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The enthalpies of formation of triphenyl vinyl germanium, triphenyl phenylethynyl germanium, bis(triphenyl germanium) oxide, and some associated Ge–C bond enthalpies

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The three compounds $(C_6H_5)_3GeCH{=}CH_2$, $(C_6H_5)_3GeC{\equiv}C(C_6H_5)$, and $\{(C_6H_5)_3Ge\}_2O$, have been burnt in an aneroid combustion calorimeter and their vapour pressures measured by an effusion method. The gas-phase enthalpies of formation:

$$\Delta_f H_m^\circ\{(C_6H_5)_3GeCH{=}CH_2, g\} = (362.6 \pm 7.5)\ \mathrm{kJ \cdot mol^{-1}},$$

$$\Delta_f H_m^\circ\{(C_6H_5)_3GeC{\equiv}C(C_6H_5), g\} = (579.0 \pm 8.4)\ \mathrm{kJ \cdot mol^{-1}},$$

$$\Delta_f H_m^\circ\{(C_6H_5)_3Ge{-}O{-}Ge(C_6H_5)_3, g\} = (259.1 \pm 11.6)\ \mathrm{kJ \cdot mol^{-1}},$$

have been used to obtain C–Ge bond-dissociation enthalpies and bond-enthalpy terms.

1. Introduction

Earlier experimental work$^{(1-3)}$ on the enthalpies of formation of organo-germanium compounds allowed us to present a self-consistent bond-enthalpy scheme for these compounds. The present work extends the scheme to Ge–C(sp), Ge–C(sp^2), and Ge–O bonds, and throws some light on the possibility of π-bonding, using the unoccupied d-orbitals of the metal.

2. Experimental

Triphenyl vinyl germanium was prepared by adding a solution of triphenyl germanium bromide in THF to vinyl magnesium bromide. The mixture was refluxed for 5 h, the excess Grignard reagent was hydrolysed with saturated aqueous ammonium chloride, and the organic layer was separated and dried over magnesium sulphate. The sample was then filtered and evaporated to give an oil which dissolved in petroleum ether. When this was poured through a column containing Kieselgel two fractions were collected which produced white crystals. Thin-layer chromatography of the two samples revealed identical spots; they were combined and recrystallized twice from petroleum ether. Melting-temperature

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curves obtained using d.s.c. indicated a purity of 99.9 moles per cent. Analysis gave carbon and hydrogen mass percentages of 73.0 and 5.5 compared with the theoretical values of 72.6 and 5.5.

Triphenyl phenylethynyl germanium was prepared by adding a solution of phenylethyne in ether to a mixture of butyl lithium and ether to give an orange-yellow liquid. After refluxing for 15 min, a solution of triphenyl germanium bromide in benzene was added. The ether was distilled off, the mixture was refluxed for 5 h, the excess butyl lithium reagent was hydrolysed with aqueous saturated ammonium chloride, and the organic layer was separated. Evaporation yielded yellow crystals which were dissolved in 60-80 ligroin and passed through a column containing Kieselgel. Three fractions were collected; on evaporation the first gave a pale green oil and the second and third gave white crystals. Thin-layer chromatography of the second and third fractions revealed identical spots; they were combined and recrystallized from ligroin and methanol. Melting-temperature curves obtained using d.s.c. indicated a purity of 99.9 moles per cent. Analysis gave carbon and hydrogen mass percentages of 77.8 and 4.9 compared with the theoretical values of 77.1 and 5.0.

Bis(triphenyl germanium) oxide was prepared by adding silver nitrate to a solution of triphenyl germanium bromide in ethanol and refluxing for 15 min. The sample was filtered and recrystallized from petroleum ether (80-100) to yield white crystals. Melting-temperature curves obtained using d.s.c. indicated a purity of 99.9 moles per cent. Analysis gave carbon and hydrogen mass percentages of 69.1 and 4.9 compared with the theoretical values of 69.3 and 4.9.

The aneroid rotating combustion bomb combines the functions of a combustion calorimeter and a solution calorimeter in one instrument. Accounts of its use in studying the enthalpies of formation of organo-germanium compounds have already been given.(1, 3) Since they were first described several changes had been made both to the calorimeter and its ancillary equipment. The drive-belt which previously caused rotation had been replaced by shafts and gears. The change in thermometer resistance with time was measured with a new a.c. bridge (Automatic Systems Laboratories Ltd. Model F17), connected to a computer, printer, and monitor. The computer was programmed to use the Regnault–Pfaundler method to calculate the corrected resistance change.

