD, UK*

Received 1 October 2001; in final form 15 October 2001

Abstract

Gas-phase rate constants for the title reactions have been obtained by laser flash photolysis at 297 K, by use of photoprecursors, 3,4-dimethyl-1-germacyclopent-3-ene for GeH_2 and pentamethyldigermane for $GeMe_2$. The values obtained were (k (cm^3 $molecule^{-1}$ s^{-1})): $(2.38 \pm 0.11) \times 10^{-10}$ for GeH_2, $(2.26 \pm 0.10) \times 10^{-13}$ for $GeMe_2$. These results show that the insertion reaction of $GeMe_2$ is 1050 times slower than that of GeH_2 into the Ge—H bonds of Me_2GeH_2. This is explained in terms of a general mechanism involving an intermediate H-bridged complex, applicable to both silylene and germylene insertions. For the $GeMe_2$ insertion, reactants are in equilibrium with the complex, which rearranges to the product in the rate controlling step. © 2002 Published by Elsevier Science B.V.

1. Introduction

Studies of the so-called 'heavy carbenes', MR_2, where M = Si, Ge and R = H, Me are of fundamental interest because of the ubiquitous involvement of these intermediates in the breakdown mechanisms of organosilicon and organogermanium compounds [1,2]. Moreover the particular prototype species, SiH_2 and GeH_2, are important in the mechanisms of chemical vapour deposition (CVD) leading to formation of electronic device materials [3,4].

Gas-phase kinetic studies of silylenes [5] have shown that $SiMe_2$ is significantly less reactive than SiH_2. For example, at 298 K, rate constants for the Si—H insertion reactions of $SiMe_2$ (with the methylsilanes), are in the range 0.2×10^{-12}–5.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} [6], while those for SiH_2 lie in the range $2.5 \times 10^{-10} - 4.0 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} [7–10]. The decrease in

---

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

0009-2614/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0009-2614(01)01257-X

reactivity has been attributed to the electron withdrawing effect of the methyl groups in the silylene [5,6].

We have recently begun a series of direct, time-resolved, measurements of the rate constants of germylenes, both GeH_2 [11–13] and $GeMe_2$ [14]. Until now these studies have mainly focussed on GeH_2, and indeed we have investigated its Ge—H insertion reactions with GeH_4 [12] and Et_3GeH [13]. In our studies with $GeMe_2$ we were unable to detect the insertion reaction with Me_3GeH [14], although there is other evidence that $GeMe_2$ can undergo Ge—H insertion [15]. In this Letter, we report a reinvestigation of the question of the Ge—H insertion reaction of $GeMe_2$, using Me_2GeH_2 as substrate. Me_2GeH_2 was chosen as substrate, since by analogy with $SiMe_2+ Me_2SiH_2$, it appears to offer the best prospect of obtaining a measurable reaction rate. For comparison purposes the reaction of GeH_2 with Me_2GeH_2 was also studied. Neither of these reactions has previously been studied.

2. Experimental

Germylene kinetic studies have been carried out by the laser flash photolysis technique, details of which have been published previously [11,13,14]. Only essential and brief details are therefore included here. Germylenes were produced by the 193 nm flash photolysis of gaseous mixtures containing suitable precursors using a Coherent Complex 100 exciplex laser, operating with ArF. Photolysis pulses were fired, at right angles, into a variable temperature reaction vessel with demountable windows which were regularly cleaned. The system is a static reactor. Although a flow system might offer some benefits, limited supplies of reagents precluded this. Photolysis pulse energies were typically 50–70 mJ with a variation of ±5%. The monitoring laser beam was multipassed 32 times along the vessel axis, through the reaction zone, to give an effective path length of 1.2 m. A portion of the monitoring beam was split off before entering the vessel for reference purposes. Light signals were measured by a dual photodiode/differential amplifier combination and signal decays were stored in a transient recorder (Datalab DL910) interfaced to a BBC microcomputer. This was used to average the decays of up to five photolysis laser shots (at a repetition rate of 1 or 2 Hz). Typical decay traces can be seen in our earlier publications [11,14]. The averaged decay traces were processed by fitting the data to an exponential form using a non-linear least-squares package. This analysis provided the values for first-order rate coefficients, k_{obs}, for removal of GeH_2 and $GeMe_2$ in the presence of known partial pressures of Me_2GeH_2.

