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Thermochemistry of Organic Derivatives of Non-transition Elements

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Studies of the enthalpies of formation (ΔH_f°) of a wide variety of organic derivatives of non-transition Group I-VI elements (450 substances), described in the literature, are discussed. The recommended values of ΔH_f° are tabulated and different versions of the enthalpy of combustion method and reaction calorimetry, used to determine the enthalpies of formation, are examined; the characteristic features, advantages, and disadvantages of specific experimental techniques are noted. All the thermochemical quantities quoted have been recalculated taking into account up to date initial data. The average dissociation energies ($\bar{D}$) of 115 chemical bonds, formed by non-transition elements (E^{nt}) in their organic compounds, have been calculated from the enthalpies of formation. The regular variation of the quantity $\bar{D}(E^{ent}-R)$, where R is an organic group, with the atomic number of the element E^{nt} down the corresponding Group in the Periodic System is demonstrated. The influence of the nature of the organic group on $\bar{D}(E^{nt}-R)$ is described.

The bibliography includes 260 references.

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I. INTRODUCTION

In the last 20 years many organic derivatives of non-transition elements have found extensive applications in the national economy. For example, the use of organomagnesium halides (Grignard reagents) as intermediates in the industrial synthesis of a large number of organic substances and the use of alkyl and alkyl halide compounds of aluminium as well as lithium alkyls as components of catalytic mixtures for polymerisation processes are well known. Organosilicon compounds are used to prepare lubricating agents, rubber-like polymers with a wide temperature range of high elasticity, and polymeric films with selective gas permeability, and for other purposes. In recent years methods have been developed for the use of alkyl derivatives of a number of Group II–VI non-transition elements in the industrial synthesis of semiconductor compounds of the type $A^{III}-B^{V}$,

$A^{II}-B^{VI}$, and $A^{II}-B^{IV}$. There are also other important possibilities for the applications of the compounds under consideration.

On the other hand the thermodynamic parameters of the syntheses and reactions of many industrially important organic derivatives of non-transition elements have still not been determined or have been merely estimated. This hinders the development and improvement of the technology of the processes involved in their manufacture and their applications. Calculations of the thermodynamic parameters of the above reactions are in many instances impossible owing to the lack of literature data on the thermodynamic properties of the initial compounds. On the other hand, in other cases such data are available, but they are scattered among different literature sources and the most reliable results have not been selected. This applies in the first place to the enthalpies of formation.

The present review considers critically the enthalpies of formation of all 450 organic derivatives of non-transition elements, relevant information about which has been published in 250 papers in scientific journals of different countries up to 1977† and reliable standard enthalpies of formation of the substances indicated are recommended.

The standard enthalpy of formation of a compound $\Delta H^{\circ}_{f,298}$ is the term given to the enthalpy of its synthesis under standard conditions (298 K; 101325 Pa), in the stable physical state under the given conditions, from the elements in their stable state under standard conditions. In many instances such reactions do not really occur, since their enthalpies cannot be measured, but the above quantities can be calculated on the basis of Hess's law from the enthalpies of other (real) reactions involving the relevant compounds.

The standard enthalpies of formation of the compounds have in fact been selected as the fundamental thermochemical quantities for the calculation of the enthalpies of a wide variety of other reactions under standard conditions on the basis of Hess's law by means of the equation

$$\Delta H^{0}_{r,298} = \sum_{i} \nu_i \Delta H^{0}_{f,298}(i) - \sum_{j} \nu_j \Delta H^{0}_{f,298}(j), \qquad (1)$$

where ν is the stoichiometric coefficient of the reactant in the reaction equation and the indices i and j denote the reaction products and the starting materials respectively#. The enthalpies of reaction at 298 K can be adjusted to any temperature T by means of the Kirchhoff formula:

$$\Delta H^{0}_{r,T} = \Delta H^{0}_{r,298} + \int_{298}^{T} \Delta(\nu C_p)\,dT, \qquad (2)$$

where $\Delta(\nu C_p) = \sum_i \nu_i C_p(i) - \sum_j \nu_j C_p(j)$ and $C_p = f(T)$ is the heat capacity of the reactant at constant pressure. Here one usually employs polynomials of the type $C_p = a + bT + cT^2$, which are fitted to the experimental data. In Eqn.(2) it is assumed that in the range 298–T (K) the reactants do not undergo phase transformations. Otherwise it would be necessary to take into account also the enthalpies of these transitions.

The enthalpies of formation of organic compounds (OC) are as a rule calculated from their experimental enthalpies of combustion (ΔH°_{c}) in oxygen§ (the enthalpy of combustion method) by means of Eqn.(3) which follows from Eqn.(1):

$$\Delta H^{0}_{f,298}(\mathrm{OC}) = \sum_{i} \nu_i \Delta H^{0}_{f,298}(i) - \Delta H^{0}_{c,298}(\mathrm{OC}), \qquad (3)$$

where the index i denotes the combustion product (CO_2, H_2O, and other oxides). In many instances the quantities ΔH°_{f}(OC) are calculated from the enthalpies of other reactions involving the given organic compound (reaction calorimetry). In calculations by Eqn.(1) and (3) the values of $\Delta H^{\circ}_{f,298}$ for all the reactants except for the test substance are tabulated quantities[1,2].

The combustion of organoelemental compounds in order to determine their enthalpies of combustion is carried out in stationary or rotating bomb calorimeters. Combustion of such substances in a stationary bomb was carried out in early investigation by Berthelot[3] (1899) in a study of the thermochemistry of dimethyl- and diethyl-mercury. The specific difficulties arising in the study of organoelemental compounds in a stationary bomb calorimeter were first discovered much later when Long and Norrish[4] (1949) made a detailed study of the combustion products of a number of alkyl derivatives of zinc, cadmium, boron, and aluminium formed in the bomb. These investigators established two factors which reduce the accuracy of the measurement of enthalpies of combustion: incomplete oxidation of the initial substances and the possibility of additional reactions between the combustion products.

However, despite the experimental complications which are frequently encountered, the method of combustion in a stationary bomb calorimeter has been widely used and is at present the principal procedure for the study of the thermochemistry of organoelemental compounds. In particular it is used successfully in the investigation of organic derivatives of mercury, tin, germanium, and certain other metals, whose oxidation products in the bomb calorimeter are not difficult to identify.

In order to overcome difficulties characteristic of the combustion of substances in a stationary bomb calorimeter, Good and coworkers[5-9] developed a method for the determination of the enthalpies of combustion of organoelemental compounds of certain classes by combusting them in a rotating bomb calorimeter. This method provides for the dissolution of the combustion products in a specially selected solvent in order to obtain a thermodynamically unambiguous final state of the reaction system. This combustion method has been applied successfully to organic derivatives of boron, silicon, germanium, lead, phosphorus, arsenic, bismuth, and selenium. Nevertheless, the need to choose an appropriate solvent in each specific instance, the appearance of new sources of error, and the difficulty of many operations prevent the wide-scale employment of the rotating bomb calorimeter method.

Among the different versions of reaction calorimetry, the determinations of the enthalpies of hydrolytic and halogenation reactions have been most widely used. During the fairly rapid course of the selected reactions close to room temperature and in the absence of side reactions, these methods lead to more accurate results than the combustion of a test compound in a bomb calorimeter. However, they are difficult to apply to new relatively little investigated classes of compounds, for which it is difficult to select reactions suitable for calorimetric measurements.

†The properties of ~200 such compounds are quoted in a monograph[1] published in England in 1970 (there is no Russian translation).

#If useful work is not performed in the given process (for example, electrical work) and the process takes place at constant pressure, then its enthalpy is equal to the evolved heat or the heat absorbed from outside, corresponding to a specific mass of the substances which have reacted.

§The enthalpy of formation of molecular oxygen is zero at any temperature, like that of any other elements.

Tables 1–5 present the enthalpies of formation of organic derivatives of non-transition elements, which we selected as the most reliable as a result of the analysis of the corresponding literature sources. In choosing these quantities, we turned attention to the method of their determination, the purities of the initial preparations, the unambiguity of the analytical results for the reaction products, and the precision of the calorimetric experiment (allowance for the necessary corrections and errors of the measurements and calculations). In cases where the given substance has been investigated more than once Tables 1–5 present all the references (in chronological order) and those from which the most reliable value of ΔH_f° has been selected are printed bold. After the references to the original literature, the method of determination of the given quantity is indicated in brackets and the following notation is used: SB—combustion in a stationary bomb; RB—combustion in a rotating bomb; R—reaction calorimetry. The enthalpies of vaporisation or sublimation, required for the calculation of ΔH_f° in the gaseous monomeric state, are in most cases quoted in the reports in which the experimental enthalpies of formation in the condensed state are given. In the remaining cases they were taken from other literature sources[1,10,11].

Analysis of the literature data showed that the real accuracy of the determination of the ΔH_f° for the compounds under consideration is usually not better than to within 1 kcal mol^{-1} and only in the most favourable conditions (mainly when reaction calorimetry is used) is it approximately to within 0.5 kcal mol^{-1}. The attainment of a higher accuracy is restricted, on the one hand, by the specific features of the given calorimetric experiment, and, on the other hand, by the need to use in the calculations a number of auxiliary thermochemical quantities. The values of the latter, quoted in modern handbooks[10,11], are frequently insufficiently accurate and their agreement with one another is inadequate. The authors of the present review therefore thought it desirable to round off appropriately the selected experimental values of ΔH_f°.

All the enthalpies of formation and the average bond dissociation energies taken from the original reports were recalculated taking into account the new enthalpies of formation of the compounds and atoms quoted in Ref. 11. In the absence of the necessary information in the given handbook[11], the latter was taken from other publications[2,10,12–14].

Together with compounds containing element–carbon bonds, we examined also certain compounds without such bonds but with compositions and physicochemical properties close to those of organoelemental compounds. The review does not include organic derivatives containing, apart from C–H and C–C bonds, only bonds formed by carbon with oxygen, the halogens, nitrogen, or sulphur. For these substances, there are very many thermochemical data[1,2] and it is desirable to consider them separately.

In each of Tables 1–5 the substances are arranged in order of increasing atomic number of their non-transition elements in the given Group of the Periodic System. For the same element, related compounds are grouped together. Compounds containing, apart from the given element, only carbon and hydrogen are indicated first; next follow compounds containing also oxygen, the halogens, nitrogen, or sulphur. Heterocyclic compounds have been isolated in individual groups and have been arranged in an analogous sequence. The physical states of the substances, to which the values of ΔH_f° refer, are denoted by the following symbols: (c) = crystal; (l) = liquid (appended to the formulae of the compounds), and (g) = gas [appended in brackets to the symbol of the enthalpy of formation: $\Delta H_{f\,(g)}$].

The enthalpies of formation (ΔH_f°) examined in this review are expressed in thermochemical kilocalories (1 kcal = 4.1840 kJ) and are referred to the standard pressure of 101325 Pa (this is indicated by superscript 0) and the standard temperature of 298.15 K.

II. COMPOUNDS OF GROUP I NON-TRANSITION ELEMENTS

The recommended enthalpies of formation of these substances are listed in Table 1.

Table 1. Standard enthalpies of formation of organic derivatives of Group I non-transition elements (kcal mol^{-1}).*

Compound	ΔH_f^0	References	Compound	ΔH_f^0	Refs.
CH_3Li (c)	−17.9±0.5	15 (R)	p-$CH_3C_6H_4Li$ (c)	+0.9±0.5	15 (R)
C_2H_5Li (c)	−13.5±0.5	16 (SB), 15 (R)	p-ClC_6H_4Li (c)	+1.3±0.5	15 (R)
C_3H_5Li (l)	−1.4±0.5	15 (R)	CH_3NHLi (c)	−22.5±0.5	18 (R)
$(CH_3)_2CHLi$ (l)	−13.8±0.5	15 (R)	C_2H_5OLi (c)	−109±1	19 (R)
n-C_4H_9Li (l)	−31.6±0.5	17 (R), 16 (SB) 15 (R)	C_2H_5ONa (c)	−98±1	19 (R)
s-C_4H_9Li (l)	−21.0±0.5	15 (R)	C_2H_5OK (c)	−98±1	19 (R)
t-C_4H_9Li (l)	−22.0±0.5	15 (R)	C_2H_5ORb (c)	−97±1	20 (R)
C_6H_5Li (c)	+11.8±0.5	15 (R)	C_2H_5OCs (c)	−97±1	20 (R)
$C_6H_5CH_2Li$ (c)	+3.7±0.5	15 (R)			

*For the explanation of the Table, see the introduction.

Lebedev et al.[16] determined the enthalpies of formation of ethyl-lithium and n-butyl-lithium by the enthalpy of combustion method. The above compounds were oxidised under the conditions of a stationary bomb calorimeter to LiO_2(c), CO_2(g), and H_2O(l). Chemical analysis of the solid combustion products showed that significant amounts of Li_2O_2 and Li_2CO_3 were absent.

A number of workers[15,17–20] believe that different versions of reaction calorimetry constitute a more reliable method for the determination of the enthalpies of formation of organolithium compounds. Thus the enthalpy of formation of n-butyl-lithium has been calculated[17] from the enthalpy of its hydrolysis measured calorimetrically: ΔH_f°[n-C_4H_9Li(l)] = −31.4 ± 0.7 kcal mol^{-1}. However, this value is close to that found by the enthalpy of combustion method[16] (−31.8 ± 1.7 kcal mol^{-1}). Table 1 lists the average of the above values[16,17] as the enthalpy of formation of n-butyl-lithium. The interactions of organolithium compounds with gaseous HBr are also suitable for calorimetric measurements. The study of the thermochemistry of these processes, occurring in petroleum ether at room temperature, made it possible[15] to calculate the enthalpies of formation of 11 organic derivatives of lithium.

The enthalpies of formation of alkali metal ethoxides have been found[19,20] from the enthalpies of their reactions with aqueous sulphuric acid solution determined calorimetrically. The calculation of the ΔH_f° for the compounds under consideration in the gaseous state requires, apart from the data in Table 1, the corresponding enthalpies of sublimation (vaporisation), which are not available in the literature. The temperature variation of the vapour pressures of ethyl-lithium and n-butyl-lithium has been studied[16,21]. However, the calculation of the enthalpies of sublimation (vaporisation) from these data is complicated by the fact that the above

compounds vaporise in the form of associated species. Thus ethyl-lithium sublimes in the form of tetrameric and hexameric molecules[22,23]. The association of gaseous n-C_4H_9Li has not been studied, but it is known[24] that gaseous t-butyllithium is tetrameric.

III. COMPOUNDS OF GROUP II NON-TRANSITION ELEMENTS

The recommended enthalpies of formation of the above substances are listed in Table 2.

The application of the enthalpy of combustion methods to organozinc compounds involves serious experimental difficulties. Firstly, the degree of oxidation of these compounds in the bomb calorimeter never reaches 100%. Thus, in a study of diethylzinc, Long and Norrish carried out 50 combustions of this substance, but complete combustion was never achieved, as shown both by visual inspection of the contents of the bomb calorimeter after the experiments and by chemical analysis of the combustion products. Secondly, there is a possibility of reactions between the combustion products which are difficult to take into account. For example, in the combustion of dimethylzinc the zinc oxide formed was partly hydrated and partly (to the extent of ~8%) reacted with carbon dioxide to form zinc carbonate. The interpretation of the experimental results[4] therefore involved the calculation of corrections due to both the incomplete combustion of the zinc compounds investigated and to the occurrence of side reactions between their combustion products.

In order to find the ΔH_f° for the methyl and ethyl compounds of zinc and cadmium, Skinner and coworkers[30,34] measured the enthalpies of their hydrolysis, iodination, and reaction with aqueous sulphuric acid solution. The hydrolytic reactions led to the formation of the metal hydroxides and the modifications of the $Zn(OH)_2$ and $Cd(OH)_2$ formed were not established, which introduced an error into the calculation of the ΔH_f° for the test compounds.

