Direct time-resolved study of the kinetics of the gas-phase reaction of germylene with triethylgermane: a negative activation energy for the Ge–H insertion process

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Gas-phase rate constants, obtained from 292–557 K, yield an activation energy of –10.6 ± 1.1 kJ mol^{-1} for the insertion reaction of GeH_2 into a Ge–H bond (of triethylgermane); these results indicate the likely involvement of an intermediate complex.

We have recently obtained the first experimental rate constants[1] for reactions of germylene, GeH_2, in the gas phase. This species is important in the chemical vapour deposition of semiconductor germanium,[2,3] and is a key intermediate in the breakdown mechanisms of germanium hydrides.[4] Our kinetic results[1] confirm that GeH_2 reacts rapidly with O_2 and with the π-bonds of alkenes and alkynes, and also inserts readily into Si–H bonds but not C–H bonds. GeH_2 is known to insert into Ge–H bonds[5,6] but to date only relative rate studies of this process have been carried out.[7] We report here an absolute rate study of the reaction of GeH_2 with Et_3GeH, the first for GeH_2 with a molecule containing a Ge–H bond. We also report the first temperature variation study, and thereby the first activation energy measurement, for a germylene reaction.

These kinetic studies were carried out by the laser flash photolysis technique, the details of which have been published previously.[1,8,9] GeH_2 was created by photodecomposition of 3,4-dimethylgermacyclopentene-3 (DMGCP) using the 193 nm ArF line of a pulsed excimer laser (Coherent, Compex 100). GeH_2 was detected and monitored in real time by use of a single-mode dye laser tuned into the strong vibration–rotation transition (17111.31 cm^{-1}) in the visible $A \leftarrow X$ absorption band, discovered by us previously.[1] Signal decays from 3–5 photolysis laser shots were averaged and found to give first-order kinetic fits. End product analysis was not undertaken here since the products of the Ge–H insertion process are already known.[5–7]

Experiments were carried out with gas mixtures containing a few millitorr of DMGCP, varying quantities of Et_3GeH up to 500 mTorr and inert diluent bath gas (SF_6) at a total pressure of 10 Torr. The reaction was studied at five temperatures in the range 292–557 K. A few experiments were carried out at other total pressures in the range 1 to 100 Torr (at 292 and 485 K), which showed that there was no effect of total pressure on the decay constants. Second order kinetics were demonstrated by finding good linear dependencies of the first-order decay constants, k_{obs}, upon Et_3GeH substrate pressures. These are shown in Figure 1, for each of the five temperatures at which the reaction was studied. The rate constants obtained from the least-squares values of the slopes of these lines are shown in Table 1. An Arrhenius plot of the data gave the following parameters:

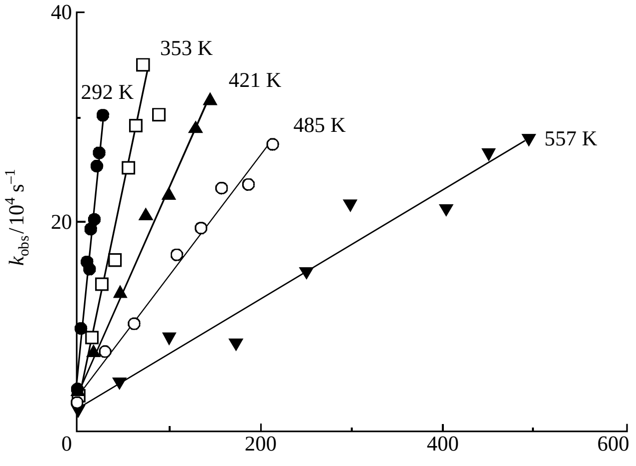

Figure 1 Second-order plots showing the dependence of decay constants, k_{obs}, on pressure of triethylgermane.

$$\log(A/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = -11.43 \pm 0.15,\ E_a = -10.64 \pm 1.11\ \text{kJ mol}^{-1}$$