The photoprecursors for the germylenes were 3,4-dimethyl-1-germacyclopent-3-ene (DMGCP) for GeH_2 and pentamethyldigermane (PMDG) for $GeMe_2$, although 1,1,2,2-tetramethyldigermane (TMDG) was also used in a few experiments. The monitoring lasers were a CW argon ion laser (Coherent Innova 90-5) for $GeMe_2$ and a single mode dye laser (Coherent 699-21) pumped by the Ar ion laser for GeH_2. Both germylenes were detected via absorption in their strong $A(^1B_1)$ *arrow*$X(^1A_1)$ absorption bands, $GeMe_2$ at 488 nm [14] and GeH_2 at 584.41 nm (17111.31 cm^{-1}), a strong vibration–rotation transition [11,16].

Gas mixtures for photolysis were made up containing a small pressure of precursor (DMGCP, 2.6 mTorr; PMDG, 12.2 mTorr; TMDG, 10.0 mTorr), varying pressures of Me_2GeH_2 substrate (0–36 mTorr for the GeH_2 studies; 0–30 Torr for the $GeMe_2$ studies) together with inert diluent, SF_6, at a total pressure of 10 Torr (GeH_2 studies only).

All gases used in this work were thoroughly degassed prior to use. The organogermanium compounds used in this work were synthesised by literature methods described previously for DMGCP [11] and PMDG [14]. TMDG was prepared by a similar method to that of PMDG. Me_2GeH_2 was prepared by the $LiAlH_4$ reduction of Me_2GeBr_2 in dried *n*-Bu_2O solution. The crude product was purified by vacuum distillation at −95 °C. All compounds were subjected to low temperature distillation prior to use and were checked for purity by GC. Purities were DMGCP (>90%), PMDG (>93%) TMDG (92.5%) and Me_2GeH_2 (98.0 ± 0.5%). SF_6 (no GC detectable impurities) was from Cambrian Gases.

3. Results

Preliminary 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 each germylene, GeH_2 itself, or $GeMe_2$, a set of runs was carried out in which the Me_2GeH_2 substrate pressure was varied over a suitable range in order to explore the systematic dependence of k_{obs} upon it. The results of these experiments are shown in Fig. 1, where the main graph shows this dependence on a common pressure (Torr) scale. However, because the reaction of GeH_2 is so fast, the results for these experiments are also shown as an inset using a mTorr pressure scale. The k_{obs} data used in these plots were often themselves averages of more than one set of 5-shot averages (up to four sets in some cases). The sets of results for both germylene species can be seen to show good linear fits, which support second-order kinetics. It is also worth noting that, for the $GeMe_2$ reaction, data points using TMDG as precursor are consistent with the majority for which PMDG was used as the precursor. This is the first use of TMDG as a $GeMe_2$ precursor. The second-order rate constants, obtained from the least-squares values of the slopes of these lines, are as follows:

$GeH_2 + Me_2GeH_2$;

$$k = (2.38 \pm 0.11) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$GeMe_2 + Me_2GeH_2$;

$$k = (2.26 \pm 0.10) \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

These reactions are not likely to be pressure dependent. For $GeH_2 + Me_2GeH_2$, the rate constant is either at or close to its upper limit of pressure dependence both by analogy with $SiH_2 + Me_2SiH_2$ [7,9,10], and the fact that it is close to the maximum collisional rate. For $GeMe_2 + Me_2GeH_2$ the lack of a pressure dependence was indicated by the fact that the total pressure was variable (dependent on $[Me_2GeH_2]$) during the experiments and no curvature in the second-order plot was found. The low rate constant obtained for the latter reaction, must strictly be regarded as an upper limit, because of the slight possibility of $GeMe_2$ reacting at close to the collision rate with an impurity. This is unlikely since most of the ca 2% impurity in Me_2GeH_2 is Me_3GeH, a molecule of similar reactivity.