The study of iodination processes[30,34] was complicated by side reactions. For example, in the case of ethyl compounds the main process

$$(C_2H_5)_2M + 2I_2 \rightarrow MI_2 + 2C_2H_5I,$$

where M = Zn or Cd, was accompanied by the reactions

$$(C_2H_5)_2M + I_2 \rightarrow MI_2 + C_4H_{10},$$

$$(C_2H_5)_2M + 2I_2 \rightarrow MI_2 + C_2H_4I_2 + C_2H_6.$$

The thermal corrections caused by the above side reactions were taken into account by the authors[30,34] in their calculations of the enthalpies of formation of the test substances. The interaction of zinc and cadmium alkyls with aqueous sulphuric acid proved to be more convenient for the calorimetric study than hydrolysis and iodination of the same compounds in view of its high rate and the lack of uncertainty as to the products.

The application of these versions of reaction calorimetry to each of the above compounds yielded satisfactorily concordant results. Thus the authors[30] obtained +4.7 ± 0.3 kcal mol^{-1} (by the hydrolytic reaction), +4.0 ± 1.0 kcal mol^{-1} (by the iodination reaction), and + 2.8 ± 0.5 kcal mol^{-1} (by the reaction with sulphuric acid) for $\Delta H_f^\circ[(C_2H_5)_2Zn(l)]$, while the corresponding values found in the same way[30,34] for $\Delta H_f^\circ[(CH_3)_2Cd(l)]$ were respectively +15.2 ± 0.2, +17.0 ± 0.1, and +15.7 ± 0.3 kcal mol^{-1}.

For organozinc compounds, a satisfactory agreement has been observed in addition between the values of ΔH_f° found by reaction calorimetry[30] and by the enthalpy of combustion method[4]. We therefore based the choice of the ΔH_f° for the above compounds on the results obtained by both methods.

In the case of organocadmium compounds there are significant differences between the values of ΔH_f° obtained by different calorimetric methods. Thus the enthalpies of formation of liquid $(CH_3)_2Cd$ and $(C_2H_5)_2Cd$ by the combustion method were found to be[4,31-33] +20.5 ± 2.8 and +20.9 ± 0.8 kcal mol^{-1}, while the values obtained by reaction

Table 2. Standard enthalpies of formation of organic derivatives of Group II non-transition elements (kcal mol^{-1}).*

Compound	ΔH_f^0	ΔH_f^0 (g)	References	Compound	ΔH_f^0	ΔH_f^0 (g)	References
$(C_6H_5)_2Be$ (c)	+37±1	+73±5	25(R)	$(n\text{-}C_4H_9)_2Hg$ (l)	−23±2	−7±2	38(SB)
$(C_5H_7O_2)_2Be$ (c)	−298±1	−276±1	26(R)	$(iso\text{-}C_4H_9)_2Hg$ (l)	−24±2	−9±2	38(SB)
$(C_{10}H_{16}O_2)_2Be$ (c)	−386±2	−362±2	26(R)	$(iso\text{-}C_5H_{11})_2Hg$ (l)	−37±2	−20±3	38(SB)
$(C_5H_4F_3O_2)_2Be$ (c)	−597±2	−574±2	26(R)	$(C_6H_5)_2Hg$ (c)	+67.3±0.5	+94.3±0.5	36(SB), 40(R), 41(SB), 42(SB)
$(cyclo\text{-}C_7H_5O_2)_2Be$ (c)	−208±1	−184±5	26(R)				
$(C_5H_5)_2Mg$ (c)	+16±1	+32±1	27(R(	$(C_2H_5Hg)_2O$ (c)	−23±2	—	43(R)
$n\text{-}C_4H_9MgCl$ (c)**	−107.7±0.5	—	28(R)	$C_2H_5HgO_2C(CH_3)_2C_6H_5$ (c)	−18±2	—	43(R)
$(C_5H_7O_2)_2Ca$ (c)	−313±1	−300±4	29(R)	$(CN)_2Hg$ (c)	+63±2	+89±2	44(R)
$(CH_3)_2Zn$ (l)	+5.7±0.5	+12.8±0.5	4(SB), 30(R)	CH_3HgCl (c)	−28.6±0.5	−13.1±0.5	35(R)
$(C_2H_5)_2Zn$ (l)	+3.9±0.5	+13.4±0.5	4(SB), 30(R) 31—33(SB)	CH_3HgBr (c)	−21±1	−5±1	35(R)
				CH_3HgI (c)	−10.6±0.5	+5±1	35(R)
$(n\text{-}C_3H_7)_2Zn$ (l)	−14±6	−3±6	4(SB)	C_2H_5HgCl (c)	−34±1	−16±1	37(R)
$(n\text{-}C_4H_9)_2Zn$ (l)	−25±6	−12±6	4(SB)	C_2H_5HgBr (c)	−26±1	−8±1	37(R)
$(C_5H_7O_2)_2Zn$ (c)	−223±1	−208±4	29(R)	C_2H_5HgI (c)	−16±1	+3±1	37(R)
$(C_{10}H_9O_2)_2Zn$ (c)	−179±1	−166±4	29(R)	$n\text{-}C_3H_7HgCl$ (c)	−40.8±0.5	−21±2	39(R)
$(CH_3)_2Cd$ (l)	+16±1	+25±1	4(SB), 34(R)	$n\text{-}C_3H_7HgBr$ (c)	−32.3±0.5	−12±2	39(R)
$(C_2H_5)_2Cd$ (l)	+13±1	+24±1	30(R), 31—33(SB)	$n\text{-}C_3H_7HgI$ (c)	−21.9±0.5	−1±2	39(R)
$(CH_3)_2Hg$ (l)	+13±1	+21±1	35(R), 36(SB)	$iso\text{-}C_3H_7HgCl$ (c)	−40.5±0.5	−20±2	39(R)
$(C_2H_5)_2Hg$ (l)	+7.3±0.5	+18±1	37(R), 36(SB) 31—33(SB)	$iso\text{-}C_3H_7HgBr$ (c)	−32.8±0.5	−13±2	39(R)
				$iso\text{-}C_3H_7HgI$ (c)	−22.4±0.5	−1±2	39(R)
$(n\text{-}C_3H_7)_2Hg$ (l)	−5.6±0.5	+7.4±0.5	38(SB), 39(R)	C_6H_5HgCl (c)	+0.1±0.5	+25±2	40(R)
$(iso\text{-}C_3H_7)_2Hg$ (l)	−4±1	+9±1	38(SB), 39(R)	C_6H_5HgBr (c)	+8±1	+33±2	40(R)
				C_6H_5HgI (c)	+18±1	+43±2	40(R)

*For the explanation of the Table, see the introduction.

**The enthalpies of formation of etheral solutions of a series of halogen-containing organomagnesium compounds are quoted by Carson and Skinner[55] and Holm[46].

calorimetry[30,32] were +16 ± 1 and +13 ± 1 kcal mol^{-1} respectively. The authors[4] note that, when organocadmium compounds are combusted in a bomb calorimeter, the solid combustion products always contain appreciable amounts of metallic cadmium and unoxidised carbon in addition to the oxide CdO. The exact calculation of the relevant corrections is difficult, which might have been the reason for the erroneous results in a number of studies[4,31–33]. Therefore, in choosing the values of ΔH_f° for cadmium compounds, we took into account only the results[30,34] obtained by reaction calorimetry.

The study of organomercury compounds has attracted much attention by thermochemists. When these substances are combusted in a bomb calorimeter, they are converted into carbon dioxide, water, and liquid mercury. A small amount of mercury (up to 10%) is then oxidised to HgO and $HgNO_3$, which requires allowance for the corresponding heat corrections. When the latter are applied correctly, it is possible to obtain fairly reliable results, as shown by the agreement, to within 1 kcal mol^{-1}, between the values of ΔH_f° for dimethyl-, diethyl-, and diphenyl-mercury found, on the one hand, by the combustion method[36,41,42], and, on the other hand, by reaction calorimetry[35,37,40].

The enthalpies of formation of the compounds R_2Hg, where $R = CH_3$, C_2H_5, C_3H_7, or C_6H_5, were obtained by Skinner and coworkers[35,37,39,40] by studying the enthalpies of bromination and iodination of the above substances.

The same workers investigated the thermochemistry of processes

$$R_2Hg + HgX_2 \rightarrow 2RHgX,$$

where X = Cl, Br or I, which made it possible to calculate the ΔH_f° for the products RHgX from the enthalpies of formation of the compounds R_2Hg found beforehand (Table 2).

IV. COMPOUNDS OF GROUP III NON-TRANSITION ELEMENTS

The recommended enthalpies of formation of the above substances are listed in Table 3.

The thermochemistry of organoboron compounds has been studied comparatively thoroughly. In the first studies in this field[4,47,48,54] the enthalpies of combustion of a number of alkylboron compounds were measured using a stationary bomb calorimeter. A number of methodological difficulties, characteristic of these substances were discovered. However, the above studies did not lead to the creation of a thoroughly developed method for the determination of the enthalpies of combustion of these compounds. Furthermore, some of the above workers expressed doubts concerning the possibility of the successful combustion of such substances in a stationary bomb calorimeter.

Gal'chenko[128], who developed a reliable method for the combustion of organoboron compounds in a stationary bomb calorimeter and applied it to a large number of organic substances containing 5–75 wt.% of boron (Table 3), made a major contribution to the development of the thermochemistry of such compounds. He established[128] that the products of their incomplete combustion include boron carbide, free carbon, and boron, and, in the case of nitrogen-containing compounds, also boron nitride. Furthermore, the combustion of the initial substance is accompanied by secondary reactions between the combustion products: the hydration of the boron oxide formed and the dissolution of part of boric acid in the water present in the bomb. However, for a high degree of combustion of the test compounds, which constitutes a necessary condition for the application of this method and is readily achieved by varying the oxygen pressure in the bomb, the mass of the specimen, the size of the crucible, and other conditions, the calculation of corrections for the incomplete combustion and secondary processes does not present special difficulty.

The correction for incomplete combustion, calculated from the determinations of carbon dioxide and boric acid in the combustion products, did not exceed 1% of the total amount of energy evolved during the experiment in most instances. It was also shown that the hydration of boron oxide and dissolution of the boric acid thus formed proceed comparatively rapidly and do not distort the variation of the temperature in the final period of the experiment. This method was used by Gal'chenko and coworkers for both liquid[50,52,53,56,60,61,63–65,74–80,85,90,103] and solid[91–102] boron compounds, the accuracy of the determination of their enthalpies of combustion being to within 0.05–0.10%.

The difficulties in the combustion of boron-containing compounds in a stationary bomb calorimeter led Good and coworkers[8,9] to develop a method involving their combustion in a rotating bomb calorimeter. By this procedure, the authors[8,9] measured the enthalpies of combustion of trimethyl- and tirethyl-amineborane. Specimens of the test substances mixed with vinylidine fluoride $(CH_2CF_2)_n$ were placed in polyester tubes. The combustion was carried out in a platinised bomb calorimeter containing an excess of aqueous HF solution. On rotation of the bomb, the combustion products interacted with the hydrogen fluoride solution and a solution of $HBF_4.14.67HF.58.72H_2O$, preliminary values of the enthalpy of which had been found in other experiments, was obtained. No solid combustion products were detected after the experiments.

The use of this combustion method involves certain difficulties as regards the assignment of the experimental results to a standard state. For example, there are not data for the solubility and enthalpy of solution of the resulting carbon dioxide in aqueous HBF_4 and HF solutions. In order to take into account the corresponding corrections, the authors[8,9] performed the so called "comparison experiments" in addition to the main experiments. In the "comparison experiment" a substance (benzoic acid or paraffin) with an accurately established enthalpy of combustion was used instead of the test compound. The amount of this substance as well as the concentration and volume of the aqueous HBF_4 and HF solution introduced into the bomb calorimeter were selected so that the final states of the reaction systems in both the comparison experiments and in the experiments designed to combust the boron compound were as far as possible similar.

The methods of reaction calorimetry have come to be widely used in the thermochemical studies of organoboron compounds. This is due to the high reactivity of the above compounds and the availability for many of them of reactions suitable for thermochemical measurements. The enthalpies of hydrolysis of the compounds have been measured most frequently. In many cases such reactions rapidly reach completion at room temperature and give rise to products whose properties have been studied in detail and which can be easily identified. Thus, in order to find the enthalpies of formation of alkoxyboron compounds, Skinner and coworkers[59] measured the enthalpies of the reactions

$$(C_nH_{2n+1}O)_3B\ (l) + 3H_2O\ (l) \rightarrow H_3BO_3\ (c) + 3C_nH_{2n+1}OH\ (l).$$

Table 3. Standard enthalpies of formation of organic derivatives of Group III non-transition elements (kcal mol^{-1}).*