3. Results

Tables 1 to 6 give the results for the combustions of the germanium compounds and for the corresponding comparison experiments in which an amount of benzoic acid, sufficient to produce the same amount of carbon dioxide as in the organo-germanium combustions, was burnt in the presence of the soluble form of germanium dioxide. The following symbols were used: M, the molar mass; m, the mass of sample; ρ, the density; q_T the total energy change; q_f, the energy correction for the fuse; q_c, the energy correction for incomplete combustion; q_B, the energy of combustion of benzoic acid.

The enthalpies of sublimation of the germanium compounds were measured using a combined mass-loss torsional-recoil effusion method.(6) The values were reduced to 298.15 K by using the heat capacities of the solids (measured by d.s.c.) and of the vapours (estimated by using the Benson group parameters).(7)

$$\Delta H^\circ_{sub}\{(C_6H_5)_3Ge\text{–}CH{=}CH_2\} = (98.7 \pm 1.6)\ \mathrm{kJ \cdot mol^{-1}},$$

$$\Delta H^\circ_{sub}\{(C_6H_5)_3Ge\text{–}C{\equiv}C\text{–}C_6H_5\} = (107.5 \pm 1.5)\ \mathrm{kJ \cdot mol^{-1}},$$

$$\Delta H^\circ_{sub}\{(C_6H_5)_3Ge\text{–}O\text{–}Ge(C_6H_5)_3\} = (98.0 \pm 1.5)\ \mathrm{kJ \cdot mol^{-1}}.$$

Therefore

$$\Delta_f H^\circ_m\{(C_6H_5)_3Ge\text{–}CH{=}CH_2, g\} = (362.6 \pm 7.5)\ \mathrm{kJ \cdot mol^{-1}},$$

$$\Delta_f H^\circ_m\{(C_6H_5)_3Ge\text{–}C{\equiv}C\text{–}C_6H_5, g\} = (579.0 \pm 8.4)\ \mathrm{kJ \cdot mol^{-1}},$$

$$\Delta_f H^\circ_m\{(C_6H_5)_3Ge\text{–}O\text{–}Ge(C_6H_5)_3, g\} = (259.1 \pm 11.6)\ \mathrm{kJ \cdot mol^{-1}}.$$

4. Discussion

The gaseous enthalpies of formation of the germanium compounds may be combined with the following quantities to yield bond-dissociation enthalpies.

TABLE 1. Results of the comparison experiments for triphenyl vinyl germanium $M = 330.9565\ \mathrm{g \cdot mol^{-1}}$; $\rho = 1.18\ \mathrm{g \cdot cm^{-3}}$

$m(C_6H_5CO_2H)/g$	q_T/kJ	q_B/kJ	q_f/kJ	q_{comp}/kJ [a]
0.165735	5.16283	4.37789	0.05124	0.73370
0.168055	5.20780	4.43917	0.04937	0.71925
0.167104	5.19998	4.41405	0.05069	0.73524
0.168938	5.24036	4.46250	0.04985	0.72801
0.167291	5.19594	4.41899	0.05077	0.72618
0.168023	5.22965	4.43833	0.05130	0.74002
			mean value:	0.7304±0.0061

[a] $q_{comp} = q_T - q_f - q_B$.

TABLE 2. Results of the combustion experiments on triphenyl vinyl germanium

m(cpd)/g	q_T/kJ	q_c/kJ	q_f/kJ	$-\Delta U^\circ_c/(\mathrm{kJ \cdot g^{-1}})$ [a]
0.164299	6.37681	0.02924	0.09143	33.98816
0.163025	6.34174	0.02609	0.09448	34.00061
0.162978	6.33758	0.02775	0.09653	33.98250
0.160629	6.24464	0.02697	0.08567	33.96361
0.162120	6.30283	0.02941	0.09611	33.96083
0.164798	6.40715	0.02994	0.10147	34.01267
			mean value:	33.985±0.017

[a] $-\Delta U^\circ_c/(\mathrm{kJ \cdot g^{-1}}) = (q_T + q_c - q_f - q_{comp})/m$.