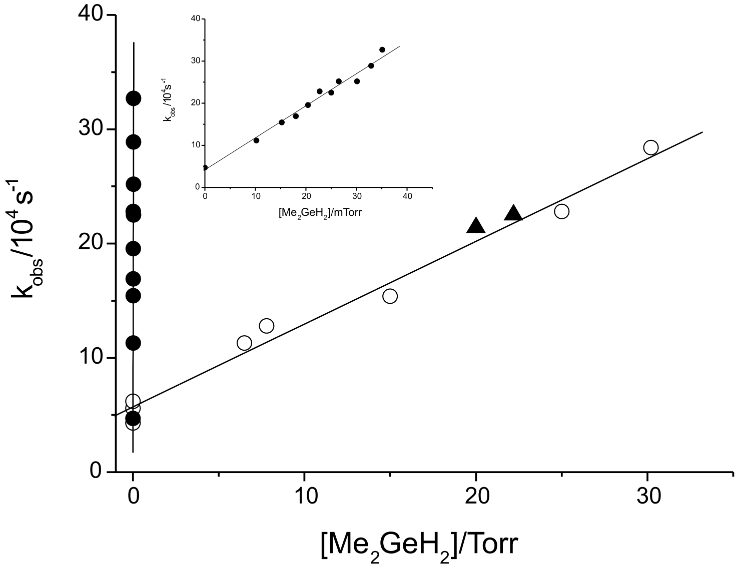

Fig. 1. Second-order plots for reactions of $GeMe_2 + Me_2GeH_2$ (○, $GeMe_2$ from PMDG; ▲, $GeMe_2$ from TMDG) and $GeH_2 + Me_2GeH_2$ (●). The plot for the latter is also shown inset with a different substrate pressure scale.

4. Discussion

4.1. Rate constants and comparisons

The main experimental purpose was to measure the rate constant for the $GeMe_2 + Me_2GeH_2$ reaction at 298 K for the first time which has been achieved. Additionally the rate constant for $GeH_2 + Me_2GeH_2$ was obtained for the first time. There is little doubt that these reactions occur via Ge—H bond insertion (C—H insertion is known not to occur [11,14] and Ge—C insertion is improbable by analogy with the lack of Si—C insertion into $SiMe_4$ [17]). These rate constants are compared with one another and also with the rate constants of some other related reactions in Table 1. This brings out the dramatic rate increase for GeH_2 relative to $GeMe_2$ of 1050 in this Ge—H insertion reaction. SiH_2 is similarly faster than $SiMe_2$ in the analogous Si—H insertion reaction, but only by a factor of 60. Thus methyl-for-H substitution is more deactivating for a germylene than a silylene.

These comparisons also bring out two other features. First, germylene insertions into Ge—H bonds are slower than silylene insertions into Si—H bonds. This we have noted before [13], but it can now be seen that the relative rates are highly variable. For example, the comparison of $SiMe_2 + Me_2SiH_2$ with $GeMe_2 + Me_2GeH_2$ gives a factor of 24, much larger than the value of 1.4 for the comparison of $SiH_2 + Me_2SiH_2$ with $GeH_2 + Me_2GeH_2$. The rate ratio for $SiH_2 + SiH_4$ relative to $GeH_2 + GeH_4$ is 8.4 and lies in between. Clearly $GeMe_2$ is significantly less reactive than $SiMe_2$. Secondly the methyl groups have a significant activation effect in the substrate germane. Thus methyl-for-H substitution ($GeH_2 + Me_2GeH_2$ compared with $GeH_2 + GeH_4$) gives a factor of 4.36 or, in fact, 8.7 on a per Ge—H bond basis. This we have noted before for ethyl-for-H substitution [12,13]. These methyl substituent effects and reaction selectivities can be understood in terms of a mechanism involving an intermediate complex.

4.2. The intermediate complex mechanism

We have shown in earlier work that the rates of silylene [5,6,8] and germylene insertion [12,13] processes can be explained by a mechanism involving an intermediate complex. For the present work the mechanism may be written:

$$R_2Ge + HGeHMe_2 \underset{-1}{\overset{1}{\rightleftharpoons}} R_2Ge\cdots H\cdots GeHMe_2 \xrightarrow{2} R_2HGeGeHMe_2$$

$$(R = H,\ Me)$$

For the GeH_2 insertion, the rate constant is relatively high, suggesting that the overall process is largely controlled by step (1) the molecular encounter, and the rearrangement of the complex, step (2), is fast compared with redissociation, step (−1). This is more like the silylene analogue, and can be understood in terms of the substrate methyl group effects, viz. that methyl substitution lowers the barrier (E_2) for the second step. Exactly this effect is found in both the reaction series $SiH_2 + Me_nSiH_{4-n}$ ($n = 1$–3) [7–10] and $SiMe_2 + Me_nSiH_{4-n}$ ($n = 1$–3) [6]. It is worth noting that ab initio calculations [13] have shown that for the