Compound	ΔH_f^0	ΔH_f^0 (g)	References
$(CH_3)_3B$ (l)	−34±6	−30±6	4(SB), 47(SB),
$(C_2H_5)_3B$ (l)	−45±2	−36±2	48(SB), 47(SB), 49(R)
$(n\text{-}C_3H_7)_3B$ (l)	−66±3	−56±3	48(SB), 50(SB),
$(iso\text{-}C_3H_7)_3B$ (l)	−70±3	−60±3	50(SB)
$(n\text{-}C_4H_9)_3B$ (l)	−83±1	−68±1	51(SB), 47(SB), 52(SB), 53(SB)
$(iso\text{-}C_4H_9)_3B$ (l)	−81±2	−67±2	49(R), 50(SB)
$(s\text{-}C_4H_9)_3B$ (l)	−73±6	−58±6	54(SB)
$(iso\text{-}C_5H_{11})_3B$ (l)	−108±2	−91±2	50(SB)
$(n\text{-}C_6H_{13})_3B$ (l)	−116±1	−95±1	55(R), 56(SB)
$(cyclo\text{-}C_6H_{11})_3B$ (c)	−115±2	−95±3	57(R)
$(n\text{-}C_7H_{15})_3B$ (l)	−133±2	−109±2	55(R)
$(n\text{-}C_8H_{17})_3B$ (l)	−152±2	−124±2	55(R)
$(s\text{-}C_8H_{17})_3B$ (l)	−148±2	−121±2	55(R)
$(C_6H_5)_3B$ (c)	+12±2	+31±2	57(R)
$(CH_3O)_2BH$ (l)	−144.5±0.5	−138.4±0.5	58(R)
$(CH_3O)_3B$ (l)	−222.9±0.5	−214.6±0.5	59(R)
$(CH_3O)B(n\text{-}C_4H_9)_2$ (l)	−132±1	—	60(SB), 61(SB)
$(C_2H_5O)_3B$ (l)	−250.4±0.5	−239.8±0.5	59(R)
$(iso\text{-}C_3H_7O)_2BH$ (l)	−183.0±0.5	—	62(R)
$(n\text{-}C_3H_7O)_3B$ (l)	−269.4±0.5	−258±1	59(R)
$(n\text{-}C_4H_9O)B(n\text{-}C_4H_9)_2$ (l)	−155±1	—	63(SB)
$(n\text{-}C_4H_9O)_2B(n\text{-}C_4H_9)$ (l)	−224±2	—	65(SB)
$(n\text{-}C_4H_9O)_3B$ (l)	−286±1	−273±1	59(R), 64(SB), 43(R)
$(C_6H_5O)_3B$ (c)	−159.9±0.5	−140±1	66(R)
$(m\text{-}CH_3C_6H_4O)_3B$ (l)	−183±1	−163±1	67(R)
$(p\text{-}CH_3C_6H_4O)_3B$ (l)	−181±1	−160±1	67(R)
$(n\text{-}C_4H_9)_2BOH$ (l)	−146±1	−131±2	68(R)
$C_6H_5B(OH)_2$ (c)	−172.0±0.5	—	69(R)
$[(n\text{-}C_4H_9)_2B]_2O$ (l)	−213±1	—	64(SB)
$[(C_6H_5)_2B]_2O$ (c)	−84±2	—	69(R)
$s\text{-}C_4H_9O_2B(O\text{-}n\text{-}C_4H_9)_2$ (l)	−276±2	−264±2	43(R)
$(s\text{-}C_4H_9O_2)_2BO\text{-}n\text{-}C_4H_9$ (l)	−265±2	−254±2	43(R)
$(CH_3)_4NB_3H_8$ (c)	−38±1	—	84(SB)
$(C_2H_5)_4NB_3H_8$ (c)	−63±2	—	84(SB)
$(n\text{-}C_4H_9)_4NB_3H_8$ (c)	−106±3	—	84(SB)
$(n\text{-}C_4H_9)B(OCH_3)N(C_2H_5)_2$ (l)	−146±1	−132±1	85(SB)
$[(CH_3)_2N]_2BCl_2$ (l)	−107±2	−98±2	86(R)
$[(CH_3)_2N]_2BCl$ (l)	−94±1	−84±1	86(R)
$B(SCH_3)_3$ (l)	−50±1	−37±1	87(R)
$B(SC_2H_5)_3$ (l)	−81±1	−67±1	88(R)
$B(S\text{-}n\text{-}C_3H_7)_3$ (l)	−100±1	−79±1	87(R)
$B(S\text{-}n\text{-}C_4H_9)_3$ (l)	−117±1	−94±1	87(R)
$B(S\text{-}n\text{-}C_5H_{11})_3$ (l)	−135±1	−110±1	87(R)
$B(SC_6H_5)_3$ (c)	+16±1	+46±2	87(R)
$CH_2(CH_2)_3B(n\text{-}C_4H_9)$ (l)	−46±1	—	52(SB), 61(SB)
$CH_2(CH_2)_3B(n\text{-}C_6H_{13})$ (l)	−67±1	—	61(SB)
$CH_2(CH_2)_3B(OCH_3)$ (l)	−93±1	—	60(SB), 61(SB)
$O(CH_2)_3B(n\text{-}C_4H_9)$ (l)	−108±1	−97±1	80(SB)
$cyclo\text{-}(C_6H_5BO)_3$ (c)	−301±2	—	69(R)
$O(CH_2)_2OBCl$ (l)	−186±1	—	89(R)
$O(CH_2)_3OBCl$ (l)	−183±3	—	89(R)
$OCH(CH_3)CH_2OBCl$ (l)	−191±1	—	89(R)
$O[CH(CH_3)]_2OBCl$ (l)	−200±1	—	89(R)
$N(C_2H_5)(CH_2)_3B(n\text{-}C_4H_9)$ (l)	−71±2	−57±2	80(SB), 90(SB)
$N(n\text{-}C_3H_7)(CH_2)_3B(n\text{-}C_3H_7)$ (l)	−73±2	—	80(SB), 90(SB)
$S(CH_2)_2SBC_6H_5$ (l)	−32±1	—	88(R)
$S(CH_2)_3SBC_6H_5$ (l)	−37±1	—	88(R)
$S(CH_2)_2SBCl$ (l)	−66±1	—	88(R)
$S(CH_2)_3SBCl$ (l)	−73±1	—	88(R)
$SCH_2CH(CH_3)SBCl$ (l)	−72±1	—	88(R)
$o\text{-}B_{10}C_2H_{12}$ (c)	−42±4	−27±4	91—94(SB)
$m\text{-}B_{10}C_2H_{12}$ (c)	−59±3	−45±3	94—98(SB), 93(SB)
$p\text{-}B_{10}C_2H_{12}$ (c)	−76±4	−61±4	96(SB), 99(SB),
$(C_7H_5O_2)_3Al$ (c)	−317±1	−287±5	116(R)
$(C_7H_4CH_3O_2)_3Al$ (c)	−330±2	−300±6	116(R)
$(C_{10}H_{17}O_2)_3Al$ (c)	−572±3	−543±3	118(R)
$(C_5H_4F3O_2)_3Al$ (c)	−893±3	−867±3	118(R)
$(C_2H_5)_2AlCl$ (l)	−97±1	—	119(R), 120(R)
$(iso\text{-}C_4H_9)_2AlCl$ (l)	−118±1	—	119(R)
$(C_2H_5)AlCl_2$ (l)	−133±4	—	120(R)
$(C_2H_5)_3Al_2Cl_3$ (l)	−230±4	—	120(R)
$(C_2H_5)_2AlBr$ (l)	−83±2	—	120(R)
$(C_2H_5)AlBr_2$ (l)	−104±4	—	120(R)
$(C_2H_5)_3Al_2Br_3$ (l)	−188±4	—	120(R)
$(t\text{-}C_4H_9O_2)_3B$ (l)	−254±2	−243±2	43(R)
$(n\text{-}C_4H_9)_2BCl$ (l)	−99±2	−88±2	68(R)
$(C_6H_5)BCl_2$ (l)	−72±1	−64±1	57(R), 70(R)
$(C_6H_5)_2BCl$ (l)	−32±2	−22±2	57(R), 70(R)
$o\text{-}CH_3C_6H_4BCl_2$ (l)	−71.9±0.5	−60.7±0.5	71(R)
$p\text{-}CH_3C_6H_4BCl_2$ (c)	−81±1	−70±1	71(R)
$(CH_3O)_2BCl$ (l)	−186.2±0.5	−178.0±0.5	1(R)
$C_2H_5OBCl_2$ (l)	−157±1	−149±1	72(R)
$(C_2H_5O)_2BCl$ (l)	−205±1	−196±1	72(R)
$(m\text{-}ClC_6H_4O)_3B$ (l)	−180±6	−166±6	67(R)
$(p\text{-}ClC_6H_4O)_3B$ (l)	−177±6	−168±6	67(R)
$(n\text{-}C_4H_9)_2BBr$ (l)	−84±1	−72±1	68(R)
$C_6H_5BBr_2$ (l)	−41±1	−31±0.8	57(R), 70(R)
$(C_6H_5)_2BBr$ (l)	−17±2	−3±2	57(R), 70(R)
$(n\text{-}C_4H_9)_2BI$ (l)	−67±1	−54±1	68(R)
$[(CH_3)_2N]_3B$ (l)	−77±1	−66±1	73(R)
$[(C_2H_5)_2N]_3B$ (l)	−111±2	—	74(SB)
$(n\text{-}C_4H_9)_2BNH_2$ (l)	−88±1	—	75(SB), 76(SB)
$(iso\text{-}C_4H_9)_2BNH_2$ (l)	−90±1	—	75(SB)
$(n\text{-}C_4H_9)_2BNH(n\text{-}C_4H_9)$ (l)	−108±1	—	76(SB)
$(n\text{-}C_4H_9)B[NH(n\text{-}C_4H_9)]_2$ (l)	−120±3	—	77(SB), 78(SB)
$(n\text{-}C_4H_9NH)_3B$ (l)	−142±2	—	77(SB), 78(SB)
$(n\text{-}C_3H_7)_2B(CH_2)_3NH_2$ (l)	−75±2	—	77(SB)
$(n\text{-}C_3H_7)_2B(CH_2)_3N(CH_3)_2$ (l)	−78±2	−60±2	80(SB)
$(n\text{-}C_4H_9)_2B(CH_2)_3NH_2$ (l)	−94±2	—	79(SB), 80(SB)
$(n\text{-}C_3H_7)_2BN(n\text{-}C_3H_7)_2$ (l)	−104±1	−89±2	80(SB)
$(n\text{-}C_4H_9)_2BN(n\text{-}C_4H_9)_2$ (l)	−127±2	−107±2	80(SB)
$CH_3H_2NBH_3$ (c)	−31.6±0.5	−13±1	81(R)
$(CH_3)_2HNBH_3$ (c)	−32.5±0.5	−14±1	81(R)
$(CH_3)_2NBH_3$ (c)	−34±1	−20±1	8(RB), 81(R)
$(C_2H_5)_2NBH_3$ (l)	−47.4±0.5	−32.9±0.5	9(RB)
$(CH_3)_4NBH_4$ (c)	−17±1	—	82(SB)
$(C_2H_5)_4NBH_4$ (c)	−34±2	—	83(SB)
$(n\text{-}C_4H_9)_4NBH_4$ (c)	−63±4	—	83(SB)
$(CH_3)_2NB_2H_5$ (l)	−35±1	−28+1	1(R)
$o\text{-}B_{10}C_2H_{11}CH_3$ (c)	−60±4	−45±4	98(SB), 94(SB) 98(SB), 100(SB), 94(SB)
$m\text{-}B_{10}C_2H_{11}CH_3$ (c)	−74±3	−59±3	100(SB), 94(SB)
$p\text{-}B_{10}C_2H_{11}CH_3$ (c)	−66±4	−54±4	100(SB), 94(SB)
$o\text{-}B_{10}C_2H_{10}\text{-}1.2\text{-}(CH_3)_2$ (c)	−68±4	−52±4	98(SB), 94(SB)
$m\text{-}B_{10}C_2H_{10}\text{-}1.7\text{-}(CH_3)_2$ (c)	−75±4	−61±4	98(SB), 94(SB)
$p\text{-}B_{10}C_2H_{10}\text{-}1.12\text{-}(CH_3)_2$ (c)	−88±4	−72±4	98(SB), 94(SB)
$o\text{-}B_{10}C_2H_{11}CH_2OH$ (c)	−83±4	−65±4	98(SB), 101(SB), 94(SB)
$m\text{-}B_{10}C_2H_{11}CH_2OH$ (c)	−108±3	−89±3	98(SB), 101(SB), 94(SB)
$p\text{-}B_{10}C_2H_{11}CH_2OH$ (c)	−110±3	−90±3	98(SB), 101(SB), 94(SB)
$o\text{-}B_{10}C_2H_{11}COOH$ (c)	−131±3	−108±3	98(SB), 102(SB), 94(SB)
$m\text{-}B_{10}C_2H_{11}COOH$ (c)	−159±3	−136±3	98(SB), 102(SB), 94(SB)
$p\text{-}B_{10}C_2H_{11}COOH$ (c)	−151±4	−128±4	98(SB), 102(SB), 94(SB)
$o\text{-}B_{10}C_2H_{11}C_6H_{13}$ (l)	−108±4	−88±4	94(SB), 103(SB),
$cyclo\text{-}[HBN(CH_3)]_3$ (l)	−227±1	−217±1	104(R)
$cyclo\text{-}[ClBN(CH_3)]_3$ (c)	−262±1	—	104(R)
$cyclo\text{-}[BrBN(CH_3)]_3$ (c)	−245±1	—	105(R)
$(CH_3)_3Al$ (l)	−36±1	−21±1	4(SB), 106(R), 107(SB)
$(C_2H_5)_2AlH$ (l)	−74±4	—	108(SB)
$(C_2H_5)_3Al$ (l)	−52±2	−35±2	44(R), 108(SB), 109(SB), 107(SB)
$(n\text{-}C_3H_7)_3Al$ (l)	−69±3	−48±3	110(R, SB)
$(iso\text{-}C_4H_9)_2AlH$ (l)	−96±4	—	108(SB)
$(iso\text{-}C_4H_9)_3Al$ (l)	−70±7	—	111(SB)
$(C_2H_5)_2Al(OC_2H_5)$ (l)	−125±1	−110±2	112(SB)
$(C_2H_5)_2Al(O\text{-}n\text{-}C_3H_7)$ (l)	−156±3	−141±4	112(SB)
$(C_2H_5)_2Al(O\text{-}t\text{-}C_4H_9)$ (l)	−185±4	—	112(SB)
$[(iso\text{-}C_3H_7O)_3Al]_3$ (l)	−692.5±0.5	—	113(R)
$[(iso\text{-}C_3H_7O)_3Al]_4$ (l)	−1230.8±0.5	—	113(R)
$(CH_3COO)_3Al$ (c)	−452±1	—	106(R)
$(C_5H_7O_2)_3Al$ (c)	−428±1	−399±1	114(SB); 115(R), 116(R) 117(SB)
$(C_2H_5)_2All$ (l)	−65±2	—	120(R)
$(C_2H_5)All_2$ (l)	−69±4	—	120(R)
$(CH_3)_3Ga$ (l)	−19±1	−11±1	121(SB), 122(R)
$(C_2H_5)_3Ga$ (l)	−24±2	−14±1	123(SB), 124(SB)
$(n\text{-}C_4H_9)_3Ga$ (l)	−68±1	−54±1	124(SB)
$(iso\text{-}C_4H_9)_3Ga$ (l)	−70±1	−57±1	124(SB)
$(C_5H_7O_2)_3Ga$ (c)	−354±2	−325±3	125(R), 117(SB)
CH_3GaI_2 (c)	−51±1	—	122(R)
$(CH_3)_3In$ (c)	+34±2	+48±2	126(R)
$(C_5H_7O_2)_3In$ (c)	−336±1	−307±2	117(SB)
C_5H_5Tl (c)	+26±1	—	127(R)

*For the explanation of the Table, see the introduction.

The reactions were carried out by breaking under water a glass bulb containing a specific amount of the test compound. The water also served as the calorimetric liquid. The process reaches completion rapidly and unambiguously at room temperature. From the results of the measured enthalpies of hydrolysis, Skinner and coworkers[59,68,72,73,86] as well as

Finch, Gardner, and coworkers[57,70,87-89], calculated the enthalpies of formation of a large number of organoboron compounds of different classes: alkoxy- and alkylthio-compounds, substances containing halogens, etc.

The enthalpies of formation of a series of trialkylboron compounds were calculated by Skinner and coworkers[49,55] from the enthalpies of hydroboration of olefins measured by a calorimetric method[49,55]:

$$B_2H_6\,(g) + 6C_nH_{2n}\,(g) \rightarrow 2\,(C_nH_{2n+1})_3B\,(l)$$

This process was carried out by passing diborane through a saturated solution of the olefin in diglyme. Owing to the possible occurrence of side reactions, the hydroboration reactions are less convenient for the determination of the enthalpies of formation of boron compounds than the hydrolytic reactions. For example, when $n = 6$, 7, 8, the main olefin hydroboration product is accompanied by the formation of ~6% of its isomers in which the boron atom is attached to the second and not the first carbon atom, which requires the calculation of the appropriate corrections in the interpretation of the experimental results.

The thermochemistry of organoaluminium compounds has been less thoroughly investigated than that of boron-containing substances. Furthermore, the results obtained by different workers for the same compound differ markedly. Thus the literature values of the enthalpy of formation of liquid $(CH_3)_3Al$ include -28.7 ± 2.3 and -21.4 ± 3 kcal mol^{-1} found by the method of combustion in a stationary bomb calorimeter[4,107] and -36.1 ± 1.3 kcal mol^{-1} obtained[106] by reaction calorimetry. Bearing in mind the difficulty of attaining the complete combustion of organoaluminium compounds, we gave preference to the value[106] calculated from the measurements of the enthalpy of reaction of trimethylaluminium with acetic acid.

Even more contradictory data are available for triethylaluminium, the enthalpy of formation of which has been found to be -32.4 ± 3, -51.9 ± 2.2, -41.4 ± 1.1, and -56.6 ± 0.8 kcal mol^{-1} by the combustion method in Refs. 107–109 and 129 respectively and -36.5 ± 5 kcal mol^{-1} by reaction calorimetry[44]. The last value, calculated from the experimental enthalpy of hydrolysis of $(C_2H_5)_3Al$, cannot be regarded as reliable owing to the lack in the relevant report[44] of a detailed analysis of the gaseous products of the above reactions and the inaccuracy of the value of ΔH_f° of the amorphous product $Al(OH)_3$ formed in the hydrolysis.

The most accurate value $\Delta H_f^\circ[(C_2H_5)_3Al(l)] = -52 \pm 2$ kcal mol^{-1} has been obtained by the combustion method in a study[108] where the combustion products were analysed quantitatively and in the interpretation of the experimental results account was taken of the corresponding corrections for the incomplete combustion of the initial compound.