This refers to the reaction: $C_{20}H_{18}Ge + 25.5O_2 = 20CO_2 + 9H_2O + GeO_2$: $-\Delta_c U^\circ_m = (11247.6 \pm 6.0)\ \mathrm{kJ \cdot mol^{-1}}$; $-\Delta_c H^\circ_m = (11261.3 \pm 6.0)\ \mathrm{kJ \cdot mol^{-1}}$. Using the values $\Delta_f H^\circ_m(CO_2, g) = -(393.51 \pm 0.13)\ \mathrm{kJ \cdot mol^{-1}}$,(4) $\Delta_f H^\circ_m(H_2O, l) = -(285.83 \pm 0.04)\ \mathrm{kJ \cdot mol^{-1}}$,(4) and $\Delta_f H^\circ_m(GeO_2, \text{hex}) = -(554.7 \pm 1.0)\ \mathrm{kJ \cdot mol^{-1}}$:(5) $\Delta_f H^\circ_m(C_{20}H_{18}Ge, \text{cr}, 298.15\ \mathrm{K}) = (263.9 \pm 7.0)\ \mathrm{kJ \cdot mol^{-1}}$. The uncertainty is twice the standard deviation of the mean and includes the uncertainties in the comparison and calibration experiments.

TABLE 3. Results of the comparison experiments for triphenyl phenylethynyl germanium $M = 405.0393\ \mathrm{g \cdot mol^{-1}}$; $\rho = 1.15\ \mathrm{g \cdot cm^{-3}}$

$m(C_6H_5CO_2H)$/g	q_T/kJ	q_B/kJ	q_f/kJ	q_{comp}/kJ
0.160986	5.02566	4.25245	0.05333	0.71988
0.163262	5.11981	4.31257	0.07664	0.73060
0.161125	5.02615	4.25612	0.05052	0.71951
0.164803	5.17973	4.35327	0.07868	0.74778
0.161874	5.04538	4.27590	0.05877	0.71071
0.162965	5.09477	4.30472	0.05371	0.73634
			mean value:	0.7275 ± 0.0100

TABLE 4. Results of the combustion experiments for triphenyl phenylethynyl germanium

m(cpd)/g	q_T/kJ	q_c/kJ	q_f/kJ	$-\Delta U^\circ_c/(\mathrm{kJ \cdot g^{-1}})$
0.146313	5.86470	0.02540	0.07136	34.79711
0.145164	5.81586	0.02365	0.05629	34.82785
0.147668	5.90170	0.02496	0.05652	34.82589
0.143558	5.78329	0.02304	0.08474	34.78817
0.147024	5.89771	0.02470	0.07405	34.83030
0.143831	5.78016	0.02278	0.06839	34.81224
			mean value:	34.8134 ± 0.0144

This refers to the reaction: $C_{26}H_{20}Ge + 32O_2 = 26CO_2 + 10H_2O + GeO_2$: $-\Delta_c U^\circ_m = (14100.8 \pm 7.0)\ \mathrm{kJ \cdot mol^{-1}}$; $-\Delta_c H^\circ_m = (14115.7 \pm 7.0)\ \mathrm{kJ \cdot mol^{-1}}$; $\Delta_f H^\circ_m(C_{26}H_{20}Ge, \mathrm{cr}, 298.15\ \mathrm{K}) = (471.4 \pm 7.9)\ \mathrm{kJ \cdot mol^{-1}}$.

TABLE 5. Results of the comparison experiments for bis(triphenyl germanium) oxide $M = 623.82\ \mathrm{g \cdot mol^{-1}}$; $\rho = 1.20\ \mathrm{g \cdot cm^{-3}}$

$m(C_6H_5CO_2H)$/g	q_T/kJ	q_B/kJ	q_f/kJ	q_{comp}/kJ
0.134470	4.35538	3.55203	0.08117	0.72218
0.138813	4.46197	3.66675	0.07235	0.72287
0.144528	4.62125	3.81771	0.07114	0.73240
0.148185	4.71738	3.91431	0.07136	0.73171
0.132572	4.29090	3.50189	0.07095	0.71806
0.140648	4.51272	3.71522	0.07121	0.72629
			mean value:	0.7256 ± 0.0046

TABLE 6. Results of the combustion experiments for bis(triphenyl germanium) oxide

m(cpd)/g	q_T/kJ	q_c/kJ	q_f/kJ	$-\Delta U^\circ_c/(\mathrm{kJ \cdot g^{-1}})$
0.140339	5.20983	0.02339	0.07519	31.58374
0.136398	5.07984	0.02304	0.06910	31.58536
0.131801	4.93901	0.02365	0.07368	31.58838
0.127557	4.81380	0.02269	0.08588	31.55460
0.145326	5.35604	0.02103	0.06036	31.59180
0.138940	5.16543	0.02347	0.07378	31.59292
			mean value:	31.5828 ± 0.0116