Table 1
Comparison of gas-phase rate constants for Ge—H insertion ($GeMe_2, GeH_2$) and Si—H insertion ($SiMe_2, SiH_2$) at 298 K

Reaction	k ($cm^3\ molecule^{-1}\ s^{-1}$)	k_{rel}	Ref.
$GeMe_2 + Me_2GeH_2$	2.3×10^{-13}	1[a]	This work
$GeH_2 + Me_2GeH_2$	2.4×10^{-10}	1050	This work
$SiMe_2 + Me_2SiH_2$	5.5×10^{-12}	1[a]	[6]
$SiH_2 + Me_2SiH_2$	3.3×10^{-10}	60	[7]
$GeH_2 + GeH_4$	5.5×10^{-11}	1[a]	[13]
$SiH_2 + SiH_4$	4.6×10^{-10}	8.4	[8]

[a] Reference reaction (of each pair).

prototype reactions the complex $H_2Ge \cdots H \cdots GeH_3$ is less strongly bound than the complex $H_2Si \cdots H \cdots SiH_3$. This means that step (−1) occurs more readily in the germylene case, meaning that germylene complexes are intrinsically more likely to redissociate and therefore anything which lowers E_2 will have a more marked effect on germylene insertions than on silylene insertions. A more detailed analysis of this will given in a future publication describing a systematic study of the kinetics of the reactions $GeH_2 + Et_nGeH_{4-n}$ ($n = 1$–3) [18].

For the $GeMe_2$ insertions, the rate constant is so low, that it suggests that step (2) is fully rate determining, i.e., $k_2 \ll k_{-1}$. Baggott et al. [6] have analysed the factors which affect the ratio k_2/k_{-1} in the case of $SiMe_2$ insertions and shown that rate factors of 10^{-3} can arise between different cases as a result of rate controlling step switching from (1) to (2). For the $SiMe_2 + Me_2SiH_2$ case at 298 K the situation is in between. Thus while step (2) in this case is rate determining, it does not produce the highest retardation effect. For $GeMe_2 + Me_2GeH_2$, however, the measured factor is close to 10^{-3}. Thus this reaction is close to one extreme limit of behaviour. This will be the case when $E_{-1} \approx E_2$. The implication of this is that this reaction should have an overall activation energy close to zero. We plan to test this. The underlying reason why the insertion reactions of both $SiMe_2$ and $GeMe_2$ are so much slower than those of their SiH_2 and GeH_2 prototypes has been attributed, in the silicon case [5,6], to the electron withdrawing ability of the methyl groups. This arises from the fact that C is more electronegative than Si. It was argued that orbital contraction in $SiMe_2$ (and therefore also $GeMe_2$) would result and therefore require shorter range, closer contact with substrates for reaction to take place. However, although this may be a contributing factor we are now more inclined to believe that it is due to the weakness of initial bond making in the complex. Methyl groups are known to stabilise $SiMe_2$. It has a higher divalent state stabilisation energy (DSSE) value (128 kJ mol^{-1}) than SiH_2 (94 kJ mol^{-1}) [19]. The more stable the silylene, the weaker is likely to be the bonding in the intermediate complex. Some support for this comes from a comparison of the zwitterionic complexes $R_2Si \cdots OMe_2$. Kinetic studies [20] give a binding energy of ca 37 kJ mol^{-1} for $Me_2Si \cdots OMe_2$, whereas kinetic studies [21] supported by theory [22] suggest a binding energy of ca 84 kJ mol^{-1} for $H_2Si \cdots OMe_2$. This is further supported by calculations [23] on analogous water complexes, $R_2Si \cdots OH_2$. If the same considerations apply to $R_2Ge \cdots H \cdots GeHMe_2$, then the weakness of this complex, when R = Me, will lower the binding energy, which corresponds to E_{-1}, relative to R = H. Such a lowering could account for the switch to step (2) being fully rate determining and the high overall retardation effect for $GeMe_2 + Me_2GeH_2$.