Measurements of the enthalpies of combustion of 30 aluminium-containing substances, including alkylaluminium hydrides and alkylaluminium chloride have been reported[129,130]. However, the above studies were carried out using insufficiently accurate calorimetric measurements. For example, the chlorine-containing substances were combusted without the use of reducing agents (hydrazine or arsenic oxide), which ensure unambiguously the state of chlorine in the combustion products; the internal surface of the bomb was not protected from the action of chlorine-containing products formed in the oxidation of the initial compound, etc. Furthermore, insufficiently purified specimens of the test compounds were used in the combustion experiments. Thus the purity of aluminium trialkyl and dialkylaluminium hydrides studied by Pawlenko[129] was between 94 and 99.5%, while that of alkylaluminium chlorides investigated in another study by Pawlenko[130] ranged from 93 to 97%.

Owing to the above deficiencies, Pawlenko[129] obtained $\Delta H_f^\circ[(\text{iso-}C_4H_9)_3Al(l)] = -92.8 \pm 2$ kcal mol^{-1}, while more careful measurements[111] lead to -69.9 ± 7.2 kcal mole^{-1}; he obtained[129] $\Delta H_f^\circ[(C_2H_5)_2AlH(l)] = -48.7 \pm 1$ kcal mol^{-1}, which does not agree with the more reliable value -73.5 ± 4.5 kcal mol^{-1} found by Shaulov et al.[108]; he quotes[130] $\Delta H_f^\circ[(C_2H_5)_2 \cdot AlCl(l)] = -56.9 \pm 1.0$ kcal mol^{-1}, while the values found in other investigations[119,120] are respectively -99.2 ± 1.3 and -96.0 ± 1.5 kcal mol^{-1}, etc. For these reasons, Pawlenko's results[129,130] have not been included in Table 3.

Smith[120] believes that calorimetric study of reactions of the type

$$^2/_3R_3Al + {}^1/_3AlX_3 \rightarrow R_2AlX,$$

where R = alkyl group and X = Cl, Br, or I, constitutes a convenient method for the determination of the enthalpies of formation of alkylaluminium halides. To reduce the rate, these processes were carried out[120] in hexadecane, where they reached completion in the course of several minutes at room temperature. The ΔH_f° for halogen-containing aluminium compounds, calculated from the experimental enthalpies of the above reactions, are listed in Table 3.

Smith[120] also discusses the agreement between the literature values of ΔH_f° for different classes of organoaluminium compounds and his own results. He examined (1) the variation of ΔH_f° within each class of organoaluminium compounds as a function of their alkyl group, (2) the difference between the enthalpies of formation of aluminium compounds of different classes, and (3) the agreement between the enthalpies of reaction found experimentally (directly) and calculated from the enthalpies of formation of the reactants. This analysis showed, in particular, that Pawlenko's results discussed above[129,130] are incorrect. Thus, direct measurements[120] of the enthalpies of the reactions

$$^2/_3(C_2H_5)_3Al\,(l) + {}^1/_3AlCl_3\,(c) \rightarrow (C_2H_5)_2AlCl\,(l),$$

$$^1/_3(C_2H_5)_3Al\,(l) + {}^2/_3AlCl_3\,(c) \rightarrow C_2H_5AlCl_2\,(l)$$

yielded -5.3 ± 0.1 and -1.2 ± 0.3 kcal mol^{-1} respectively, while calculations of the corresponding enthalpies from the ΔH_f° for the reactants, obtained by Pawlenko[129,130], lead to unrealistic values for the above reactions of $+37 \pm 1$ and $+56 \pm 1$ kcal mol^{-1}.

There have been several studies[117,121-127] devoted to the investigation of the thermochemical properties of organic derivatives of gallium, indium, and thallium (Table 3). The satisfactory agreement between the values of ΔH_f° for liquid trimethylgallium calculated from its enthalpy of combustion[121] ($\Delta H_f^\circ = -19.1 \pm 1.7$ kcal mol^{-1}) and enthalpy of iodination[122] ($\Delta H_f^\circ = -18.6 \pm 2.2$ kcal mol^{-1}) suggests that the combustion method can be used successfully also for other gallium compounds.

V. COMPOUNDS OF GROUP IV NON-TRANSITION ELEMENTS

The recommended enthalpies of formation of the above substances are listed in Table 4.

In connection with the applications of organosilicon compounds in technology, numerous studies have been made on their thermochemistry. In most instances the enthalpies of formation of the compounds were calculated from their enthalpies of combustion measured in a stationary bomb calorimeter. The use of this method in such cases is extremely difficult owing to the formation of a film of silicon dioxide on combustion of the test compounds. The film

covers the test substance and hence hinders contact between it and oxygen, which precludes the attainment of complete combustion. In the present instance the combustion products can contain, together with CO_2, H_2O and SiO_2, elemental carbon and silicon, carborundum, carbon monoxide, and a wide variety of pyrolysis products of the initial compound. The exact analysis of the combustion product formed is frequently impossible, so that reliable heat corrections, associated with the incomplete oxidation of the initial compounds, could not be found.

Table 4. Standard enthalpies of formation of organic derivatives of Group IV non-transition elements (kcal mol^{-1}).*

Compound	ΔH_f^0	ΔH_f^0 (g)	References
$C_2H_3SiH_3$ (l)	−4±3	+1±3	131(SB)
$(CH_3)_2SiH_2$ (l)	−52±3	−47±3	131(SB)
$(CH_3)_2Si(n\text{-}C_3H_7)_2$ (l)	−56±8	—	131(SB)
$(CH_3)_3SiH$ (l)	−72±4	−66±4	131(SB)
$(CH_3)_3SiC_2H_3$ (l)	+4±1	—	133(RB)
$(CH_3)_4Si$ (l)	−61±1	−55±1	131(SB), 33(SB)
$C_2H_5SiH_3$ (l)	−32±3	−27±3	131(SB)
$(C_2H_5)_2SiH_2$ (l)	−49±5	−42±5	131(SB)
$(C_2H_5)_3SiH$ (l)	−49±5	−40±2	131(SB), 134(SB)
$(C_2H_5)_4Si$ (l)	−66±4	−56±4	131(SB), 33(SB), 135(SB), 136 (SB), 137(RB)
$(n\text{-}C_4H_9)SiH_3$ (l)	−38±5	−31±5	131(SB)
$(iso\text{-}C_4H_9)SiH_3$ (l)	−36±5	−29±5	131(SB)
$(C_6H_5)_4Si$ (c)	+44±1	+80±1	133(RB), 138(SB), 139(SB), 140(RB), 141(RB), 132(RB)
$(C_6H_5CH{=}CH)_4Si$ (c)	+174±6	—	142(SB)
$[(CH_3)_3Si]_2$ (l)	−96±2	−87±2	137(RB)
$[(C_2H_5)_3Si]_2$ (l)	−97±3	−82±3	135(SB), 136(SB)
$[(C_2H_5)_3Si]_2Hg$ (l)	−40±1	−26±2	143(SB)
$(CH_3)_3Si(OH)$ (l)	−130±1	−119±1	144(R)
$(CH_3)_3SiOC_2H_5$ (l)	−126±1	−117±1	145(R), 146(R)
$(CH_3)_2Si(OC_2H_5)_2$ (l)	−206±1	−196±1	147—149(SB)
$(CH_3)_3SiO\text{-}n\text{-}C_3H_7$ (l)	−133±1	−124±1	146(R)
$(CH_3)_3SiO\text{-}iso\text{-}C_3H_7$ (l)	−135±1	−127±1	146(R)
$(CH_3)_3SiO\text{-}t\text{-}C_4H_9$ (l)	−144±1	−135±1	146(R)
$(CH_3)_3SiOOC(CH_3)_3$ (c)	−126±3	−115±3	150(SB)
$(CH_3)_2HSiO(C_6H_4)(C_6H_5)$ (l)	—	−67±3	151(SB)
$(CH_3O)_3SiH$ (l)	−198±3	−189±3	152(SB)
$(CH_3O)_3SiCH_3$ (l)	−233±2	−225±2	153(SB)
$(CH_3O)_4Si$ (l)	−303±3	−293±3	152(SB), 154(SB)
$(C_2H_5)_2Si(OH)_2$ (c)	−218±1	—	147—149(SB)
$(C_2H_5O)Si(C_6H_5)_3$ (c)	−154±4	—	133(RB), 155(RB), 156(RB)
$(C_2H_5O)_2Si(n\text{-}C_3H_7)_2$ (l)	−224±2	—	147—149(SB)
$(C_2H_5O)_3SiH$ (l)	−228±2	−218±2	152(SB), 157(SB)
$(C_2H_5O)_3SiC_2H_3$ (l)	−247±1	−235±1	158(SB)
$(C_2H_5O)_4Si$ (l)	−330±5	−318±5	152(SB), 159(R), 157(SB)
$(C_2H_5OC_2H_4O)_3Si(C_2H_3)$ (l)	−470±3	—	160(SB)
$(iso\text{-}C_3H_7O)_4Si$ (l)	−355±5	−343±5	152(SB)
$[(CH_3)_3Si]_2O$ (l)	−195±1	−186±1	161(SB), 7(RB), 137(RB), 162(RB)
$[(CH_3O)_3Si]_2$ (l)	−458±1	−445±1	154(SB)
$[(CH_3O)_3Si]_2O$ (l)	−552±1	−539±1	154(SB)
$[(CH_3O)_2CH_3Si]_2O$ (l)	−424±3	−415±3	153(SB)
$[(CH_3O)_2C_2H_5Si]_2O$ (l)	−435±4	−425±4	153(SB)
$[(CH_3)_3SiO]_2Si(CH_3)_2$ (l)	−355±7	−345±7	161(SB)
$[(CH_3O)_3SiO]_2Si(OCH_3)_2$ (l)	−816±1	−803±1	154(SB)
$[(CH_3O)_2CH_3SiO]_2Si(CH_3)(OCH_3)$ (l)	−608±5	−598±5	153(SB)
$[(CH_3)_3SiOSi(CH_3)_2]_2O$ (l)	−534±8	−522±8	161(SB)
$[(CH_3)_3SiOSi(CH_3)_2O]_2Si(CH_3)_3$ (l)	−674±10	−661±10	161(SB)
CH_3SiCl_3 (l)	−146±1	−138±1	163—165(RB)
$(CH_3)HSiCl_2$ (l)	−104±1	−98±1	166(RB)
$(CH_3)_2HSiCl$ (l)	−97±1	−73±1	166(RB)
$(CH_3)_2SiCl_2$ (l)	−116±1	−108±1	163(RB), 167(R), 166(RB)
$(CH_3)_3SiCl$ (l)	−91.9±0.5	−84.5±0.5	163—165(RB), 168(R), 144(R), 146(R)
$(CH_3)_3SiBr$ (l)	−77±1	−69±1	144(R)
$C_2H_5SiCl_3$ (l)	−132±6	−126±6	169(SB)
$(C_6H_5)_2SiCl_2$ (l)	−66±1	−49±1	167(R), 156(RB)
$(C_6H_5)_3SiCl$ (c)	+12±4	—	156(RB)
$(C_2H_5O)_3SiCl$ (l)	−297±1	—	159(R)
$(CH_3)_3SiNHCH_3$ (l)	−63±1	−54±1	144(R)
$(CH_3)_3SiN(CH_3)_2$ (l)	−67±1	−59±1	144(R)
$(CH_3)_3SiN(C_2H_5)_2$ (l)	−89±1	−80±2	170(R)
$[(CH_3)_3Si]_2NH$ (l)	−124±1	−114±1	168(R), 144(R)
$[(CH_3)_3Si]_2NCH_3$ (l)	−116±1	−107±1	144(R)
$[(CH_3)_3Si]_3N$ (c)	−173±2	−160±3	144(R)
$(CH_3)_3Si(CH_2)_2NCH_2CH_2$ (l)	−26±1	—	174(SB)
$(CH_3)_3SiN{=}N{\equiv}N$ (l)	+9±1	+17±2	175(R)
$(C_2H_5)_3SiN(C_2H_5)_2$ (l)	−88±1	−78±1	171(SB)
$[(C_2H_5)_2N]_3SiH$ (l)	−131±1	−117±1	171(SB)
$(CH_3)_2(C_2H_5O)Si(CH_2)_3NH_2$ (l)	−154±2	—	160(SB)

Table 4 (contd.).

