THERMODYNAMIC PROPERTIES OF SELECTED BORON COMPOUNDS WITH PARTICULAR REFERENCE TO THE PEROXYBORANES

AND THEIR RÔLE IN HYDROCARBON OXIDATION

A Thesis submitted by

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ABSTRACT

The standard enthalpy of formation of tri(tertiary-butylperoxy)borane has been determined from a thermochemical study of its hydrolysis in an isoperibol reaction calorimeter and the enthalpy of vaporisation has been determined using tensimetry. The strength of the peroxide bond, E(BO-OR), and the boron-to-peroxide bond, E(B-OOR), were derived and the corresponding values for tri(normal-butylperoxy)borane estimated. The rôle of boron containing coreactants in hydrocarbon autoxidations in directing the reaction towards increased alcohol:ketone ratios was explained in terms of the formation of organoperoxyboranes as intermediates and their subsequent decomposition under oxidation conditions.

Mesityldichloroborane and ortho-, meta-, and para-tolyldichloroboranes have been studied thermochemically and their standard enthalpies of formation derived. The enthalpies of vaporisation of meta-tolyldichloroborane and mesityldichloroborane have been determined tensimetrically. Derived boron-to-carbon bond energies were interpreted in terms of steric and electronic effects of the methyl substituents. The steric effect of ortho methyl substitution caused a decrease in the boron-to-carbon bond energy whilst meta-methyl substitution caused a similar decrease through an electronic effect.

Pure samples of rubidium and caesium tetrachloroborates have been prepared using a modified synthetic procedure. Hydrolyses were studied thermochemically from which the standard enthalpies of the two salts were derived. Using a semi-empirical equation, the 'thermochemical radius' of the tetrachloroborate anion and the lattice energies of the prepared tetrachloroborates were estimated. The thermodynamic instability of the alkali-metal tetrachloroborates relative to the corresponding tetrafluoroborates was demonstrated.

A list of standard enthalpies of reaction of organoboron compounds was compiled for inclusion in 'CATCH' tables (Computer Analysis of ThermoCHemical data) processed by J.B. Pedley et al of the University of Sussex. The intent is that these tables should provide a widely accessible and readily updated source of thermodynamic data.

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'New associations and fresh ideas are more likely to come out of a varied store of memories and experience than out of a collection that is all of one kind'.

Dr. E.L. Taylor, 1948.

CONTENTS

page

CHAPTER I - Experimental Techniques

CHAPTER II - Synthesis and Analysis of Compounds

SYMBOLS, DEFINITIONS and UNITS

I. SYMBOLS

The recommendations of the International Union of Pure and Applied Chemistry have been followed with regard to symbols and nomenclature for thermodynamic quantities. These are as follows:

Quantity	Symbol
Internal energy	U
Enthalpy	H
Gibbs energy	G
Entropy	S
Heat capacity	C

The sign of energy changes etc., is always determined from the standpoint of the system, e.g. if energy is evolved from a system the energy change, ΔU, for the process is negative. Symbols for thermodynamic quantities relating to substances in their standard states (q.v.), or to reactions with all participants in their standard states, are distinguished by the superscript, ^{o}. E.g. S^{o}, ΔH^{o}.

II. DEFINITIONS

The following definitions of standard states are used:

(i) For a gas, the standard state is that of a hypothetical ideal gas at 760 Torr (symbol, g).

(ii) For a liquid, the standard state is that of the pure substance under a pressure of 760 Torr (symbol, l).

(iii) For a solid, the standard state is that of the pure crystalline substance, under a pressure of 760 Torr (symbol, c).

Temperature is not part of the definition of the standard state, and should therefore be quoted separately. The usual convention is followed in this work; a temperature dependent thermodynamic quantity written without a temperature subscript refers to 298.15 K.

If all the participants in a chemical reaction are in their standard states, the heat of reaction is referred to as the standard heat of reaction, ΔH^o.

'N', is defined as the mole ratio of water to compound in a specified chemical reaction, e.g. for the heat of solution of boric acid,

$B(OH)_3(c) + NH_2O(l) = B(OH)_3.NH_2O$ (solution).

III. UNITS

The International System of Units (SI base units) has been followed with one exception; the unit of pressure of torr (symbol, Torr) is used throughout this work. It is defined exactly in terms of SI units:

Torr = $(101325/760)\,Nm^{-2}$.