There have been no theoretical calculations on the insertion of $GeMe_2$ into Ge—H bonds. However, DFT and MP2 studies by Su and Chu [24,25] show that (a) $GeMe_2$ inserts less readily than GeH_2 into the C—H bond of CH_4, although both reactions have high activation barriers [24], and (b) $GeMe_2$ inserts more readily into the Si—H bond of SiH_4 ($E_a = 66$ kJ mol^{-1}) than into the C—H bond of CH_4 ($E_a = 164$ kJ mol^{-1}) [25].

Acknowledgements

We thank the following: INTAS-RFBR (project IR-97-1658), NATO (project PST.CLG. 975368). R.B. also thanks the DGICYT (Spain) for support under projects PB98-0537-C02-01 and BQU2000-1163-C02-01. M.P.E., I.V.K. and O.M.N. also thank RFBR (projects 01-03-32630 and 00-03-32630). R.B. also thanks EPSRC (project C7410). We thank Sergey Boganov for helpful comments and additionally Keith King and Warren Lawrance for an advance copy of their paper.

References

[1] Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, Chichester, 1998.
[2] S. Patai (Ed.), The Chemistry of Organic Germanium, Tin and Lead Compounds, vol. 1, Wiley, Chichester, 1995.
[3] J.M. Jasinski, S.M. Gates, Acc. Chem. Res. 24 (1991) 9.
[4] C. Isobe, H. Cho, J.E. Crowell, Surf. Sci. 295 (1993) 117.

[5] R. Becerra, R. Walsh, Kinetics and mechanisms of silylene reactions: a prototype for gas-phase acid/base chemistry, in: R.G. Compton, G. Hancock (Eds.), Research in Chemical Kinetics, vol. 3, Elsevier, Amsterdam, 1995, p. 263 (Chapter 6).
[6] J.E. Baggott, M.A. Blitz, H.M. Frey, R. Walsh, J. Am. Chem. Soc. 112 (1990) 8337.
[7] J.E. Baggott, H.M. Frey, P.D. Lightfoot, R. Walsh, I.M. Watts, J. Chem. Soc. Faraday Trans. 86 (1990) 27.
[8] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, M.S. Gordon, J. Chem. Soc. Faraday Trans. 91 (1995) 2723.
[9] I.W. Carpenter, Ph.D. Thesis, University of Reading, 1996.
[10] I.W. Carpenter, R. Walsh (in preparation).
[11] R. Becerra, S.E. Boganov, M.P. Egorov, O.M. Nefedov, R. Walsh, Chem. Phys. Lett. 260 (1996) 433.
[12] R. Becerra, S.E. Boganov, M.P. Egorov, O.M. Nefedov, R. Walsh, Mendeleev Commun. (1997) 87.
[13] R. Becerra, S.E. Boganov, M.P. Egorov, V.I. Faustov, O.M. Nefedov, R. Walsh, J. Am. Chem. Soc. 120 (1998) 12657.
[14] R. Becerra, S.E. Boganov, M.P. Egorov, V.Ya. Lee, O.M. Nefedov, R. Walsh, Chem. Phys. Lett. 250 (1996) 111.
[15] E.C-L. Ma, D.P. Paquin, P.P. Gaspar, J. Chem. Soc., Chem. Commun. (1980) 381.
[16] A. Campargue, R. Escribano, Chem. Phys. Lett. 315 (1999) 397.
[17] R. Becerra, R. Walsh, Int. J. Chem. Kinet. 31 (1999) 393.
[18] R. Becerra, S.E. Boganov, M.P. Egorov, I.V. Krylova, O.M. Nefedov, R. Walsh, to be published.
[19] R. Becerra, R. Walsh, Thermochemistry (Chapter 4), p. 153 in Ref. [1].
[20] J.E. Baggott, M.A. Blitz, H.M. Frey, P.D. Lightfoot, R. Walsh, Int. J. Chem. Kinet. 24 (1992) 127.
[21] U.N. Alexander, K.D. King, W.D. Lawrence, Phys. Chem. Chem. Phys. 3 (2001) 3085.
[22] M.W. Heaven, G.F. Metha, M.A. Buntine, J. Phys. Chem. A 105 (2001) 1185.
[23] S. Su, M.S. Gordon, Chem. Phys. Lett. 204 (1993) 306.
[24] M-D. Su, S-Y. Chu, J. Am. Chem. Soc. 121 (1999) 4229.
[25] M-D. Su, S-Y. Chu, J. Phys. Chem. A 103 (1999) 11011.