Compound	ΔH_f^0	ΔH_f^0 (g)	Reference
$(CH_3)(C_2H_5O)_2Si(CH_2)_3NH_2$ (l)	−212±4	—	172(SB)
$(CH_3)(C_2H_5O)_2Si(CH_2)_2CN$ (l)	−231±2	—	160(SB)
$(CH_3)(C_2H_5O)_2Si(C_6H_4)NH(CH_3)$ (l)	−198±4	—	173(SB)
$(CH_3)_2(C_2H_5O)Si(CH_2)_5CHNH_2NHCH_3$ (l)	−177±2	—	173(SB)
$(C_2H_5O)_3Si(CH_2)_3NH_2$ (l)	−282±2	−271±2	176(SB)
$(C_2H_5O)_3Si(CH_2)_2CN$ (l)	−263±1	−257±1	160(SB)
$(CH_3)_3SiS(C_4H_9)$ (l)	−91±1	−81±1	144(R)
$(CH_3)_2Si(CH_2)_2CH_2$ (l)	−28±1	−20±1	133(RB), 162(RB), 177(RB)
cyclo-$[(CH_3)_2SiCH_2]_2$ (l)	−64±2	−54±2	162(RB), 177(RB)
cyclo-$[(CH_3)_2SiCH_2]_3$ (l)	−122±7	−111±7	162(RB), 177(RB)
$(CH_3)_2SiO(C_6H_4)(C_6H_4)$ (l)	—	−25±3	151(SB)
cyclo-$[(CH_3)_2SiO]_3$ (c)	−415±1	−402±1	147—149(SB)
cyclo-$[(CH_3)_2SiO]_4$ (c)	−543±2	−532±2	178(SB)
cyclo-$[(CH_3)HSiO]_5$ (c)	−591±3	—	179(SB)
cyclo-$[(CH_3)_2SiO]_5$ (c)	−687±2	−676±2	178(SB)
cyclo-$[(C_6H_5)_2SiO]_3$ (c)	−244±5	—	147—149(SB)
cyclo-$[(C_6H_5)_2SiO]_4$ (c)	−318±2	—	141(RB)
cyclo-[*cis*-$(CH_3)(C_6H_5)SiO]_3$ (c)	−321±2	—	180(RB), 181(RB), 133(RB)
cyclo-[*trans*-$(CH_3)(C_6H_5)SiO]_3$ (c)	−327±1	—	180(RB), 181(RB), 133(RB)
cyclo-$[(CH_3)(C_6H_5)SiO]_4$ (c)	−436±2	—	180(RB), 182(RB), 133(RB)
cyclo-$[(CH_3)(iso\text{-}C_3H_7O)SiO]_3$ (c)	−619±2	−609±2	178(SB)
cyclo-$[(CH_3)(iso\text{-}C_3H_7O)SiO]_4$ (c)	−843±2	−832±2	178(SB)
$(CH_3)_4Ge$ (l)	−28±2	−21±2	183(SB)
$(C_2H_5)_3GeH$ (l)	−40±2	−30±3	134(SB), 184(SB)
$(C_2H_5)_4Ge$ (l)	−51±2	−40±2	185(SB), 186(RB), 183(SB)
$(n\text{-}C_3H_7)_4Ge$ (l)	−73±1	−58±1	185(SB)
$(n\text{-}C_4H_9)_4Ge$ (l)	−92±1	−80±1	187(SB)
$(iso\text{-}C_4H_9)_4Ge$ (l)	−111±1	−100±1	187(SB)
$(C_6H_5)_2Ge(C{=}CH)_2$ (c)	+157±2	+189±2	188(SB)
$(C_6H_5)_4Ge$ (c)	+67±3	+105±4	138(SB), 189(SB), 190(RB), 191(RB)
$(C_6H_5CH_2)_4Ge$ (c)	+52±2	+96±3	192(RB), 193(RB)
$(C_6H_5CH{=}CH)_4Ge$ (c)	+199±3	—	194(SB)
$[(C_2H_5)_3Ge]_2$ (l)	−98±2	−83±2	184(SB)
$[(C_2H_5)_3Ge]_2Hg$ (l)	−32±1	−17±2	143(SB)
$[(iso\text{-}C_3H_7)_2Ge]_2Hg$ (l)	−74±1	−61±2	143(SB)
$[(C_6H_5)_3Ge]_2$ (c)	+107±2	+157±3	191(RB), 192(RB)
$(CH_3O)_4Ge$ (l)	−206±1	−196±1	196(SB)
$(C_2H_5O)Ge(CH_3)_3$ (l)	−95±2	−87±3	145(R)
$(C_2H_5O)_4Ge$ (l)	−245±1	−235±1	196(SB)
$(C_6H_5O)_4Ge$ (l)	−113±1	−104±1	196(SB)
$[(C_2H_5)_3Ge]_2O$ (l)	−151±2	−137±2	136(SB), 150(SB)
$(C_2H_5)_3GeOOC(CH_3)_3$ (c)	−120±1	−110±1	150(SB)
$(CH_3)_3GeCl$ (l)	−72±2	−64±3	145(R)
$(CH_3)_3GeBr$ (l)	−61±2	−52±3	145(R)
$(CH_3)_3GeN(CH_3)_2$ (l)	−37±2	−29±3	145(R)
$(C_2H_5)_3GeN(C_2H_5)_2$ (l)	−86±1	−75±2	171(SB)
$(CH_3)_3GeN{=}N{\equiv}N$ (l)	28±1	+37±2	175(R)
$(CH_3)_3GeS(n\text{-}C_4H_9)$ (l)	−65±2	−55±3	145(R)
$C(C_6H_5){=}[C(C_6H_5)]_2{=}C(C_6H_5)Ge(C{=}CH_2)$ (c)	+207±2	—	195(SB)
cyclo-$[(CH_3)_2GeO]_4$ (c)	−378±2	—	197(SB)
cyclo-$[(C_2H_5)_2GeO]_4$ (c)	−380±5	—	198(SB)
$(CH_3)_2SnH_2$ (l)	+14±1	+21±1	199(SB)
$(CH_3)_3SnH$ (l)	−2±1	+6±1	199(SB)
$(CH_3)_4Sn$ (l)	−12.6±0.5	−4.5±0.5	200(SB), 201(SB), 202(SB), 203(SB), 33(SB), 136(SB)
$(CH_3)Sn(C_2H_5)_3$ (l)	−54±1	—	201(SB)
$(CH_3)_2Sn(C_2H_5)_2$ (l)	−29±5	−19±5	201(SB)
$(CH_3)_3Sn(C_2H_5)$ (l)	−16±1	−7±1	201(SB), 203(SB)
$(CH_3)_3Sn(CH{=}CH_2)$ (l)	+13±1	+22±1	33(SB), 203(R)
$(CH_3)_3Sn(iso\text{-}C_3H_7)$ (l)	−21±1	−11±1	205(SB)
$(CH_3)_3Sn(t\text{-}C_4H_9)$ (l)	−29±1	−16±2	205(SB)
$(CH_3)_3Sn(C_6H_5)$ (l)	+14±1	+27±1	203(R), 204(R)
$(CH_3)_3Sn(CH_2C_6H_5)$ (l)	+8±2	+21±2	203(R), 204(R)
$[(CH_3)_3Sn]_2$ (l)	−19±1	−7±2	206(R), 203(SB)
$(C_2H_5)_2SnH_2$ (l)	+3±1	+10±1	199(SB)
$(C_2H_5)_3SnH$ (l)	−11±2	0±2	199(SB), 134(SB),
$(C_2H_5)_4Sn$ (l)	−23.0±0.5	−11.0±0.5	38(SB), 201(SB), 202(SB) 207(SB), 33(SB), 203(SB)
$(C_2H_5)_3Sn(CH{=}CH_2)$ (l)	+9±1	+21±2	33(SB)
$(C_2H_5)_2Sn(n\text{-}C_4H_9)_2$ (l)	−54±2	—	201(SB)
$[(C_2H_5)_3Sn]_2$ (l)	−52±2	−37±3	207(SB), 136(SB)
$(CH_2{=}CH)_4Sn$ (l)	+72±1	+84±2	33(SB)
$(CH_2{=}CH{-}CH_2)_4Sn$ (l)	−41±2	—	33(SB)
$(n\text{-}C_3H_7)_3SnH$ (l)	−32±1	—	208(R)
$(n\text{-}C_3H_7)_4Sn$ (l)	−50±1	−34±1	33(SB), 203(SB)
$(iso\text{-}C_3H_7)_4Sn$ (l)	−45±1	−29±2	33(SB), 205(SB)
$(n\text{-}C_4H_9)_3SnH$ (l)	−49±1	—	208(R)
$(n\text{-}C_4H_9)_4Sn$ (l)	−72.5±0.5	−52.7±0.7	201(SB), 203(SB), 33(SB)
$(iso\text{-}C_4H_9)_4Sn$ (l)	−79±1	—	33(SB)
$(cyclo\text{-}C_6H_{11})_4Sn$ (l)	−87±7	—	33(SB)
$(C_6H_{13})_4Sn$ (l)	−112±3	—	201(SB)
$(C_6H_5)_4Sn$ (c)	+98±1	+137±1	138(SB), 33(SB), 209(SB), 139(SB), 210(SB)
$[(C_6H_5)_3Sn]_2$ (c)	+158±2	+203±2	33(SB), 139(SB), 211(SB)
$(CH_3)_3SnOH$ (c)	−91±1	−76±2	145(R)
$(CH_3)_3Sn(OC_2H_5)$ (l)	−73±1	−63±2	145(R)
$(CH_3)_3SnOCOC_6H_5$ (c)	−118±2	—	136(SB)
$(C_2H_5)_3SnOOC(CH_3)_3$ (c)	−101±4	−89±4	150(SB)
$(C_2H_5)_3SnOCOC_6H_5$ (c)	−138±2	—	207(SB), 136(SB)

Table 4 (contd.).

Compound	ΔH_f^0	ΔH_f^0 (g)	Reference
$(C_2H_5)_3SnOOC(CH_3)_2C_6H_5$ (c)	−68±2	−55±2	150(SB)
$[(C_2H_5)_3Sn]_2O$ (l)	−102±3	−90±3	150(SB)
$(C_6H_5)_3SnOH$ (c)	+12±2	+43±2	212(SB)
$[(C_6H_5)_3Sn]_2O$ (c)	+99±2	+146±3	212(SB)
$(CH_3)SnCl_3$ (l)	−109±2	—	213(R)
$(CH_3)_2SnCl_2$ (l)	−81±2	—	213(R)
$(CH_3)_3SnCl$ (l)	−52±2	—	213(R)
$(CH_3)_3SnCl$ (c)	−59±1	−47±2	145(R)
$(CH_3)_3SnBr$ (l)	−44±1	−33±1	206(R), 203(SB)
$(CH_3)_3SnBr$ (c)	−48±1	−34±1	145(R)
$(CH_3)_3SnI$ (l)	−31±1	−20±1	206(R), 203(SB)
$(n\text{-}C_4H_9)_3SnBr$ (l)	−85±1	−65±3	203(R), 204(R)
$(C_6H_5)_2SnBr_2$ (c)	−5±1	—	203(R), 204(R)
$(C_6H_5)_3SnBr$ (c)	+45±1	—	203(R), 204(R)
$(CH_3)_3SnN(CH_3)_2$ (l)	−14±1	−5±2	145(R)
$[(CH_3)_3Sn]_2N(CH_3)$ (l)	−32±1	−20±2	145(R)
$[(CH_3)_3Sn]_3N$ (c)	−30±2	−15±3	145(R)
$(CH_3)_3SnN{=}N{\equiv}N$ (c)	+45±1	+60±2	175(R)
$(C_2H_5)_3SnN(C_2H_5)_2$ (l)	−50±1	−38±2	171(SB)
$[(n\text{-}C_4H_9)_3Sn]_2{=}C$ (l)	−86±1	—	214(SB)
$(n\text{-}C_4H_9)_3SnNCO$ (l)	−88±1	—	214(SB)
$(CH_3)_3SnS(n\text{-}C_4H_9)$ (l)	−47±1	−37±2	145(R)
$(CH_3)_4Pb$ (l)	+23.3±0.5	+32.4±0.5	6(RB)
$(C_2H_5)_4Pb$ (l)	+12.5±0.7	+26.0±0.8	5(RB)
$(C_6H_5)_4Pb$ (c)	+123±4	+161±4	215(RB), 216(RB)
$(C_6H_5)_2PbBr_2$ (c)	+8±4	+42±4	217(R), 218(R)
$(C_6H_5)_3PbBr$ (c)	+63±4	+95±4	217(R), 218(R)
$(C_6H_5)_2PbI_2$ (c)	+36±4	+69±4	217(R), 218(R)
$(C_6H_5)_3PbI$ (c)	+78±4	+109±4	217(R), 218(R)

*For the explanation of the Table, see the introduction.

The above factors led a number of workers to the assumption that all the values of ΔH_f° for silicon-containing substances obtained by the combustion method in a stationary bomb calorimeter are certain to be erroneous and do not merit any consideration. In particular, the values of ΔH_f° for silicon compounds found by the above method have been fully excluded from the monograph of Cox and Pilcher[1], the handbook of Wagman et al[10], Skinner's review[44], etc. However, in the majority of studies carried out using a stationary bomb calorimeter the investigators concerned made a detailed study of the products of incomplete combustion apart from creating the best possible conditions for the complete combustion of the starting material. This made it possible to apply the corresponding thermal corrections. The results of the above investigations may be suitable for various approximate calculations in cases where more accurate data are not available. For this reason, we have omitted from the present review only clearly erroneous results. Other values of ΔH_f° for silicon-containing compounds are included in Table 4 and are discussed regardless of the method used to determine them.

The enthalpies of combustion of a series of organosilicon compounds were first determined in a stationary bomb calorimeter by Reuther[152]. The lack of a detailed description of the method used precludes an assessment of the reliability of the results.

Tannenbaum et al.[131] measured the enthalpies of combustion of eleven organosilicon compounds. The substances, contained in glass or gelatine bulbs, were ignited in a nickel crucible having a number of apertures. The degree of combustion was checked by the visual inspection of the contents of the bomb after the experiments. The incomplete combustion products, in the form of dark spots on the inner surface of the bomb were observed even in the best experiments. Tannenbaum et al.[131] noted difficulties in creating conditions in the bomb which would ensure the complete combustion of the test compounds. For example, 25 combustions were carried out for vinylsilane and the necessary degree of combustion was achieved in only two experiments. For the remaining substances, only the results of the three best experiments were taken into account in calculating ΔH_f°. The authors believe[131] that the error of the ΔH_f° obtained ranges from −1.3 to +0.5%.

In his measurements of the enthalpies of combustion of polymethylsiloxanes, Thompson[161] used a novel method to ensure their complete combustion. The substance, enclosed in two bulbs of different strength, was placed in a glass crucible in the bomb. One of the bulbs was ruptured during the filling of the bomb with oxygen as a result of which the second stronger bulb was immersed in the liquid spilled out of the first bulb. At the required instant this liquid was ignited and, as a result of the evolution of heat, the second bulb exploded and, according to the author[161], the entire mass of the substance taken for the experiment was combusted, which he inferred from a visual inspection of the contents of the bomb after the experiment. The use of this combustion procedure involves difficulties associated with the preparation of bulbs capable of withstanding the oxygen pressure in the bomb and yet exploding on heating.

A series of studies on the measurements in a stationary bomb calorimeter of the enthalpies of combustion of organosilicon compounds of different structure were published by Tanaka and coworkers[147–149,153,154,178,179]. The liquid substances were ignited in glass or gelatine bulbs and solid substances were ignited in paper bags. The degree of combustion was inferred from the visual inspection of the solid combustion products formed. In his first studies Tanaka[147–149] did not report the difficulties encountered in attaining the complete combustion of the test compound. However, in later investigations[178,179] he noted the presence in the solid combustion products of, apart from amorphous SiO_2, amorphous carbon, silicon carbide, and a polymeric silicon-containing substance. The appropriate corrections were calculated in the interpretation of the experimental results.

Lautsch et al.[33] measured the enthalpies of combustion of tetramethyl- and tetraethyl-silanes. The substances were ignited in glass bulbs rolled up in a polyethylene film. However, complete combustion could not be achieved.

Several organosilicon compounds were investigated by Shaulov and coworkers[157,160,172,173,176]. The substances were placed in a bomb in polyethylene bulbs. The combustion products were analysed for carbon dioxide, unoxidised carbon, and silicon, and in the case of nitrogen-containing compounds, silicon nitride. It was established that the corrections for the presence of silicon and silicon nitride are insignificant and can be neglected.

A series of organosilicon compounds have also been combusted in a stationary bomb calorimeter in studies by the authors of the present review[134–136,150,171,174]. The liquid substances were ignited in polyethylene bulbs and the solid substances, in the form of several 0.1 g discs, were ignited in a thin platinum crucible. The analytical results for the solid combustion products showed that they contained as impurities unoxidised carbon and traces of unoxidised silicon and silicon carbide. For each substance, the experimental amount of CO_2 in the gaseous combustion products agreed, when account was taken of the incomplete combustion, to within 0.1% with the amount calculated from the chemical formula.

The use of the rotating bomb calorimeter method for organosilicon compounds is associated with two important conditions: the choice of the auxiliary substance ensuring a high degree of oxidation of the test compound and the choice of a solvent capable of rapidly dissolving the combustion

products formed. This method was first used by Good et al.[7] in a study of hexamethyldisiloxane. The substance was ignited in a mixture with trifluoromethylbenzene ($C_6H_5CF_3$). Trifluoromethylbenzene was chosen as the auxiliary substance because of the ease with which it can be purified and because of its ability to burn in the bomb calorimeter without the formation of carbon tetrafluoride. The mixture prepared in this way was ignited in a container of polyester film and the amount of energy consumed was ~69% in the combustion of trifluoromethylbenzene, ~25% in the combustion of hexamethyldisiloxane, and ~6% in the combustion of the film relative to the total amount of energy evolved during the experiment. The bomb was first charged with a specific amount of water or an aqueous HF solution, which came into contact with the combustion products on rotation of the bomb and reacted with the latter to form a solution of H_2SiF_6.HF. .H_2O. The enthalpy of formation of the resulting solution had been determined in preliminary experiments. In order to take into account a series of side effects, for example, the dissolution of carbon dioxide in aqueous solutions of H_2SiF_6 and HF, Good et al.[7] carried out the so called comparison experiments. In these experiments they combusted benzoic acid or liquid hydrocarbons; the amounts of the latter as well as the concentration of the aqueous solution of H_2SiF_2 and HF introduced into the bomb was selected in such a way that the final states of the reacting systems in the comparison experiments and the experiments involving the combustion of siloxane were as far as possible similar.

The enthalpy of formation of hexamethyldisiloxane obtained by Good et al.[7] was subsequently confirmed by Iseard et al.[137], who used a similar combustion method. However, they employed another auxiliary compound, namely *m*-trifluoromethylbenzoic acid ($C_6H_4CF_3COOH$). Iseard et al.[137] determined also the enthalpies of combustion of two other silicon compounds: tetraethylsilane and hexamethyldisilane. The combustion method proposed by Good[7] was also used by Genchel' et al.[162,177,180], who measured the enthalpies of combustion of several cyclic silicon compounds, and by Steele[132], who obtained an accurate value of ΔH_C° for tetraphenylsilane.

