sorbates, the oil inhibits the progress of the interaction with the surface.

The interaction of the silica-supported Co adsorbent produced the same types of surface structures as the oil-supported Co. The main difference is the increased quantity and stability of the surface species on the silica-supported Co. As well as having medium-intensity bands assigned to chemisorbed CO and a surface acyl structure, methanol on silica-supported Co has a band at 2835 cm^{-1} which is interpreted as indicating the presence of a methoxide structure. On the evaporated-into-oil Co, methanol and ethanol gave only weak bands for acyl and chemisorbed CO structures together with medium-intensity bands for alkoxide structures. Ethanol on silica-supported Co gives medium intensity bands for chemisorbed CO and an acyl structure in addition to bands in the C–H stretching region. Again a comparison of the relative intensities in the C–H region to the acyl C–O stretching band with those found in transition metal acyl complexes suggests that most of the intensity in the C–H region is not due to the acyl structure. The validity of this comparison is supported by the methanol adsorption data where a specific band

for the alkoxide structure exists as well as the acyl band. The similarity of the pattern for the relative intensities of the C–H stretching bands to those in the adsorbate, ethanol, together with the results for methanol, suggests the presence of some ethoxide structure from ethanol adsorption.

Similar arguments may be made for the existence of alkoxide structures on silica-supported Co in addition to the acyl structure and a small amount of CO indicated by bands in the appropriate regions for adsorbed 1-propanol, 2-propanol, and acetone. For these adsorbates, only weakly held alkoxide structures were found on oil-supported Co. Again, the inhibiting effect of the oil is exhibited.

Over-all comparison of the silica-supported and oil-supported metals shows no fundamental difference in the adsorption process on each. The oil is observed to have an inhibiting effect on dehydrogenation and alkyl migration reactions on the surface.

The Heat of Formation of Silylgermane[1]

by Stuart R. Gunn and John H. Kindsvater

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The heats of explosion of stibine–silylgermane mixtures at several composition ratios and of equivalent stibine–disilane–digermane mixtures have been measured. Comparison of the results gives $\Delta H° = -0.19 \pm 0.11$ kcal mole^{-1} for the reaction $^{1}/_{2}\mathrm{Si_2H_6}(g) + ^{1}/_{2}\mathrm{Ge_2H_6}(g) \rightarrow \mathrm{H_3SiGeH_3}(g)$, and 27.8 kcal mole^{-1} for $\Delta H_f°(\mathrm{H_3SiGeH_3}(g))$.

The heats of formation of disilane and digermane have previously been measured in this laboratory by calorimetry of explosions of the gases in mixtures with stibine.[2,3] The present study of the heat of formation of silylgermane was undertaken to see if there is any significant deviation of the thermochemical bond

energy $E(\mathrm{Si-Ge})$ from the mean of $E(\mathrm{Si-Si})$ and $E(\mathrm{Ge-Ge})$, which would be expected on the basis of the

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

(3) S. R. Gunn and L. G. Green, *ibid.*, **68**, 946 (1964).

very similar electronegativities of silicon and germanium in the absence of any perturbing interactions. After the completion of this work we learned of recent mass spectrometric appearance potential measurements by Saalfeld and Svec[4] which indicate $\Delta H_f{}^\circ$ (H_3SiGeH_3) to be some 20 kcal mole^{-1} less positive than the mean of $\Delta H_f{}^\circ(Si_2H_6)$ and $\Delta H_f{}^\circ(Ge_2H_6)$. Saalfeld and Svec[5,6] have previously measured the mass spectrometric appearance potentials of fragments from several hydrides which we have also studied calorimetrically; the heats of formation and thermochemical bond energies deduced therefrom are generally in good agreement with the calorimetric values. For silicon and germanium hydrides, agreement is improved if the heats of atomization of silicon and germanium selected by the National Bureau of Standards[7] are used[3] rather than the higher values selected by Cottrell[8] which were used[2] in our original calculations, but the current measurements of Saalfeld and Svec[4] do not depend on any heats of atomization to derive $\Delta H_f{}^\circ$ (H_3SiGeH_3).

Experimental Section

Materials. Monosilane was prepared by the acid hydrolysis of magnesium silicide and monogermane by the reduction of germanium dioxide with aqueous hydroborate. A mixture of the two was then subjected to an electric discharge as described by Spanier and MacDiarmid.[9] The disilane, digermane, and silylgermane produced were finally purified by gas–liquid chromatography, using a column of silicone oil supported on firebrick. The infrared spectrum of the silylgermane was in good agreement with that given by Spanier and MacDiarmid.[9] The principal evidences of purity were the infrared spectra and the hydrogen yields obtained in the explosion measurements.

Calorimetry. The method used was a comparative one involving matched pairs of runs wherein the heat of explosion of a mixture of stibine and silylgermane was compared with the heat of explosion of an equivalent mixture of stibine, disilane, and digermane. In this way the uncertain interaction heats in the ternary antimony–silicon–germanium system produced could be made to cancel out.