Many thermodynamics texts use the 'thermochemical calorie' as energy units and for purposes of comparison it is defined here in SI units:

1 thermochemical calorie, $cal_{th} = 4.184J$.

The precision of results is quoted throughout as twice the standard deviation of the mean, $\bar{s}$:

$$\bar{s} = \frac{\sum (x_1 - \bar{x})^2}{n(n-1)}$$

where $\bar{x}$ is the arithmetic mean of n results. All results are quoted in the form $x \pm 2\bar{s}$, i.e. to within 95% confidence limits assuming a normal distribution. Net errors are calculated as the root of the sum of the squares of constituent errors.

INTRODUCTION

Thermochemistry is concerned with the energy changes of chemical reactions and of associated physical processes involving substances of defined composition and may be regarded as a branch of the larger science of thermodynamics. One of the fundamental measurements in thermochemistry is the determination of heats of chemical reaction and this constitutes the experimental science of calorimetry. Such measurements are used to calculate standard heats of formation of compounds and these in turn may be used to predict (i) the heat changes in other chemical reactions and (ii) estimate the temperature coefficient of equilibrium constants.

The revival of interest in thermochemical measurements was due in part to the suggestion[1, 2] that the heat of formation of a compound from its constituent atoms could be taken as a measure of the strengths of the bonds in a molecule. Very soon the qualitative concept of bond strength was precisely defined in terms of bond-energy and bond dissociation energy (BDE). There is now a large body of thermochemical information for covalent compounds containing a diversity of elements and from these data it is possible to examine such effects as strain and stabilisation (due to electron delocalisation) on the strengths of chemical bonds.

The aim of the research described in this thesis is concerned mainly with this latter kind of problem, viz. how heats of chemical reactions of organoboron compounds can be used to determine bond strengths and how these values can be interpreted in terms of structure and reactivity. It is first necessary to consider what thermochemical quantity can most meaningfully be related to structure. The total energy content of a molecule in its ground state includes (a) intramolecular energy due to the chemical binding of the constituent atoms, (b) translational, rotational and vibrational energy, (c) intermolecular energy due to interaction of external force fields. Energy from effect (c) can be removed from consideration by specifying that the molecule is in the ideal-gas state. It is conventional to make no attempt to separate effects (a) and (b) and to regard the measure of the total chemical binding energy to be the energy change of the process:

$$\text{Molecule (ground state, ideal gas, } T_1) \rightarrow \text{Atoms (ground state, ideal gas, } T_1)$$

This process, known as the energy of atomisation of the molecule, uses an energy reference state that is amenable to experimental study, namely the total energy of the constituent atoms at infinite separation. For most purposes, it is convenient to combine the $\Delta(pV)$ quantity for the reaction with the energy change and hence to deal with the heat of atomisation, ΔH_a^o, T_1. If the heat of atomisation is equated to the total chemical bonding energy, the problem then arises as to how this quantity can be subdivided in terms of energies of individual bonds.

There are three ways (at least) of examining the problem of bond strength.

(i) One could consider the force required to stretch or distort a bond. This information stated in terms of 'force constants' is obtained spectroscopically. Apart from the difficulties involved in their determination, stretching force constants reflect the resistance of a bond to small perturbations. There is no theoretical justification in correlating them with thermodynamic quantities although correlation in groups of compounds with related structure is often reported.

(ii) One could allocate the energy required to split a molecule completely into its constituent atoms among the various bonds in the molecule to provide an index of the 'strength' of these bonds.

(iii) One could measure the energy required to break a particular bond.

In order to obtain values for (ii) and (iii), the elements in their standard states are arbitrarily taken to have zero enthalpy of formation and define the standard enthalpy of formation of a compound, ΔH_f^o, as the heat change when it is formed from its elements in their standard states at a given temperature. In general terms the heat of any reaction, ΔH^o, can be equated to the difference between the sum of the heats of formation of the products of the reaction and the sum of the heats of formation of the reactants, or:

$$\Delta H^o = \sum \Delta H_f^o \text{ (products)} - \sum \Delta H_f^o \text{ (reactants)} \qquad \ldots \qquad (I.1)$$

If the heat of a reaction is measured, and all but one of the heats of formation are known, this unknown standard heat of formation is easily calculated. From the standard heat of formation of a gaseous compound, it is possible to calculate the heat of atomisation from the relationship:

$$\Delta H_a^o = \Delta H_f^o \text{ (atoms, ideal gas)} - \Delta H_f^o \text{ (compound, ideal gas)} \qquad (I.2)$$