These results, apart from demonstrating clearly that GeH_2 reacts with Et_3GeH, are qualitatively similar to those for the Si–H insertion reactions of silylenes.[10,11] In particular they exhibit the negative activation energy characteristic of the involvement of an intermediate complex. This suggests that the reaction studied here is a Ge–H insertion process (particularly since GeH_2 does not insert in C–H bonds[1]) and that the probable mechanism is *via* an H-bonded intermediate, *viz.*

$$Et_3Ge{-}H + GeH_2 \underset{2}{\overset{1}{\rightleftharpoons}} Et_3Ge\cdots H\cdots GeH_2 \longrightarrow Et_3GeGeH_3$$

The comparison with the silylene Si–H insertion process is instructive. The closest analogue for which data exists is the reaction of SiH_2 with Me_3SiH for which the rate constants[12] are also shown in Table 1. The Arrhenius parameters for this data[12] are:

$$\log(A/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = -10.11 \pm 0.05,\ E_a = -2.93 \pm 0.33\ \text{kJ mol}^{-1}$$

We may reasonably assume that the alkyl substituent (Et for the germane substrate, Me for the silane substrate) makes little or no difference. Thus the significant difference is the much stronger negative activation energy, in association with the lower *A* factor, for the GeH_2 reaction studied here than for the SiH_2 analogue. We have analysed the intermediate complex mechanism[10] for silylene (SiX_2) insertion reactions (into Si–H bonds) in terms of a loose collisional association process [the analogue of step (1)] followed by a tight rearrangement process [the analogue of step (2)] caused by the restriction of motion of the inserting SiX_2 fragment. The same model offers a

Table 1 Experimental rate constants for insertion reactions of germylene and silylene.

(*a*) GeH_2 + Et_3GeH[a]		(*b*) SiH_2 + Me_3SiH[b]	
T/K	$k/10^{-10}$ cm^3 molecule^{-1} s^{-1}	*T*/K	$k/10^{-10}$ cm^3 molecule^{-1} s^{-1}
292	2.66 ± 0.11	295	2.48 ± 0.15
353	1.53 ± 0.05	343	2.25 ± 0.16
421	0.859 ± 0.026	400	1.88 ± 0.21
485	0.588 ± 0.015	480	1.58 ± 0.18
557	0.305 ± 0.011	625	0.93 ± 0.17

[a]This work. [b]Refs. 10,12.

reasonable interpretation of these results for GeH_2 insertion into Ge–H bonds. The difference appears to be that, whereas the SiH_2 insertion into Si–H bonds is largely controlled by step (1), for GeH_2 insertion into Ge–H bonds (at least in this case) the control is intermediate between steps (1) and (2). This can be surmised from the fact that the experimental A factor found here is lower than those for SiH_2[10,12] but higher than those for $SiMe_2$[10,13] in their insertion reactions. In fact, the closest resemblance is with the Si–H insertion reactions of MeSiH.[10,14]

From these findings we may draw the inference that, in general, the second step is slightly more difficult for germylenes inserting into Ge–H bonds. This may be because the intermediate complex has an increased energy barrier to reorganisation. This conclusion would be consistent with our observations[15] that $GeMe_2$ does not apparently insert into Ge–H bonds, at least not at room temperature on the time scale of the present experiments ($k_{\text{ins}} < 4\times10^{-13}$ cm^3 molecule^{-1} s^{-1}). It is also consistent with the potential energy calculations of Trinquier,[16] who has found that, as one descends the Group 14 elements, M, the hydrides M_2H_6 (ground state structure H_3MMH_3) possess an increasingly stable alternative bridged structure $H_3M\cdots H\cdots MH_2$ with an increasing barrier between the two isomeric forms. Work on the insertion reactions of GeH_2 into Ge–H and Si–H bonds is continuing.[17]

This work has been supported by the Royal Society under its joint project scheme. RB also thanks the Direccion General de Investigacion Cientifica y Technica (DGICYT) for support under project PB94-02180-C02-01.

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Received: Cambridge, 8th February 1997
Moscow, 21st February 1997; Com. 7/00901A