Samples of the gases were first measured approximately by the *P–V–T* method, then transferred to 50-ml bulbs and weighed, and finally condensed in a reaction cell[10] of about 90-ml volume which was subsequently sealed off. Following the run, a break-seal on the cell was attached to a Toepler pump and buret system for measurement of the hydrogen.

Calorimeter XXIX[11] was used with a copper resistance thermometer. Explosions were initiated at 25.0 ±

0.2°. Following the heat measurement the cell was removed, covered with a manganin wire heater, and reinserted after cooling the calorimeter. Calibration was then performed by electrical heating over nearly the same temperature interval as that of the explosion measurement.

The platinum-fuse ignition technique[10] previously used was discontinued. It was found that the 0.010-in. diameter tungsten electrodes with considerably oxidized surfaces when constrained to lie in loose contact with one another constituted a spark gap which upon discharge of a 0.1-mf capacitor charged to 600 v would consistently initiate the explosion of stibine. The fraction of the energy dissipated in the firing switch and leads external to the calorimeter is uncertain and probably highly variable, but since the total energy involved is only 0.009 cal, the correction and its uncertainty are negligible.

Since the calorimetric procedure involves holding the gaseous mixture in the reaction cell at 25° for *ca.* 40 min before firing, it is necessary that no rearrangement of stibine–silylgermane or stibine–disilane–digermane mixtures occur during this period; that is, that the mixtures be energetically equivalent to the separate gases. It was found that a disilane–digermane mixture stored in a Pyrex tube 3 days at room temperature showed no change in infrared spectrum, the limit of detection for silylgermane being *ca.* 3%. Stibine–silylgermane and stibine–disilane–digermane mixtures comparable with those employed in the calorimetric runs gave infrared spectra a few minutes after mixing showing all the absorption peaks of the separate components and no additional features; after storage for 1 hr at room temperature in Pyrex tubes containing tungsten wires (these being the only materials contacting the gas in the calorimeter cells) the spectra were completely unchanged. Finally, two auxiliary runs were performed in the calorimeter in which *ca.* 1 mmole of stibine was injected into a cell containing *ca.* 0.5 mmole of silylgermane or 0.25 mmole each of disilane and digermane. In both runs the heat effect was 0 ±

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(8) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworth and Co. Ltd., London, 1958.

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(11) S. R. Gunn, *Rev. Sci. Instr.*, **35**, 183 (1964).

Table I: Heats of Decomposition of H_3SiGeH_3 and Si_2H_6–Ge_2H_6 Mixtures

Run	A	B	C	D	E	B'	q_{obsd}, cal	Q_x, kcal mole^{-1}
				mmoles				
1	2.118	0.423	0.409	...	5.665	0.003	96.00	1.42
2	2.110	...	...	0.842	5.685	0.002	95.95	1.14
3	2.117	0.426	0.418	...	5.691	0.006	96.27	1.37
4	2.123	...	...	0.847	5.727	0.000	96.44	0.99
5	2.127	0.528	0.510	...	6.248	0.007	102.02	1.01
6	2.124	...	...	1.061	6.362	0.002	102.81	0.94
7	2.138	0.542	0.518	...	6.361	0.008	103.05	1.11
8	2.128	...	...	1.080	6.421	0.004	103.44	0.89
9	2.090	0.633	0.623	...	6.851	0.016	107.18	0.95
10	2.079	...	...	1.254	6.851	0.010	106.97	0.94
11	2.143	0.643	0.646	...	7.056	0.008	110.26	0.96
12	2.154	...	...	1.288	7.078	0.006	110.35	0.75

0.03 cal (after subtracting the PV compressional heat due to entering stibine).

Results

Twelve runs were performed, constituting six matched pairs, two pairs at each of the three approximate stibine:silylgermane ratios 2:0.8, 2:1.0, and 2:1.2. The data are given in Table I. A, B, C, and D denote amounts of stibine, disilane, digermane and silylgermane taken, respectively, and E is the amount of hydrogen found. The assumption is made that the deficiency in hydrogen found compared with that calculated to be produced from the amounts of reactants is all present as disilane, whether the original mixture contained disilane and digermane or silylgermane. The justification for this is that digermane was found to explode quantitatively at low stibine:digermane ratios,[2] whereas disilane required a much higher stibine: disilane ratio, and that the apparent heat of decomposition of disilane, calculated from hydrogen found, was substantially independent of the apparent percentage decomposed.[2] This hypothetical remaining disilane is then designated B' and calculated from

$$B' = \frac{1}{3}(1.5A + 3B + 3C + 3D - E) \quad (1)$$

Column 7 gives q_{obsd}, the observed heat of the run. The energy of explosion of stibine,[2,10] q_A, is taken to be $34.98A$; q_B is taken[2] as $18.30(B - B')$; q_C is taken[2,3] as $(39.96 - 3.14R)C$, where R is the antimony:germanium atom ratio in the mixture. For silylgermane, the heat of formation is tentatively assumed to be the mean of those of disilane and digermane, so that the energy of explosion, q_D, is $(29.13 - 1.57R)D - 18.30B'$. An excess heat, Q_x, is then defined as