Here, ΔH_f^o (atoms, g) is the sum of the heats of formation of the gaseous atoms in their ground state from their standard state. Equation (I.2) corresponds to the dissocation of the compound into the separate constituent atoms, with the complete rupture of the chemical bonds. The heat change of this dissociation is put equal to the sum of the bond-energies in the molecule, $\sum E(b)$, and therefore:

$$\Delta H_a^o = \sum E(b) \qquad \ldots \qquad (I.3)$$

The various relationships are shown in Figure 1. For a molecule of the type AB_n, containing only A–B bonds, it is reasonable to divide the heat of atomisation of the compound amongst the n bonds A – B, so that the bond-energy of the A – B bond, E (A – B) in the gaseous state is defined by the expression:

$$n.E(A\text{–}B) = \Delta H_a^o = \Delta H_f^o A(g) + n.\Delta H_f^o B(g) - \Delta H_f^o ABn(g) \qquad \ldots \qquad (I.4)$$

The bond energy, E(A–B) or bond-energy term, as it is generally known, is therefore identified with case (ii) above.

However, the idea of the energy of a molecule being 'localised' in a number of bonds between atoms is a highly artificial one, in that the total energy of a molecule is the resultant of the attractive and repulsive energies between bonded and non-bonded atoms. Nevertheless, it is still convenient to consider the net attractive energy as the sum of the bond-energies. It is undisputed that whatever values are attributed to individual bond-energies in a polyatomic molecule, their sum must be equal to the enthalpy of atomisation of the gaseous molecule. The original assumption made[3, 4] was that the bond-energy term for a bond of a given type has a characteristic value, independent of the environment and factors such as the hybridisation states of the bonded atoms, i.e. bond-energy terms were considered to be additive and transferable from one molecular structure to another. It is this assumption that underlies the application of bond-energy terms to structure and reactivity studies of molecules.

