Electronic Supplementary Material for PCCP

Supplementary Information

Time-resolved gas-phase kinetic study of the germylene addition reaction, GeH_2 + $CH_3C{\equiv}CCH_3$

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Calculation of the enthalpies of products and transition states in the reaction of GeH_2 with $CH_3C{\equiv}CCH_3$

This was done using an additivity method based on the reactions:

$SiH_2 + C_2H_2 \rightarrow product_1$ (or TS1) (1)
$SiH_2 + CH_3C{\equiv}CCH_3 \rightarrow product_2$ (or TS2) (2)
$GeH_2 + C_2H_2 \rightarrow product_3$ (or TS3) (3)
$GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow product_4$ (or TS4) (4)

Values for $\Delta H^o(4)$ were derived using equation (5):

$$\Delta H^o(4) = \Delta H^o(3) + \Delta H^o(2) - \Delta H^o(1) \quad (5)$$

This assumes bond additivity, but is a close approximation to group additivity[s1]. Equation (5) was used as is, for derivation of $\Delta H^o(4)$ values in Tables S1a-S1e and S2b-S2d. For $\Delta H^o(4)$ values in Tables S1f and S2a, the further group correction incorporated into equation (6) was applied.

$$\Delta H^o(4) = \Delta H^o(3) + \Delta H^o(2) - \Delta H^o(1) + \Delta H^o([Ge\_(C)_2(H)_2)] - [Ge\_(C)(H)_3)] - [Si\_(C)_2(H)_2)] + [Si\_(C)(H)_3)]) \quad (6)$$

The additional bracketed quantity in (6) has the value of + 17 kJ mol^{-1} [s2,s3].

Tables of ΔH^o values are given on p.2 (Tables S1a-S1d), p.3 (Tables S1e, S1f, S2a, S2b) and p.4 (Tables S2c, S2d). References are given on p.5.

Calculation of LJ collision number for GeH_2 + $CH_3C{\equiv}CCH_3$

This was done by the method recommended by Troe[s7]. The LJ parameters for GeH_2 were taken to be the same as those for GeH_4, as used previously[s8]. The LJ parameters for $CH_3C{\equiv}CCH_3$ were obtained by extrapolation of those for C_2H_2 and $CH_3C{\equiv}CH$[s9]. The parameters themselves are given in Table S3 (p.4). References are given on p.5.

Table S1a Data for derivation of standard enthalpy at 298 K of reaction:
$GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ 2,3-dimethylgermirene.

Reaction	ΔH^o/kJ mol^{-1}	Method	Reference
$SiH_2 + C_2H_2 \rightarrow$ silirene	-218	G3	s4
$SiH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ 2,3-dimethylsilirene	-216	G3	s5
$GeH_2 + C_2H_2 \rightarrow$ germirene	-107	G2//QCISD	s6
$GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ 2,3-dimethylgermirene	-105	Additivity	derived

Table S1b Data for derivation of standard enthalpy at 298 K of reaction:
$GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ HGeCMe=CHMe(cis).

Reaction	ΔH^o/kJ mol^{-1}	Method	Reference
$SiH_2 + C_2H_2 \rightarrow HSiCH{=}CH_2$	-186	G3	s4
$SiH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ HSiCMe=CHMe(cis)	-167	G3	s5
$GeH_2 + C_2H_2 \rightarrow HGeCH{=}CH_2$	-166	G2//QCISD	s6
$GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ HGeCMe=CHMe(cis)	-147	Additivity	derived

Table S1c Data for derivation of standard enthalpy at 298 K of reaction:
$GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ EtC(Me)=Ge.

Reaction	ΔH^o/kJ mol^{-1}	Method	Reference
$SiH_2 + C_2H_2 \rightarrow CH_3CH{=}Si$	-192	G3	s4
$SiH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ EtC(Me)=Si	-158	G3	s5
$GeH_2 + C_2H_2 \rightarrow CH_3CH{=}Ge$	-172	G2//QCISD	s6
$GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ EtC(Me)=Ge	-138	Additivity	derived

Table S1d Data for derivation of standard enthalpy at 298 K of reaction:
$GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ 2,3-dimethylgermiranylidene.

Reaction	ΔH^o/kJ mol^{-1}	Method	Reference
$SiH_2 + C_2H_2 \rightarrow$ siliranylidene	-203	G3	s4
$SiH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ 2,3-dimethylsiliranylidene	-158	G3	s5
$GeH_2 + C_2H_2 \rightarrow$ germiranylidene	-183	G2//QCISD	s6
$GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow$ 2,3-dimethylgermiranylidene	-138	Additivity	derived

Table S1e Data for derivation of standard enthalpy at 298 K of reaction: $GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow Ge(^3P_1) +$ trans-2-butene.