This refers to the reaction: $C_{36}H_{30}Ge_2O + 45O_2 = 36CO_2 + 15H_2O + 2GeO_2$: $-\Delta_c U^\circ_m = (19702.0 \pm 7.4)\ \mathrm{kJ \cdot mol^{-1}}$; $-\Delta_c H^\circ_m = (19724.3 \pm 7.4)\ \mathrm{kJ \cdot mol^{-1}}$; $\Delta_f H^\circ_m(C_{36}H_{30}Ge_2O, \mathrm{cr}, 298.15\ \mathrm{K}) = (161.1 \pm 10.6)\ \mathrm{kJ \cdot mol^{-1}}$.

$$\Delta_f H^\circ_m(\mathrm{O, g}) = 249.17\ \mathrm{kJ \cdot mol^{-1}},^{(13)}$$

$$\Delta_f H^\circ_m(\mathrm{C_6H_5C{\equiv}C \cdot}) = 642\ \mathrm{kJ \cdot mol^{-1}},^{(8)}$$

$$\Delta_f H^\circ_m(\mathrm{CH_2{=}CH \cdot}) = 288\ \mathrm{kJ \cdot mol^{-1}},^{(7)}$$

$$\Delta_f H^\circ_m\{\mathrm{(C_6H_5)_3Ge \cdot}\} = 460\ \mathrm{kJ \cdot mol^{-1}}.$$

This last is an assumed value† based on $\Delta_f H^\circ_m\{(C_6H_5)_3Sn \cdot\} = 519\ \mathrm{kJ \cdot mol^{-1}}$,(9) $\langle D \rangle(Sn{-}C_6H_5) = 268\ \mathrm{kJ \cdot mol^{-1}}$, and $\langle D \rangle(Ge{-}C_6H_5) = 322\ \mathrm{kJ \cdot mol^{-1}}$.(2) There might be a considerable uncertainty in this assumption, but this is not important from the point of view of comparison, since all the compounds being considered contain this radical. The values obtained are

$$D\{\mathrm{(C_6H_5)_3Ge{-}C_2H_3}\} = 385\ \mathrm{kJ \cdot mol^{-1}},$$

$$D\{\mathrm{(C_6H_5)_3Ge{-}C_2C_6H_5}\} = 523\ \mathrm{kJ \cdot mol^{-1}},$$

$$\langle D \rangle\{\mathrm{(C_6H_5)_3Ge{-}O}\} = 455\ \mathrm{kJ \cdot mol^{-1}}.$$

If Ge or Sn is linked directly to an aromatic ring, to an olefinic group, or to an acetylenic group, there is the possibility of partial π-bonding using the unoccupied d-orbitals of the metal. There has been controversy about the existence of this effect in Ge,(10) and the evidence seems to indicate that if it is present, it will be to a lesser extent than in Sn compounds. The above dissociation enthalpies when compared with the values for the corresponding Sn compounds:(11)

$$D\{\mathrm{(C_6H_5)_3Sn{-}C_2H_3}\} = 282\ \mathrm{kJ \cdot mol^{-1}},$$

$$D\{\mathrm{(C_6H_5)_3Sn{-}C_2(C_6H_5)}\} = 427\ \mathrm{kJ \cdot mol^{-1}},$$

$$\langle D \rangle\{\mathrm{(C_6H_5)_3Sn{-}O}\} = 339\ \mathrm{kJ \cdot mol^{-1}},$$

do not appear to support this. The dissociation enthalpy of a bond would normally be increased by about 80 $\mathrm{kJ \cdot mol^{-1}}$ in going from an essentially sp^2 configuration to an sp one and for both the Ge and Sn cases the change is about 60 $\mathrm{kJ \cdot mol^{-1}}$ greater than this, indicating that there is some interaction with the π-electrons of the triple bond. $D\{(C_6H_5)_3Ge{-}C_6H_5\} = 360\ \mathrm{kJ \cdot mol^{-1}}$, so that $D\{Ge{-}C(sp^2)\}$ is greater than $D\{Ge{-}C(ar)\}$ by about 25 $\mathrm{kJ \cdot mol^{-1}}$. This may be attributed to the stability of the phenyl radical.

The bond-dissociation enthalpies $D/(\mathrm{kJ \cdot mol^{-1}})$:

Ge–C(sp)	Ge–O	Ge–C(sp^2)	Ge–C(ar)
523	455	385	360

lie on a smoothly descending curve.

The standard molar enthalpies of formation of the gaseous compounds from their constituent atoms may be used to obtain the bond-enthalpy terms: $E\{Ge{-}C(sp^2)\}$, $E\{Ge{-}C(sp)\}$, and $E\{Ge{-}O\}$, as follows.

The standard molar enthalpy of atomization of $(C_6H_5)_3GeCH{=}CH_2$ is

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† We are grateful to Dr G. Pilcher, Manchester University, for a discussion on this point.