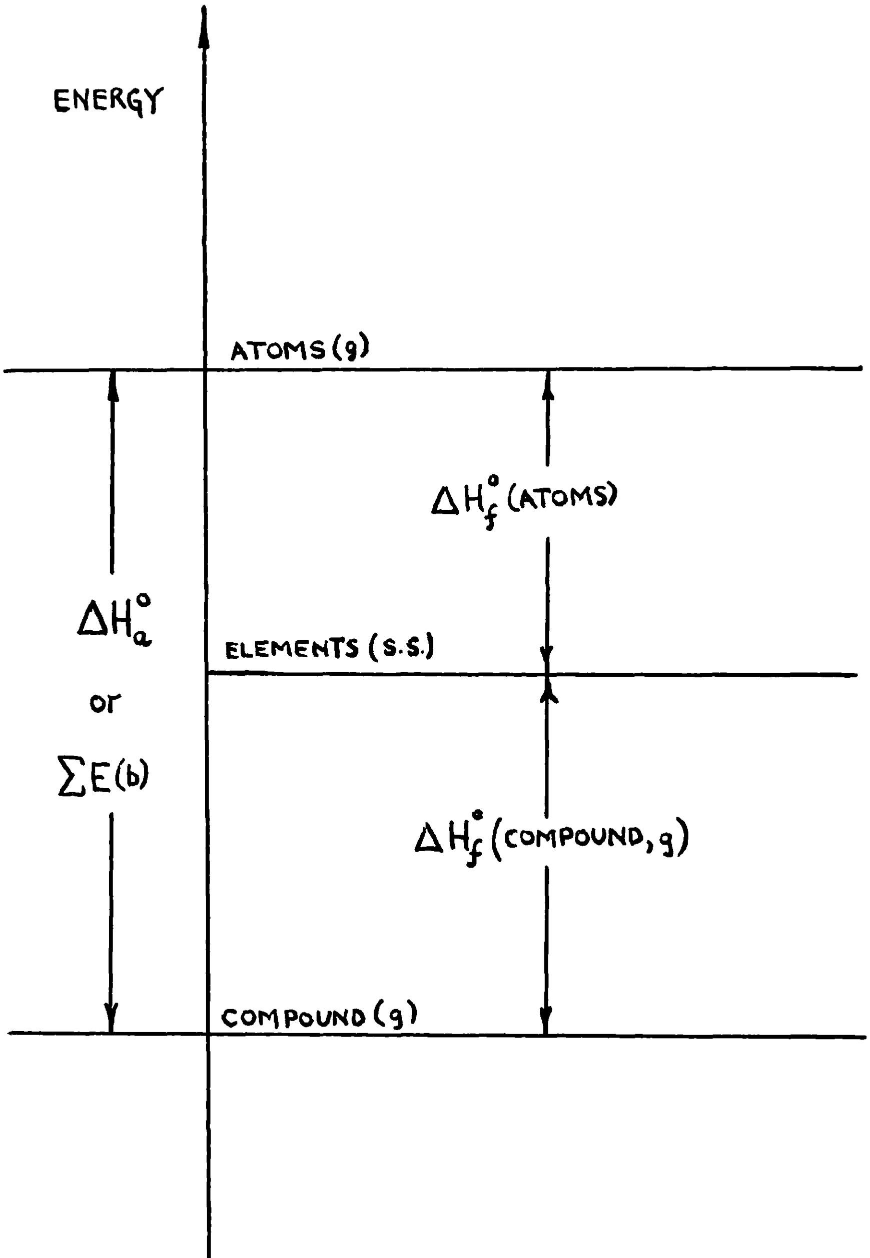

ENERGY
ATOMS (g)
ELEMENTS (S.S.)
COMPOUND (g)
ΔH_a°
or
$\sum E(b)$
ΔH_f° (ATOMS)
ΔH_f° (COMPOUND, g)

figure I.1

The energy required to break a specific bond in a molecule, case (iii) above, is the most direct measure of the strength of a bond and is generally referred to as the bond-dissociation energy, BDE. The BDE is defined as the enthalpy change associated with the reaction in which one mole of a bond is homolytically broken, reactants and products being in the ideal gas state. It follows that for a diatomic molecule, the bond-energy term is the same as the BDE (at 298.15K). The BDE, for example, D(R-X) is more strictly defined as $\Delta U(0K)$ for the reaction:

$$R\text{-}X(g) \longrightarrow R^{\bullet}(g) + X^{\bullet}(g) \qquad \ldots \qquad (I.5)$$

where R-X, $R^{\bullet}$ and $X^{\bullet}$ are in their ground vibrational states, and it is this quantity D_0^o which is generally derived from spectroscopic measurements. Dissociation energies derived from equilibrium studies and from activation energies are generally quoted as ΔH^o (298.15K) values. Fortunately, ΔH (298.15K) is not very different from $\Delta U(0K)$ and it has been shown[5] that the maximum difference would be $\approx$10.8 kJ. For the dissociation of bonds in polyatomic molecules, the uncertainty of the determination is rarely less than ± 4kJ and therefore the use of data at 298.15K for dissociation energies should not cause confusion.

Bond-energy terms defined above have been critisised on the ground that the heats of atomisation used refer to the atoms in their ground states, whereas the valence state should be the relevant state. However, this lack of an absolute 'valence' basis in the bond-energy terms used is not important as far as the uses to which they are usually put. One use of bond-energy terms is that of calculating heats of formation of compounds for which experimental data are lacking. Another use is to compare calculated heats of formation with those observed for compounds in which perturbing effects are expected. The difference between the two can then be used as a measure of these effects, for example, in terms of 'strain' energy or similar concepts. Modern bond-energy schemes, which are based on the additivity properties of bond-energy terms for specific kinds of bonds in molecules, allow the calculation of standard heats of formation of a wide range of covalent molecules. These schemes are discussed in Appendix I.

The experimental aspects of calorimetry of organometallic compounds are manifold. The field can be conveniently divided into combustion calorimetry and reaction calorimetry, and it is the latter with which this thesis is concerned. 'Reaction calorimetry' refers to the measurement of the energy or heat of any reaction other than combustion, usually one in which the carbon skeleton remains intact. The technique finds application to compounds that readily undergo unique quantitative reactions at moderate temperatures. For example, the hydrolytic instability of many organoboron compounds provides a simple aqueous hydrolysis reaction highly suited for solution reaction calorimetry. Thus the difficulty found in preparing and handling such moisture sensitive compounds is compensated by the ease with which calorimetric studies can be made.

Solution reaction calorimetry of a number of mainly aliphatic boron compounds has been studied extensively[6 - 12] using simple reactions such as hydrolysis, hydroboration, aqueous oxidation and reduction reactions. Similar reactions have been exploited in the thermochemistry of some arylboron compounds[13 - 15] and these have provided some important 'key' data i.e. standard heats of formation of simple arylboron compounds that occur as products in other reactions. Indeed, one of the main points to observe in selecting a reaction for calorimetric study is the availability of standard heats of formation for the products and reactants in calculating the unknown ΔH_f^o of the compound. Details of a compilation of standard heats of formation of organoboron compounds processed by computer is given in Appendix II.