Another approach to the problem of the application of bomb calorimetric methods to silicon compounds was proposed by Gadzhiev[156]. He determined the enthalpies of combustion of a series of liquid chloromethylsilanes[156] by the explosive combustion method, which he developed[163–166]. This method consists in the vaporisation of part of the substance (not more than 10%) during the experiment and subsequent ignition of the mixture of its vapour with oxygen, which is stated[156,163–166] to cause the explosive combustion of both the gaseous and liquid parts of the substance with formation, apart from CO_2 and H_2O, of a stoichiometric amount of amorphous SiO_2. Gadzhiev and coworkers[133,140,141,155,156,181,182] recommend that solid organosilicon compounds be combusted in the presence of certain oxidants (potassium nitrate, potassium hypochlorite, benzoyl peroxide), which they say ensures the complete oxidation of the starting materials. However, one should point out that the value of ΔH_f° obtained in their studies[133,181,182] differ sharply from the corresponding data of other investigators[162,177,180] found using the more sophisticated combustion method developed by Good et al.[7] and used successfully in a later investigation[137]. This factor indicates the preliminary nature of both the methodological recommendations of Gadzhiev et al.[133,181,182] and of their results.

Failure to attain the complete combustion of organosilicon compounds in a stationary bomb calorimeter and the complexity of the experiments in a rotating bomb calorimeter led many investigators to resort to other methods for the thermochemical investigation of such substances. The study of their hydrolytic reactions proved to be extremely fruitful[144–146,159,167,168,170]. These reactions frequently take place at room temperature with formation of readily identifiable products. The widescale employment of the above procedure for the investigation of the methyl compounds of silicon has been favoured to a large extent by the fact that the enthalpy of formation of their main hydrolysis product (hexamethyldisiloxane) had been reliably established in the above investigations[7,137].

Despite the large number of organogermanium compounds synthesised and their practical importance, the study of their thermochemistry began comparatively recently, namely in 1963, when the authors of the present review published the results of measurements of the enthalpies of combustion of tetraethylgermane and hexaethyldigermane[184]. As shown in one of the subsequent studies of the present authors[134,136,143,150,171] and also in the studies of Skinner[185] and Shaulov[183,187,189,196–198], organogermanium compounds are readily oxidised under the conditions of the stationary bomb calorimeter and the attainment of a high degree of their oxidation does not present special difficulties. All the above investigators ignited the test substances in polyethylene or polyester bulbs placed in a quartz crucible. In some cases the solid combustion products contained, together with hexagonal germanium dioxide, small amounts of unoxidised carbon and germanium, which were reliably taken into account by the appropriate corrections.

The combustion of organogermanium compounds in a rotating bomb calorimeter was first used by Bills and Cotton[186], who measured the enthalpy of combustion of liquid tetraethylgermane. The liquid in the bomb, used to dissolve the condensed combustion products, was an aqueous HF solution, which led to the formation of an aqueous solution of H_2GeF_6. This method was subsequently used in other studies[190,192] to determine the enthalpies of combustion of tetraphenylgermane, hexaphenyldigermane, and tetrabenzylgermane; however, the bomb liquid consisted of aqueous KOH. The enthalpies of solution in the above solvent of the germanium and carbon dioxides formed in the experiments were determined beforehand. The combustion products also contained a "solid residue", which did not dissolve in the bomb liquid. The authors[190,192] suggested that it consisted of a mixture of unoxidised carbon and the initial germanium compound. The correction taking into account the presence of this "solid residue" did not exceed 0.5% of the overall amount of energy evolved in the experiment.

It has been suggested[186] that the exact determination of the enthalpy of combustion of organogermanium compounds in a stationary bomb calorimeter is impossible owing to their incomplete oxidation in the corresponding experiments. However, the similarity of the values of ΔH_f° found for tetraethylgermane by the method of combustion in a stationary bomb calorimeter[183–185] (-52.2 ± 1.0, -52.6 ± 1.5, and -48.9 ± 1.0 kcal mol^{-1} respectively) and by the method of combustion in a rotating bomb calorimeter[186] (-50.4 ± 1.5 kcal mol^{-1}) suggests that reliable values of ΔH_f° can be obtained for germanium compounds also in stationary bomb calorimeters¶.

¶There is a sharp difference between the individual values of ΔH_f° for tetraphenylgermane found in a stationary bomb calorimeter[138,189] and between these and the result obtained by the rotating bomb calorimeter method[190]. However, it is apparently associated with the inadequate purity of the specimens investigated[138,189]. The error of Birr's result[138] and its possible cause were pointed out by Tel'noi and Rabinovich[139].

The only study in which reaction calorimetry was used to investigate the thermochemistry of germanium compounds is that of Baldwin et al.[145], who measured the enthalpies of hydrolysis of several trimethylgermane derivatives. The comparatively high error of the enthalpies obtained (±2 kcal mol^{-1}) is mainly due to the inaccuracy of the estimated enthalpy of formation of hexamethylgermanoxane (−136 ± 4 kcal mol^{-1}), formed in the hydrolysis of the above substances, which was used in the calculations.

The measurement of the enthalpies of combustion of organotin compounds presents no difficulties, since the latter are fully oxidised under the conditions of the stationary bomb calorimeter. This factor led to the accumulation in the literature of a large number of thermochemical data obtained by the combustion of organotin compounds in the stationary bomb calorimeter. Their combustion products contained in some cases unoxidised tin and carbon. However, in these experiments corrections for incomplete combustion could be determined exactly by heating the solid combustion product to constant weight and by the simultaneous determination of the carbon dioxide produced in this process[134,203]. In order to improve the combustion, the test substances are frequently placed in polyethylene or polyester bulbs. One should note that some of the investigations[138,200,201] in which the stationary bomb calorimeter method was applied to organotin compounds were experimentally imprecise and the difference between their results and those of the corresponding exact data[203,209,210] (Table 4) did not indicate any methodological complications arising in the study of the given substances in a stationary bomb calorimeter.

The existence of a large number of chemical reactions of organotin compounds suitable for calorimetric studies made it possible to determine the enthalpies of formation of many of these substances by reaction calorimetry. A study of the enthalpies of halogenation[204,205,208,213] and hydrolysis[145] proved to be the most fruitful. The methods of reaction calorimetry are particularly suitable for the determination of the enthalpies of formation of halogen-containing tin compounds whose combustion in a bomb calorimeter is complicated by a number of side reactions.

The combustion of organolead compounds in a stationary bomb calorimeter does not yield exact enthalpies of combustion because of the formation on combustion of a mixture of inorganic lead compounds which cannot be subjected to a reliable quantitative analysis. Good and coworkers[5,6] therefore used the method of combustion in a rotating bomb calorimeter in the study of tetramethyl- and tetraethyl-lead. A solution of nitric and arsenous acids was used as the bomb liquid, as a result of which the entire lead present in the combustion products was converted into Pb^{2+} ions. The test substances were combusted in a quartz crucible which was fairly inert in relation to the hot lead oxides formed. The use of glass bulbs and of a platinum crucible is inconvenient in this instance, since fused lead oxides or unoxidised lead react with glass and are fused together with platinum. Since explosive combustion is characteristic of tetramethyl-lead, it was diluted with a liquid-hydrocarbon before combustion and was placed in a polyester bag. The enthalpy of solution of tetramethyl-lead in the hydrocarbon as well as the enthalpy of solution of the carbon dioxide (formed in the experiments) in the final bomb solution were determined in special experiments. A combustion method analogous to that examined above was also used[215] in a study of tetraphenyl-lead.

The use of methods of reaction calorimetry for the determination of the enthalpies of formation of organolead compounds is limited to the studies of Butler et al.[217,218], who measured the enthalpies of halogenation of crystalline tetraphenyl-lead. The enthalpies of formation of certain bromo- and iodo-derivatives of the above compounds were calculated from the results (Table 4).

One must note that the literature values of the enthalpies of formation of organolead compounds, obtained by combustion in a stationary bomb calorimeter, are erroneous for the reasons examined above. For example, according to data[33] obtained in a stationary bomb calorimeter, the standard enthalpy of formation of crystalline $(C_6H_5)_4Pb$ is +221 ± 3 kcal mol^{-1}, while the use of the rotating bomb calorimeter[215] yields $\Delta H_f^\circ = +123 \pm 4$ kcal mol^{-1} for the same substance. All

Table 5. Standard enthalpies of formation of organic derivatives of Group V non-transition elements (kcal mol^{-1}).*

Compound	ΔH_f^0	ΔH_f^0 (g)	References	Compound	ΔH_f^0	ΔH_f^0 (g)	References
$(CH_3)_3P$ (l)	−30±1	−23±1	220(SB)	$(CH_3)_3PN(C_2H_5)$ (l)	−36±2	−22±2	230(R)
$(C_2H_5)_3P$ (l)	−21±3	−12±3	31(SB), 32(SB)	$(C_6H_5)_3PN(C_2H_5)$ (c)	+16±1	+34±2	230(R)
$(n\text{-}C_4H_9)_3P$ (l)	−28±7	—	221(R)	$[(C_2H_5)_2N]_3P$ (l)	−67±2	−53±3	235(R)
$(n\text{-}C_6H_{13})_3P$ (l)	−177±9	—	222(R)	$(CH_2)(C_6H_5NH)_2PO$ (c)	−86±6	—	226(SB)
$(C_6H_5)_3P$ (c)	+55±2	+78±3	223(SB), 224(SB)	$(C_2H_5)(C_6H_5NH)_2PO$ (c)	−89±3	—	226(SB)
$(CH_3O)_3P$ (l)	−176±1	−167±2	225(R)	$(C_2H_5)_2NPCl_2$ (l)	−81±1	—	236(R)
$(C_2H_5O)_3P$ (l)	−203±1	−193±1	225(R), 226(R)	$[(C_2H_5)_2N]_2PCl$ (l)	−78±2	—	236(R)
$(iso\text{-}C_3H_7O)_3P$ (l)	−232±2	−221±2	226(R)	$(n\text{-}C_4H_9)_3PS$ (l)	−56±7	—	237(R)
$(n\text{-}C_4H_9O)_3P$ (l)	−262±4	—	222(R)	$(C_2H_5O)_3PS$ (l)	−229±1	—	237(R)
$(C_6H_5)(OH)_2P$ (c)	−132±5	—	227(SB)	$(C_6H_5)_5C_4P$ (c)	+94±3	—	238(SB)
$(CH_3)(OH)_2PO$ (c)	−252±6	−240±6	228(R)	$(C_6H_5)(C_6H_4)_2P$ (c)	+45±2	—	238(SB)
$(C_2H_5)(OH)_2PO$ (c)	−251±2	−239±3	228(R), 231(R)	$(C_6H_5)_5C_4PO$ (c)	+53±5	—	238(SB)
$(C_6H_5)(OH)_2PO$ (c)	−211±3	—	227(SB)	$(C_6H_5)(C_6H_4)_2PO$ (c)	−21±6	—	238(SB)
$(C_6H_5)_2(OH)PO$ (c)	−125±6	—	227(SB)	cyclo-$[PN(CH_3)_2]_3$ (c)	−123±3	−105±4	239(SB)
$(CH_3)(ON)_2PO$ (c)	−350±2	—	229(SB)	cyclo-$[PN(C_6H_5)_2]_4$ (c)	+43±12	+61±12	239(SB)
$(CH_3)_3PO$ (c)	−115±2	−103±2	230(R)	cyclo-$[(CH_3N)_6P_4]$ (c)	−57±6	−42±6	240(SB)
$(n\text{-}C_4H_9)_3PO$ (c)	−110±7	—	232(SB)	cyclo-$[PN(cyclo\text{-}C_6H_{11}O_2)_2]_3$ (c)	−580±4	−562±5	239(SB)
$(n\text{-}C_6H_{13})_3PO$ (c)	−263±9	—	222(SB)	cyclo-$[C_6H_5NHP(O)NC_6H_5]_2$ (c)	−122±5	−92±5	240(SB)
$(C_6H_5)_3PO$ (c)	−26±1	+5±2	224(SB), 233(RB)	cyclo-$(CH_3NPCl_3)_2$ (c)	−209±2	−192±3	240(SB), 241(R)
$(C_2H_5O)_2(CH_3)PO$ (l)	−244±6	−231±7	226(R)	$(CH_3)_3As$ (l)	−4±1	+3±1	242(SB)
$(C_2H_5O)_3PO$ (l)	−296±1	−282±1	221(R), 224(SB) 234(SB)	$(C_2H_5)_3As$ (l)	+3±2	+13±2	31(SB), 32(SB)
				$(C_6H_5)_3As$ (c)	+71±2	+95±2	243(SB), 244(RB)
$(n\text{-}C_3H_7O)_3PO$ (l)	−315±4	−299±5	232(SB)	$(CH_3O)_3As$ (l)	−141.9±0.5	−131.6±0.5	245(R)
$(iso\text{-}C_3H_7O)_2(C_2H_5)PO$ (l)	−267±4	−252±4	226(R)	$(C_2H_5O)_3As$ (l)	−168.3±0.5	−156,2±0.6	245(R)
$(iso\text{-}C_3H_7O)_3PO$ (l)	−310±2	—	228(R)	$(n\text{-}C_3H_7O)_3As$ (l)	−189±1	−175±2	245(R)
$(n\text{-}C_4H_9O)(n\text{-}C_4H_9)_2PO$ (l)	−183±9	—	232(SB)	$(CH_3)_3Sb$ (l)	0±3	+8±3	247(SB)
$(n\text{-}C_4H_9O)_3PO$ (l)	−348±3	−331±3	232(SB), 234(SB)	$(C_2H_5)_3Sb$ (l)	+1±1	+11±1	31(SB), 32(SB)
$(iso\text{-}C_4H_9O)_3PO$ (l)	−347±8	—	234(SB)	$(C_6H_5)_3Sb$ (c)	+79±2	+104±3	223(SB)
$(C_6H_5O)_3PO$ (c)	−180±3	—	234(SB)	$(CH_3)_3Bi$ (l)	+37±2	+46±2	248(SB)
$(C_2H_5)PCl_2$ (l)	−72±4	—	228(R)	$(C_2H_5)_3Bi$ (l)	+40±2	+51±2	31(SB), 32(SB)
$(CH_3)POCl_2$ (c)	−148±6	−133±6	226(R)	$(C_6H_5)_3Bi$ (c)	+117±1	+143±2	243(SB), 219(RB)
$(C_2H_5)POCl_2$ (l)	−146±3	−136±3	226(R)				

*For the explanation of the Table, see the introduction.

the values of ΔH_f° calculated from the results of the combustion of organolead compounds in a stationary bomb calorimeter are therefore disregarded in this review and are not included in Table 4.

VI. COMPOUNDS OF GROUP V NON-TRANSITION ELEMENTS

The recommended enthalpies of formation of the above substances are listed in Table 5.

The determination of the enthalpies of combustion of organophosphorus compounds in a stationary bomb calorimeter has a number of characteristic features, which make it difficult to obtain sufficiently reliable results. Their combustion products contain, apart from CO_2 and H_2O, orthophosphoric acid (in aqueous solution), which, however, may be accompanied by other phosphorus-containing acids in solution: H_3PO_3, $H_4P_2O_7$, and $H_5P_3O_{10}$; the concentrations of the acids formed in different parts of the bomb differ significantly. This factor may appreciably distort the results of the calculation of the ΔH_f° of the test substance owing to the comparatively high enthalpies of solution of phosphoric acids in water. Furthermore, it is difficult to achieve the complete combustion of organophosphorus compounds—all the investigators have noted the presence of significant amounts of unoxidised carbon in their combustion products. In view of the corrosive nature of phosphoric acids in relation to the material of the crucible in which the test substance is to be combusted, the choice of the crucible is important.

The method of combustion in a stationary bomb calorimeter was used[226] in a study of two phosphoric acid dianilides. The combustion products were analysed for ortho-, pyro-, and meta-phosphoric acids. It was found that 93–96% of the phosphorus was oxidised to orthophosphoric acid. The authors[226] disregarded corrections for the formation of other acids. They also established that the concentration of the H_3PO_4 solution formed on combustion of the test substances was 0.5 M on the walls of the bomb and 2 M in the crucible and that the main bulk of the acid (~85%) was on the walls of the bomb. The difference between the concentrations of orthophosphoric acid in different parts of the bomb was taken into account in the interpretation of the experimental data. The error of the calculated ΔH_f° (Table 5) is several kcal mol^{-1}.