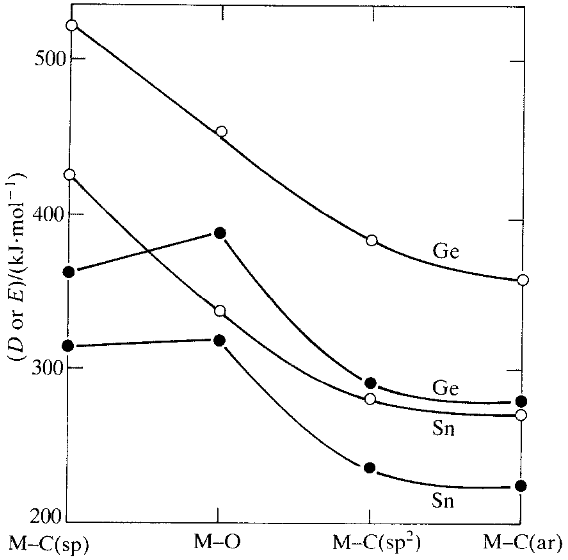

FIGURE 1. For Ge–C, Ge–O, Sn–C, and Sn–O bonds: ○, dissociation enthalpies; ●, bond enthalpies.

18239.6 kJ · mol^{-1}, which may be represented by the contributions:†

$$\begin{aligned}&-3\Delta_a H^\circ_m(C_6H_5\cdot)+3E\{\mathrm{Ge{-}C(ar)}\}+E\{\mathrm{Ge{-}C(sp^2)}\}+2E\{\mathrm{C(sp^2){-}H}\}_2\\&\qquad+E\{\mathrm{C(sp^2){-}H}\}_1+E\{\mathrm{C(sp^2){-}C(sp^2)}\}\\&=(15284.2+840)\ \mathrm{kJ\cdot mol^{-1}}+E\{\mathrm{Ge{-}C(sp^2)}\}\\&\quad+(846.8+420.6+556.5)\ \mathrm{kJ\cdot mol^{-1}}\\&=18239.6\ \mathrm{kJ\cdot mol^{-1}},\ E\{\mathrm{Ge{-}C(sp^2)}\}=291.5\ \mathrm{kJ\cdot mol^{-1}}.\end{aligned}$$

The standard molar enthalpy of atomization of $(C_6H_5)_3GeC{\equiv}C(C_6H_5)$ is 22749.6 kJ · mol^{-1} which may be represented by the contributions:

$$\begin{aligned}&-4\Delta_a H^\circ_m(C_6H_5\cdot)+3E\{\mathrm{Ge{-}C(ar)}\}+E\{\mathrm{Ge{-}C(sp)}\}+E\{\mathrm{C(sp){-}C(sp)}\}+\{\mathrm{C(sp){-}}\\&\mathrm{C(ar)}\}\\&\quad=(20379.0+840.0)\ \mathrm{kJ\cdot mol^{-1}}+E\{\mathrm{Ge{-}C(sp)}\}+(766.9+402.1)\ \mathrm{kJ\cdot mol^{-1}}\\&\quad=22749.6\ \mathrm{kJ\cdot mol^{-1}},\ E\{\mathrm{Ge{-}C(sp)}\}=361.6\ \mathrm{kJ\cdot mol^{-1}}.\end{aligned}$$

The standard molar enthalpy of atomization of $(C_6H_5)_3Ge{-}O{-}Ge(C_6H_5)_3$ is 33026.0 kJ · mol^{-1} which may be represented by the contributions:

$$\begin{aligned}&-6\Delta_a H^\circ_m(C_6H_5)+6E\{\mathrm{Ge{-}C(ar)}\}+2E\{\mathrm{Ge{-}O}\}\\&\quad=(30568.4+1680.0)\ \mathrm{kJ\cdot mol^{-1}}+2E\{\mathrm{Ge{-}O}\}=33026.0\ \mathrm{kJ\cdot mol^{-1}},\\&\qquad\qquad\langle E\rangle\{\mathrm{Ge{-}O}\}=388.8\ \mathrm{kJ\cdot mol^{-1}}.\end{aligned}$$

As would be expected these values are consistently higher than the corresponding Sn ones. The increase in E in passing from M–C(sp²) to M–C(sp) is about the same

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† These are the Laidler parameters recommended by Cox and Pilcher.(12) The molar enthalpies of formation of the gaseous atoms are also taken from reference 12.

in each case (about 70 kJ · mol^{-1}). The trends in the bond-dissociation enthalpies and the bond enthalpies terms are illustrated in figure 1.

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