Reaction	ΔH^o/kJ mol^{-1}	Method	Reference
$SiH_2 + C_2H_2 \rightarrow Si(^3P_1) + C_2H_4$	+7	G3	s4
$SiH_2 + CH_3C{\equiv}CCH_3 \rightarrow Si(^3P_1)$ + trans-2-butene	+27	G3	s5
$GeH_2 + C_2H_2 \rightarrow Ge(^3P_1) + C_2H_4$	-37	G2//QCISD	s6
$GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow Ge(^3P_1)$ + trans-2-butene	-17	Additivity	derived

Table S1f Data for derivation of standard enthalpy at 298 K of reaction: $GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow MeC{\equiv}CGeH_2Me$.

Reaction	ΔH^o/kJ mol^{-1}	Method	Reference
$SiH_2 + C_2H_2 \rightarrow HC{\equiv}CSiH_3$	-261	G3	s4
$SiH_2 + CH_3C{\equiv}CCH_3 \rightarrow MeC{\equiv}CSiH_2Me$	-294	G3	s5
$GeH_2 + C_2H_2 \rightarrow HC{\equiv}CGeH_3$	-170	G2//QCISD	s6
$GeH_2 + CH_3C{\equiv}CCH_3 \rightarrow MeC{\equiv}CGeH_2Me$	-186	Additivity	derived

Table S2a Data for derivation of standard enthalpy at 298 K of the transition state for the reaction: 2,3-dimethylgermirene $\rightarrow MeC{\equiv}CGeH_2Me$.

Reaction	ΔH_{rel}^o/kJ mol^{-1} [a]	Method	Reference
silirene $\rightarrow HC{\equiv}CSiH_3$	-41	G3	s4
2,3-dimethylsilirene $\rightarrow MeC{\equiv}CSiH_2Me$	+66	G3	s5
germirene $\rightarrow HC{\equiv}CGeH_3$	+47	G2//QCISD	s6
2,3-dimethylgermirene $\rightarrow MeC{\equiv}CGeH_2Me$	+171	Additivity	derived

[a] Relative to SiH_2 (or GeH_2) + C_2H_2 (or $CH_3C{\equiv}CCH_3$)

Table S2b Data for derivation of standard enthalpy at 298 K of the transition state for the reaction: 2,3-dimethylgermirene $\rightarrow$ HGeCMe=CHMe(cis).

Reaction	ΔH_{rel}^o/kJ mol^{-1} [a]	Method	Reference
silirene $\rightarrow HSiCH{=}CH_2$	-65	G3	s4
2,3-dimethylsilirene $\rightarrow$ HSiCMe=CHMe(cis)	-76	G3	s5
germirene $\rightarrow HGeCH{=}CH_2$	-26	G2//QCISD	s6
2,3-dimethylgermirene $\rightarrow$ HGeCMe=CHMe(cis)	-37	Additivity	derived

[a] Relative to SiH_2 (or GeH_2) + C_2H_2 (or $CH_3C{\equiv}CCH_3$)

Table S2c Data for derivation of standard enthalpy at 298 K of the transition state for the reaction: HGeCMe=CHMe(cis) → EtC(Me)=Ge.

Reaction	ΔH_{rel}^{o}/kJ mol^{-1} [a]	Method	Reference
$HSiCH=CH_2 \rightarrow CH_3CH=Si$	-78	G3	s4
HSiCMe=CHMe(cis) → EtC(Me)=Si	-73	G3	s5
$HGeCH=CH_2 \rightarrow CH_3CH=Ge$	-49	G2//QCISD	s6
HGeCMe=CHMe(cis) → EtC(Me)=Ge	-44	Additivity	derived

[a]Relative to SiH_2 (or GeH_2) + C_2H_2 (or $CH_3C{\equiv}CCH_3$)

Table S2d Data for derivation of standard enthalpy at 298 K of the transition state for the reaction: HGeCMe=CHMe(cis) → 2,3-dimethylgermiranylidene(cis).

Reaction	ΔH_{rel}^{o}/kJ mol^{-1} [a]	Method	Ref.
$HSiCH=CH_2 \rightarrow$ siliranylidene	-80	G3	s4
HSiCMe=CHMe(cis) → 2,3-dimethylsiliranylidene(cis)	-67	G3	s5
$HGeCH=CH_2 \rightarrow$ germiranylidene	+8	G2//QCISD	s6
HGeCMe=CHMe(cis) → 2,3-dimethylgermiranylidene(cis)	+21	Additivity	derived

[a]Relative to SiH_2 (or GeH_2) + C_2H_2 (or $CH_3C{\equiv}CCH_3$)

Table S3 Lennard-Jones Parameters for GeH_2 and $CH_3C{\equiv}CCH_3$.

Molecule	σ/Å	(ε/k)/K
GeH_2[a]	4.22	239
$CH_3C{\equiv}CCH_3$[b]	5.18	317

[a]See text and ref s8. [b]See text and ref s9.

References

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