In the combustion of trimethylphosphine[220] magnesium ribbon was used to ignite the substance and to improve its combustion. However, its employment introduced additional difficulties owing to the formation of magnesium oxide in the combustion products, which partly dissolves in aqueous orthophosphoric acid. The trimethylphosphine combustion products were analysed to determine (a) the mass of magnesium oxide dissolved in phosphoric acid (an aqueous $MgHPO_4$ solution was formed), (b) to determine the mass of unoxidised carbon, (c) to test for the presence of lower phosphorus acids, and (d) to determine the masses of meta- and pyro-phosphoric acids. The analyses showed that orthophosphoric acid amounted to not less than 95% of the overall mass of all the phosphorus-containing acids formed. In the calculation of ΔH_c° corrections were applied for the presence of phosphorous acid, free carbon, etc. in the combustion products.

In another study[223] triphenylphosphine was combusted in polyethylene bulbs, which consumed ~60% of the energy evolved in the experiment. A mixture of H_3PO_4 and H_3PO_3 was detected in the combustion products. Corrections for the auxiliary materials and the presence of unoxidised carbon and phosphorus acid in the combustion products were applied in the calculations of ΔH_c°. The value $\Delta H_f^\circ = +52.9 \pm 3.6$ kcal mol^{-1} found by the author[223] agrees within the limits of experimental error with $+54.8 \pm 2.4$ kcal mol^{-1} obtained analogously in another investigation[224].

The enthalpies of combustion of a series of organophosphorus compounds were measured by Mortimer and coworkers[224, 238,239]. To improve the combustion, certain substances (discs) were placed in polyester bulbs. To prevent the scattering of the hot substances, the crucible was covered by a platinum gauze. The mass of the combusted compound was determined from the masses of CO_2 and free carbon found in the combustion products. It was assumed that all the auxiliary substances were completely combusted. Chemical analysis of the wash water from the bomb after the experiments demonstrated the presence of only one phosphorus-containing acid (H_3PO_4).

The method of measurement of ΔH_c° for phosphorus-containing substances was improved in a number of investigations[222,232,234]. Much attention was devoted to the selection of the material of the crucible, fairly inert with respect to the combustion products of the test compounds. Corundum crucibles, which proved in this respect to be better than stainless steel, titanium, quartz, or porcelain crucibles, were used. Together with orthophosphoric acids, a certain amount of pyrophosphoric acid was found in the combustion products, which conflicts with data obtained in investigations[224,238,239] where only orthophosphoric acids was found in the products. (Nikolaev et al.[234] explained this by the inaccuracy of the analytical methods employed in the earlier investigations[224,238,239].) In the interpretation of the experimental data account was taken of the thermal corrections for the enthalpy of solution of phosphoric acids and unoxidised carbon. The authors[222,232,234] explained the comparatively large error in the values of ΔH_c° obtained, amounting in certain cases to ~0.5%, by the impossibility of attaining the complete oxidation of phosphorus-containing substances under the conditions of the stationary bomb calorimeter.

The enthalpies of combustion of the three phosphorus-containing acids have been measured[227] in an adiabatic stationary bomb calorimeter not designed for precision measurement. Discs of the test substances were placed in a platinum crucible together with a disc of benzoic acid, which ensured a more complete combustion. Part of the water introduced into the bomb before the experiment wetted its inner walls, which tended to equalise the concentrations of the orthophosphoric acid formed in different parts of the bomb according to the authors[227]. The chemical composition of the wash water from the bomb after the experiments was determined by method proposed previously[224,238,239] and, as in those investigations, the authors[227] demonstrated the quantitative oxidation of phosphorus to orthophosphoric acid without the formation of other phosphoric acids.

The enthalpies of combustion of three cyclic phosphorus compounds containing also nitrogen and chlorine were determined by Fleig and Berke-Goehring[240] using a tantalum stationary bomb calorimeter. The substances were combusted together with paraffin. In the experiment with the chlorine-containing compound the bomb was charged with quartz wool impregnated with an aqueous solution of As_2O_3. Under these conditions, molecular chlorine, formed to some extent on combustion of the test compound, was fully reduced to HCl. Together with orthophosphoric acid, the authors detected small amounts of pyrophosphoric acid in the wash water from the bomb. However, the corrections due to the presence of the latter were insignificant and were therefore disregarded.

The possibility of the combustion of phosphorus compounds in a rotating bomb calorimeter has been examined in detail[233]. It was suggested that triphenylphosphine oxide be used as the standard substance for the thermochemical study of organophosphorus compounds[233]. A disc of the above compound was ignited in a small gold crucible by means of a polyethylene ribbon. The formation of soot in this case was insignificant. The bomb liquid consisted of an aqueous solution of perchloric acid. When the combustion product dissolved in it, only one phosphoric acid was formed, namely H_3PO_4. The amount of CO_2 found in the combustion products of triphenylphosphine oxide was 99.97 ± 0.01% of the amount calculated from its chemical formula. The enthalpy of combustion of the test compound was determined to within ±0.04% (which is significantly more accurate than the results obtained in the study of phosphorus-containing compounds in a stationary bomb calorimeter). $\Delta H_f^\circ = -26.2 \pm 1.0$ kcal mol^{-1}, calculated from the above heat of combustion, differs significantly from the value $\Delta H_f^\circ = -15.1 \pm 3.0$ kcal mol^{-1} found[224] in a stationary bomb calorimeter, which is probably due to the difficulty of the analysis of the combustion products formed when the authors' method is used[224].

The thermochemistry of a number of phosphorus-containing compounds has been studied by reaction calorimetry. In these studies the enthalpies of hydrolysis[228,230,231,241] or the enthalpies of oxidation of the test compounds by an aqueous solution of hydrogen peroxide[221,222,228,230] were frequently measured. Reliable thermochemical data have been obtained also by measuring the enthalpies of reaction of chlorine-containing phosphorus compounds with a cyclohexane solution of the corresponding alcohol and a substituted amine[225,226,235]. The role of the amines consisted in binding the hydrogen chloride formed in the processes. The experimental conditions selected ensured that the reactions took place at temperatures close to the standard temperature and the duration of the experiments in most cases did not exceed 60 min. The results of these investigations are presented in Table 5.

Mortimer and Skinner[249] were the first to investigate the thermochemistry of organoarsenic compounds. They showed that many of these compounds readily interact with iodine even at room temperature and that such reactions are extremely convenient for calorimetric study. The above workers measured[249,250] the enthalpies of the reactions

$$(CH_3)_2AsAs(CH_3)_2\ (l) + I_2\ (c) \rightarrow 2(CH_3)_2AsI\ (l),$$
$$C_6H_5AsH_2\ (l) + 2I_2\ (c) \rightarrow C_6H_5AsI_2\ (l) + 2HI\ (g),$$

occurring in methanol and carbon tetrachloride respectively. However, the results did not allow the calculation of ΔH_f° of any one arsenic-containing reactant. Later the enthalpies of formation of three alkoxyarsenic compounds were determined[245] from measurements of the enthalpies of their hydrolysis in the presence of an excess of NaOH. These reactions take place rapidly and quantitatively at room temperature. The presence of alkali is necessary for the rapid dissolution of the arsenic trioxide formed.

The applicability of the enthalpy of combustion method to arsenic compounds was first investigated by Long and Sackman[242], who measured ΔH_c° for trimethylarsenic in a stationary bomb calorimeter. They established that the combustion products of the above compound have a composition very difficult to analyse. Indeed, the combustion products contained unoxidised arsenic and carbon, solid As_2O_3, As_2O_4, and As_2O_5, and a solution containing arsenic(III) and arsenic(V) compounds. This made it necessary to develop a method for the exact analysis of the above mixture. The arsenic content found in the combustion product by the method developed above amounted on average to 99.8% of the expected value, which confirmed the validity of the proposed analytical procedure. The enthalpy of combustion of triethylarsenic has been measured[31-33] in a stationary bomb calorimeter and only one arsenic oxide (As_2O_3) was found in the combustion product.

The same method has been used[243] to investigate triphenylarsenic. A method proposed previously[242] was used to analyse the combustion products, among which the oxides As_2O_3, As_2O_4, and As_2O_5 were found. However, the enthalpy of formation of the above compound thus obtained (+93.6 ± 2.0 kcal mol^{-1}) differs appreciably from the reliable value of this quantity (+71.0 ± 2.0 kcal mol^{-1}) found by Mortimer and Sellers[244], who used the method of combustion in a rotating bomb calorimeter with aqueous NaOH as the bomb liquid. In this case dissolution of the combustion products in the bomb resulted in the formation of a solution of sodium arsenate, arsenite, carbonate, and hydroxide. The enthalpies of reaction of the combustion products with the bomb liquid, necessary for the calculation of ΔH_f° for the test compound, were measured[244] in a special calorimeter.

Few data are available for the thermochemical properties of organoantimony compounds. They were all obtained by the combustion of the test substances in a stationary bomb calorimeter. The enthalpy of combustion of trimethylantimony was determined by Long and Sackman[247] who inserted the test substance in thin-walled glass bulbs and then placed them in the bomb. Analysis of the solid combustion products showed that they consisted mainly of crystalline Sb_2O_4. Sb_2O_3, unoxidised antimony, and carbon were also found as impurities. The analytical method developed for this mixture made it possible to take into account accurately the products of the incomplete oxidation of the initial compound. The enthalpy of hydration of Sb_2O_3, specially measured in preliminary experiments, proved to be insignificant and was disregarded in the interpretation of the experimental data.

The enthalpy of combustion of triethylantimony has been measured[31-33]. The selected experimental conditions ensured the formation of only a single antimony oxide, namely Sb_2O_3. The enthalpy of combustion of triphenylantimony was determined by Birr[223]. To improve the combustion, the test substance was ignited in a polyethylene bag. The resulting solid combustion product consisted of a mixture of unoxidised carbon and the oxides Sb_2O_3 and Sb_2O_4. It was analysed by the method of Long and Sackman[247].

The enthalpies of combustion of trimethyl-, triethyl-, and triphenylbismuth have also been measured[31-33,243,246], by combustion in a stationary bomb calorimeter. Long and Sackman[246] placed samples of trimethylbismuth to be combusted in thin-walled glass bulbs, on which a magnesium ribbon, connected to an iron wire used for ignition, was wound. Only the bismuth oxide Bi_2O_3 was found in the solid combustion products. Small amounts of metallic bismuth and free carbon were found as impurities. Analysis for unoxidised bismuth and carbon was carried out after each experiment and the corrections due to their presence were taken into account in the calculation of ΔH_f° for the test substance.

Steele[219] determined the enthalpy of formation of triphenylbismuth by the rotating bomb calorimeter method. The bomb liquid was an aqueous HCl solution in which the bismuth-containing combustion products were converted into $BiCl_3$. The value $\Delta H_f^\circ[(C_6H_5)_3Bi(c)] = 117.0 \pm 1.2$ kcal mol^{-1} obtained in this investigation[219] is close to $\Delta H_f^\circ = 112 \pm 2$ kcal mol^{-1} found for the same compound by combustion in a stationary bomb calorimeter[243].

VII. COMPOUNDS OF GROUP VI NON-TRANSITION ELEMENTS

Among organic compounds containing Group VI non-transition elements, only sulphur-containing substances have been investigated in fair detail. The monograph of Cox and Pilcher[1] presents the enthalpies of formation (obtained as a rule by combustion in a rotating bomb calorimeter) for approximately 170 such compounds. As already mentioned in the introduction, these data are not repeated here.

As regards the thermochemistry of organic substances containing other Group VI non-transition elements, there have been only three studies in which the enthalpies of formation of organic compounds of selenium and tellurium were determined.

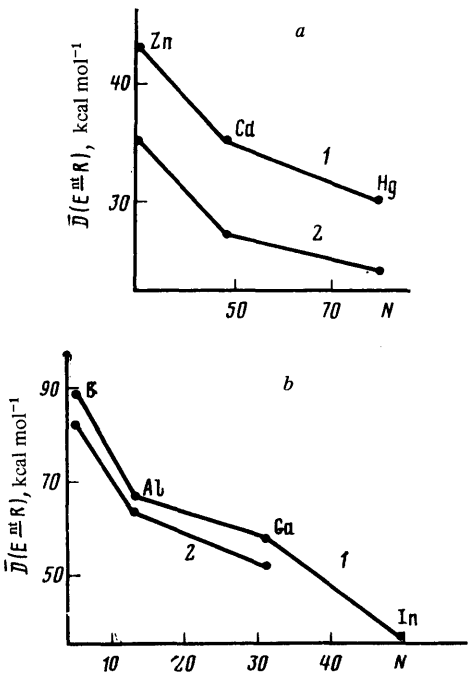


Figure 1. Variation of the average dissociation energy of the element–organic group bonds formed by Group II non-transition elements in the compounds $E^{nt}R_2$ (*a*) and Group III elements in the compounds $E^{nt}R_3$ (*b*) with increase of the atomic number of the element *N*; R: 1) CH_3; 2) C_2H_5.

The enthalpy of formation of liquid diethyl selenide, which is -23 ± 1 kcal mol^{-1}, has been calculated[251] from the results of the combustion of this substance in a stationary bomb calorimeter. It was combusted together with paraffin, which increased the degree of combustion. The same value of $\Delta H_f^\circ[(C_2H_5)_2Se(l)]$ was obtained[248] by measuring the enthalpy of reaction of diethyl selenide with an excess of bromine. After taking into account the enthalpy of vaporisation of this compound, which amounts to[248] 9.3 ± 0.4 kcal mol^{-1}, we obtain $\Delta H_f^\circ[(C_2H_5)_2Se(g)] = -14 \pm 1$ kcal mol^{-1}.

Barnes and Mortimer[252] calculated ΔH_f° for liquid diphenyl selenide from the enthalpy of combustion measured in a rotating bomb calorimeter and obtained $\Delta H_f^\circ = -54 \pm 1$ kcal mol^{-1}. The test substance was ignited in a polyester bag in a quartz crucible. Distilled water (50 cm^3), in which the combustion products obtained dissolved, was first placed in the bomb. The enthalpy of vaporisation of $(C_6H_5)_2Se$, amounting to 15.2 ± 0.6 kcal mol^{-1}, was calculated in the same study from its boiling point at different pressures. Taking into account this quantity, we have $\Delta H_f^\circ[(C_6H_5)_2Se(g)] = +69 \pm 1$ kcal mol^{-1}.

$\Delta H_f^\circ[(C_2H_5)_2Te(l)] = -3 \pm 1$ kcal mol^{-1} was calculated from measurements of the enthalpy of mixing of diethyl telluride with an excess of bromine and, after taking into account the enthalpy of vaporisation, equal to 10.0 ± 0.5 kcal mol^{-1}, the enthalpy of formation in the gaseous state was found to be $\Delta H_f^\circ[(C_2H_5)_2Te(g)] = +7 \pm 1$ kcal mole^{-1}.[248]

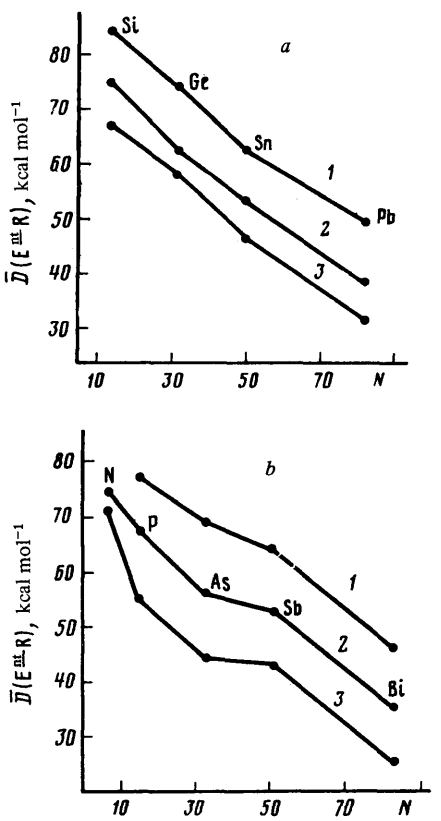


Figure 2. Variation of the average dissociation energy of the element–organic group bonds formed by Group IV non-transition elements in the compounds $E^{nt}R_4$ (*a*) and Group V elements in the compounds $E^{nt}R_3$ (*b*) with increase of the atomic number of the element; R: 1) C_6H_5; 2) CH_3; 3) C_2H_5.