$$Q_x = (q_{obsd} - q_A - q_B - q_C - q_D)/(B + C + D) \quad (2)$$

This is considered in the case of stibine–disilane–digermane runs to represent the interaction heat in the Sb–Si–Ge system produced, compared with the same amounts of an Sb–Ge system; in the stibine–silylgermane runs, it represents the same interaction heat together with the error in the assumption that $\Delta H_f°(H_3SiGeH_3) = \frac{1}{2}\Delta H_f°(Si_2H_6) + \frac{1}{2}\Delta H_f°(Ge_2H_6)$. It is seen that in all six pairs of runs, Q_x is somewhat less for the silylgermane runs, the differences from the paired disilane–digermane runs being 0.28, 0.38, 0.07, 0.22, 0.01, and 0.19 kcal mole^{-1}; silylgermane is slightly more stable than an equivalent mixture of disilane and digermane. Thus, for

$$\frac{1}{2}Si_2H_6(g) + \frac{1}{2}Ge_2H_6(g) \longrightarrow H_3SiGeH_3(g) \quad (3)$$
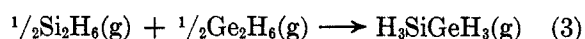
$\Delta H_3° = -0.19 \pm 0.11$ kcal mole^{-1}.

Insofar as the pairs of runs are exactly matched in Sb:Si:Ge ratios, the procedure for obtaining $\Delta H_3°$ finally involves essentially only the assumption that the energy of the solid Sb–Si–Ge mixture produced by the explosion, relative to the separated elements, is the same in corresponding silylgermane and disilane–digermane runs. X-Ray diffraction analysis of the material from runs 11 and 12 gave identical results: a (presumably metastable) solution of Ge in Sb and pure Ge, as previously reported for germane runs,[2] and no evidence of silicon or a silicon-containing phase. The source of the interaction heat Q_x is not clear. Germanium and silicon at equilibrium form a continuous range of solid solutions; perhaps some of this is formed in addition to the crystalline Ge and Ge–Sb phases seen, or the energy of the amorphous or finely divided silicon may be somehow affected by the presence of Ge to give a value different from that in the absence of Ge, or the energy of the Ge–Sb phase may be similarly affected by the presence of Si.

Using 17.1 kcal mole^{-1} for $\Delta H_f{}°(Si_2H_6)$[2] and 38.8 for $\Delta H_f{}°(Ge_2H_6)$,[2,3] $\Delta H_f{}°(H_3SiGeH_3)$ is calculated to be 27.8. The absolute value of this figure is subject to errors, mainly from the uncertainty in $\Delta H_f{}°(Si_2H_6)$ resulting from the indefinite energy of the Si produced[2] relative to the standard state and, to a lesser extent, from uncertainties in $\Delta H_f{}°(Ge_2H_6)$. The more interesting value $\Delta H_3{}°$ should however be relatively free of systematic error. Using the heats of atomization selected by Cottrell[8] and our previous values for the heats of formation of monosilane[2] and monogermane,[2,3] the thermochemical bond energies derived are 46.4 for $E(Si-Si)$, 38.2 for $E(Ge-Ge)$, and 42.5 for $E(Si-Ge)$.

Spanier and MacDiarmid observed both the boiling and melting points of silylgermane to be very close to the mean of the values for disilane and digermane. They interpreted this as evidence for a very low polarity of the molecule, consistent with the similar electronegativities of silicon and germanium. The present results are in accord with such an interpretation.

Mass Spectra of Volatile Hydrides. IV. Silylgermane[1,2]

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Mass spectra of silylgermane and the related hydrides silane, disilane, germane, and digermane have been studied. Positive ion fragmentation patterns were measured using 70-v electrons. From the appearance potentials of selected ions of these compounds the following thermochemical values have been calculated (in kcal/mole): $\Delta H_f{}°(SiGeH_6) = 7.5$; $D(H_3Si-GeH_3) = 99.9$; $D(H_3Si-SiH_3) = 84$; $D(H_3Ge-GeH_3) = 75.5$; $\Delta H_f{}°(SiH_3) = 50.4$; $\Delta H_f{}°(GeH_3) = 57$; e.a.$(SiH_3) = -39.1$; e.a.$(GeH_3) = -32.3$.

Introduction

The preparation and purification of silylgermane, $SiGeH_6$, has been described by Spanier and MacDiarmid.[3] The compound was identified from its mass spectrum but neither the fragmentation pattern nor any other mass spectral properties were reported. It is the purpose of this paper to present such data and report on thermochemical properties derived from them.

Experimental Section

Silylgermane was prepared by passing a 1:1 mixture of silane and germane, prepared individually by standard methods,[4,5] with separated isotopes ^{28}Si (99.38%)

and ^{74}Ge (96.06%), through a silent electric discharge following the procedure of Spanier and MacDiarmid.[3] Trap-to-trap distillation was employed to separate the products of the discharge reaction. A modified Con-

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