VIII. THE AVERAGE DISSOCIATION ENERGIES OF THE CHEMICAL BONDS FORMED BY NON-TRANSITION ELEMENTS IN THEIR ORGANIC COMPOUNDS

The elucidation of the dependence of the strength of chemical bonds on the nature of the atoms involved in them is of considerable theoretical interest. However, determination of the dissociation energy of an individual bond in a

specified compound is usually a very difficult experimental problem. For this purpose one therefore frequently employs the average bond dissociation energies ($\bar{D}$). $\bar{D}$ is the enthalpy of the process

$$ER_n\ (g) \rightarrow E\ (g) + nR\ (g),$$

divided by the number of bonds n, where ER_n is the molecule of the given substance in the gaseous state, E the element, and R the atom, group, or ligand, also in the gaseous state. This quantity can be calculated by the formula

$$\bar{D}\ (E-R) = \frac{1}{n}\left\{\Delta H_f^0\ [E\ (g)] + n\Delta H_f^0\ [R\ (g)] - \Delta H_f^0\ [ER_n\ (g)]\right\},$$

from experimental (tabulated) enthalpies of formation of the reactants involved in the given reaction in the gaseous state.

Table 6. Average dissociation energies ($\bar{D}$) of element–organic group chemical bonds formed by Group II–VI non-transition elements (kcal mol^{-1}).

Compound	Bond	$\bar{D}$	Compound	Bond	$\bar{D}$
$(C_6H_5)_2Be$	C_6H_5—Be	80±3	(iso-C_4H_9)$_4$Ge	iso-C_4H_9—Ge	62±2
$(CH_3)_2Zn$	CH_3—Zn	43±1	$(C_6H_5)_4Ge$	C_6H_5—Ge	74±2
$(C_2H_5)_2Zn$	C_2H_5—Zn	35±1	$(C_6H_5CH_2)_4Ge$	$C_6H_5CH_2$—Ge	43±1
(n-C_3H_7)$_2$Zn	n-C_3H_7—Zn	38±3	$(CH_3O)_4Ge$	CH_3O—Ge	74±2
(n-C_4H_9)$_2$Zn	n-C_4H_9—Zn	39±3	$(C_2H_5O)_4Ge$	C_2H_5O—Ge	75±1
$(CH_3)_2Cd$	CH_3—Cd	35±1	$(C_6H_5O)_4Ge$	C_6H_5O—Ge	62±3
$(C_2H_5)_2Cd$	C_2H_5—Cd	27±1	$[(C_2H_5)_3Ge]_2$	C_2H_5—Ge	59±1
$(CH_3)_2Hg$	CH_3—Hg	30±1	$[(C_2H_5)_3Ge]_2O$	O—Ge(C_6H_5)$_3$	90±2
$(C_6H_5)_2Hg$	C_6H_5—Hg	24±1	$[(C_6H_5)_3Ge]_2$	C_6H_5—Ge	71±2
(n-C_3H_7)$_2$Hg	n-C_3H_7—Hg	24±1	$(CH_3)_4Sn$	CH_3—Sn	53±1
(iso-C_3H_7)$_2$Hg	iso-C_3H_7—Hg	20±1	$(C_2H_5)_4Sn$	C_2H_5—Sn	60±3
(n-C_4H_9)$_2$Hg	n-C_4H_9—Hg	27±2	$(C_2H_5)_4Sn$	C_2H_5—Sn	46±1
(iso-C_4H_9)$_2$Hg	iso-C_4H_9—Hg	26±2	(n-C_3H_7)$_4$Sn	n-C_3H_7—Sn	47±2
(iso-C_5H_{11})$_2$Hg	iso-C_5H_{11}—Hg	26±2	(iso-C_3H_7)$_4$Sn	iso-C_3H_7—Sn	43±2
$(C_6H_5)_2Hg$	C_6H_5—Hg	38±1	(n-C_4H_9)$_4$Sn	n-C_4H_9—Sn	47±2
$(CN)_2Hg$	CN—Hg	65±2	$(C_6H_5)_4Sn$	C_6H_5—Sn	62±2
$(CH_3)_3B$	CH_3—B	89±2	$[(CH_3)_3Sn]_2$	CH_3—Sn	52±2
$(C_2H_5)_3B$	C_2H_5—B	82±2	$[(C_2H_5)_3Sn]_2$	C_2H_5—Sn	48±2
(n-C_3H_7)$_3$B	n-C_3H_7—B	84±2	$[(C_2H_5)_3Sn]_2O$	O—Sn(C_2H_5)$_3$	79±3
(iso-C_3H_7)$_3$B	iso-C_3H_7—B	82±2	$[(C_6H_5)_3Sn]_2$	C_6H_5—Sn	60±2
(n-C_4H_9)$_3$B	n-C_4H_9—B	84±2	$[(C_6H_5)_3Sn]_2O$	O—Sn(C_6H_5)$_3$	80±3
(iso-C_4H_9)$_3$B	iso-C_4H_9—B	81±2	$(CH_3)_4Pb$	CH_3—Pb	38±1
(s-C_4H_9)$_3$B	s-C_4H_9—B	76±2	$(C_2H_5)_4Pb$	C_2H_5—Pb	31±1
(iso-C_5H_{11})$_3$B	iso-C_5H_{11}—B	84±2	$(C_6H_5)_4Pb$	C_6H_5—Pb	49±2
(cyclo-C_6H_{11})$_3$B	cyclo-C_6H_{11}—B	88±3	$(CH_3)_3N$	CH_3—N	74±1
(n-C_6H_{13})$_3$B	n-C_6H_{13}—B	82±2	$(C_2H_5)_3N$	C_2H_5—N	71±1
(n-C_7H_{15})$_3$B	n-C_7H_{15}—B	82±2	$(CH_3)_3P$	CH_3—P	67±1
(n-C_8H_{17})$_3$B	n-C_8H_{17}—B	82±2	$(C_2H_5)_3P$	C_2H_5—P	55±1
(s-C_8H_{17})$_3$B	s-C_8H_{17}—N	80±2	$(C_6H_5)_3P$	C_6H_5—P	77±2
$(C_6H_5)_3B$	C_6H_5—B	112±2	$(CH_3)_3PO$	$(CH_3)_3P{=}O$	139±2
$(CH_3O)_3B$	CH_3O—B	118±2	$(C_6H_5)_3PO$	$(C_6H_5)_3P{=}O$	133±3
$(C_2H_5O)_3B$	C_2H_5O—B	119±1	$(CH_3O)_3P$	CH_3O—P	83±2
(n-C_3H_7O)$_3$B	n-C_3H_7O—B	120±2	$(C_2H_5O)_3P$	C_2H_5O—P	83±1
(n-C_4H_9O)$_3$B	n-C_4H_9O—B	119±2	(iso-C_3H_7O)$_3$P	iso-C_3H_7O—P	84±2
$(C_6H_5O)_3B$	C_6H_5O—B	104±2	$(C_6H_5O)_3PO$	$(C_6H_5O)_3P{=}O$	150±1
$[(CH_3)_2N]_3B$	$(CH_3)_2N$—B	96±2	$[(C_6H_5)_2N]_3P$	$(C_6H_5)_2N$—P	81±2
$(CH_3S)_3B$	CH_3S—B	87±3	(n-C_4H_9)$_3$PS	(n-C_4H_9)$_3$P=S	91±1
$(C_6H_5S)_3B$	C_6H_5S—B	79±3	$(C_2H_5O)_3PS$	$(C_2H_5O)_3P{=}S$	90±1
$(CH_3)_3Al$	CH_3—Al	67±1	$(CH_3)_3As$	CH_3—As	56±1
$(C_2H_5)_3Al$	C_2H_5—Al	64±1	$(C_2H_5)_3As$	C_2H_5—As	44±1
(n-C_3H_7)$_3$Al	n-C_3H_7—Al	63±2	$(C_6H_5)_3As$	C_6H_5—As	69±2
$(CH_3)_3Ga$	CH_3—Ga	59±1	$(CH_3O)_3As$	CH_3O—As	69±2
$(C_2H_5)_3Ga$	C_2H_5—Ga	52±2	$(C_2H_5O)_3As$	C_2H_5O—As	69±2
(n-C_4H_9)$_3$Ga	n-C_4H_9—Ga	56±2	(n-C_3H_7O)$_3$As	n-C_3H_7O—As	70±2
(iso-C_4H_9)$_3$Ga	iso-C_4H_9—Ga	55±2	$(CH_3)_3Sb$	CH_3—Sb	53±1
$(CH_3)_3In$	CH_3—In	37±1	$(C_2H_5)_3Sb$	C_2H_5—Sb	43±1
$(CH_3)_4Si$	CH_3—Si	75±1	$(C_6H_5)_3Sb$	C_6H_5—Sb	64±2
$(C_2H_5)_4Si$	C_2H_5—Si	67±1	$(CH_3)_3Bi$	CH_3—Bi	35±1
$(C_6H_5)_4Si$	C_6H_5—Si	84±2	$(C_2H_5)_3Bi$	C_2H_5—Bi	25±1
$(CH_3O)_4Si$	CH_3O—Si	102±2	$(C_6H_5)_3Bi$	C_6H_5—Bi	46±2
$(C_6H_5O)_4Si$	C_6H_5O—Si	101±2	$(CH_3)_2O$	CH_3—O	86±1
(iso-C_3H_7O)$_4$Si	iso-C_3H_7O—Si	98±3	$(C_2H_5)_2O$	C_2H_5—O	85±1
$[(CH_3)_3Si]_2$	CH_3—Si	72±1	$(C_6H_5)_2O$	C_6H_5—O	102±2
$[(CH_3)_3Si]_2O$	O—Si(CH_3)$_3$	116±3	$(CH_3)_2S$	CH_3—S	71±1
$[(C_2H_5)_3Si]_2$	C_2H_5—Si	63±2	$(C_2H_5)_2S$	C_2H_5—S	68±1
$(CH_3)_4C$	CH_3—Ge	62±1	$(C_6H_5)_2S$	C_6H_5—S	83±2
$(C_2H_5)_4Ge$	C_2H_5—Ge	58±1	$(C_2H_5)_2Se$	C_2H_5—Se	60±2
n-C_3H_7–Ge	(n-C_3H_7)$_4$Ge	58±2	$(C_6H_5)_2Se$	C_6H_5—Se	70±2
n-C_4H_9–Ge	(n-C_4H_9)$_4$Ge	59±2	$(C_2H_5)_2Te$	C_2H_5—Te	48±2

Table 6 presents the values of $\bar{D}$(E–R) for a series of compounds of Group II–VI non-transition elements calculated by the authors of the review by this method from the data in Tables 1–5 in this review and in a handbook[11]. The data in Table 6 made it possible to establish the following relations for the dissociation energies $\bar{D}$ of the bonds formed by non-transition elements in their organic compounds.

1. In compounds $E^{nt}R_n$ of non-transition elements (E^{nt}) in the same Group of the Periodic System and with the same alkyl or phenyl group (R) and the same value of n, the average dissociation energy of the E^{nt}–R bond diminishes with increasing atomic number of the element E^{nt} down the Group (Figs. 1–3)†.

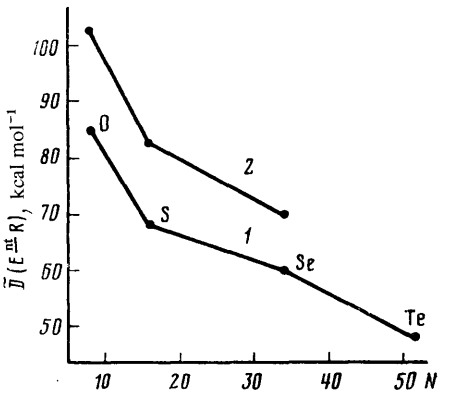


Figure 3. Variation of the average dissociation energy of the element–organic group bonds formed by Group VI non-transition elements in the compounds $E^{nt}R_2$ with increase of the atomic number of the element; R: 1) C_2H_5; 2) C_6H_5.

2. In all cases $\bar{D}(E^{nt}-C_6H_5) > \bar{D}(E^{nt}-CH_3) > \bar{D}(E^{nt}-C_2H_5) \cong \bar{D}(E^{nt}-n\text{-}C_3H_7) \cong \bar{D}(E^{nt}-n\text{-}C_4H_9)$.

3. The average dissociation energy of the E^{nt}–n-R bond exceeds by 1–4 kcal mol^{-1} $\bar{D}(E^{nt}-iso\text{-}R)$. [The failure of $\bar{D}$(Ge–n-C_4H_9) and $\bar{D}$(Ge–iso-C_4H_9) to obey this rule is probably due to the inaccuracy of experimental data used to calculate these quantities.]

4. The average dissociation energies of the E^{nt}–OR bonds, where R is an alkyl group, exceed by 14±2 kcal mol^{-1} the corresponding values of $\bar{D}(E^{nt}-OC_6H_5)$. The high dissociation energies of the bonds formed by silicon and germanium with oxygen in the compounds $(R_3E)_2O$ compared with the corresponding values for $(RO)_4E$ are striking.

5. The average dissociation energies of the E–R bonds, where R is an alkyl or phenyl group and E = Si, Ge, or Sn, in the compounds ER_4 and $(ER_3)_2$ with the same elements and groups have similar values (Table 6). This corresponds to the equality, within the limits of the error of the determination, of the E–R bond lengths in the compounds ER_4 and $(ER_3)_2$ with identical E and R.[256–259]

†As a general relation, this was first established by the present authors[253]. In the compound E^tL_n of transition elements (E^t) belonging to the same Group and with the same ligand (L) and the same n, $\bar{D}(E^t-L)$ increases with increasing atomic number of the element down the Group[254,255].

The values of $\bar{D}$(E–R) for compounds of the type $(ER_3)_2$ were calculated from the equation

$$\bar{D}(E-R) = {}^1/_6 \{6\Delta H_f^0[R(g)] + \Delta H_f^0[E_2(g)] - \Delta H_f^0[(ER_3)_2(g)]\}.$$

If, bearing in mind the observed similarity of the values of $\bar{D}$(E–R) in ER_4 and in $(ER_3)_2$, one assumes that $\bar{D}$(E–E) for the corresponding gas-phase molecules of E_2 and $(ER_3)_2$ are also similar, then we obtain the following values for the compounds $(ER_3)_2$: $\bar{D}$(Si–Si) ≅ 74 kcal mol^{-1}, $\bar{D}$(Ge–Ge) ≅ 66 kcal mol^{-1}, and $\bar{D}$(Sn–Sn) ≅ 45 kcal mol^{-1}.

Unfortunately there are no thermochemical data for the strength of the bonds between non-transition elements. a mass-spectrometric study[260] of the compounds (C_5H_5). $.(CO)_3E^1E^2(CH_3)_3$, where E^1 = Cr, Mo, or W and E^2 = Ge or Sn, led to the following results:

Bond	Cr–Ge	Mo–Ge	W–Ge	Cr–Sn	Mo–Sn	W–Sn
D, kcal mole^{-1}	46.8	60.0	64.8	53.5	71.0	75.6

Thus $\bar{D}(E^1–E^2)$ increases with increasing atomic number of both the transition and non-transition element down the Groups of the Periodic System. In this case the behaviour characteristic of the bonds formed by transition metals, considered in detail in our previous reviews[245,255], is manifested.

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