The merit of combustion calorimetry (from this point of view) lies in the drastic degradative powers of combustion reactions, thus giving products that are usually simple compounds (H_2O, CO_2 etc.,) having well-established ΔH_f^o values. From the viewpoint of the combustion thermochemist utilising this technique, boron is most definitely not a 'well-behaved' element, i.e. combustion of boron-containing compounds are not 'clean'. This means that it is difficult to define the final thermodynamic state due to incomplete combustion and undesirable side-reactions. The use of a rotating bomb calorimeter in place of a static bomb[16] and fluorine bomb calorimetry are two techniques obviating this difficulty. Only in the case of a direct synthesis from the elements is the heat of reaction a direct measure of the heat of formation.

The appeal of solution reaction calorimetry is that it can be applied to a variety of organoboron compounds having reactions which are established as quantitative and are rapid ($t_{\frac{1}{2}}$ reaction $\leqslant 5$ min.) at temperatures $\approx 298K$. An exhaustive review on the thermochemistry of boron compounds has been published.[17]

Calorimeters of various designs have been devised for the measurement of reactions in the solution phase. The most commonly used apparatus for the determination of ΔH^o for a 'fast' chemical reaction is the constant-temperature-environment, (C.T.E.) or isoperibol calorimeter, in which the surroundings are held at a constant temperature and the calorimeter-cell is insulated to some extent from these surroundings. The rate of heat exchange between the calorimeter-cell and surroundings is then small and calculable by the known laws of heat flow. A description of the calorimeter used is given in Chapter I,C.

The derivation of the standard heat of formation in the hypothetical ideal-gas state, ΔH_f^o (ideal gas) requires knowledge of the standard heat of vaporisation of the liquid at 298.15 K, ΔH_v^o and for a solid it requires knowledge of the standard heat of sublimation of the compound at 298.15 K, ΔH_s^o. Thus from the first law of thermodynamics it is evident that

$$\Delta H_f^o(g) = \Delta H_f^o(l) + \Delta H_v^o \quad \ldots \quad (I.6)$$

$$\text{and} \quad \Delta H_f^o(g) = \Delta H_f^o(c) + \Delta H_s^o \quad \ldots \quad (I.7)$$

The determination of accurate values of heats of vaporisation and sublimation is therefore an important aspect of thermochemistry. There are various methods of determining these values and a comprehensive account is available.[18] The vapour-pressure method used in this work is described in Chapter, I,F.

This work describes the thermochemical study of tri(tertiary-butylperoxy)borane, four aryldichloroboranes and some alkali-metal tetrachloroboranes, and various bond-energy terms and thermodynamic functions have been derived from the determined standard heats of formation, $\Delta H_f^o(g)$. The determination of $E(BO\text{–}OBu^t)$ and $E(B\text{–}OOBu^t)$ in tri(tertiary-butylperoxy) borane is described in Chapter III and the bond-energies are discussed in the context of hydrocarbon oxidation in the presence of boron containing co-reactants. An examination of the aryl carbon-boron bond energy forms the subject of Chapter IV and the following compounds were studied calorimetrically: mesityldichloroborane, ortho-, meta-, and para-tolyldichloroboranes. The values obtained are discussed in terms of electronic and steric features of the molecules and a comparison made with E(B-C) in phenyldichloroborane, diphenylchloroborane, triphenylborane and tricyclohexylborane.

The preparation and calorimetry of analytically pure samples of rubidium and caesium tetrachloroborates is described in Chapter V. The determined standard heats of formation are used to estimate the 'thermochemical radius' of the tetrachloroborate anion, the lattice energies of the two salts and the standard enthalpy of formation of $BCl_4^-(g)$. The thermodynamic instability of the tetrachloroborates relative to the corresponding tetrafluoroborates is discussed.

CHAPTER I

Experimental Techniques

- *A.* Proton magnetic resonance spectra.
- *B.* Raman spectra.
- *C.* Calorimetry.
- *D.* Precision resistance measurements.
- *E.* Differential scanning calorimetry.
- *F.* Measurement of enthalpies of vaporisation.
- *G.* Purification of solvents and reagents.
- *H.* Handling of moisture sensitive compounds.
- *I.* Autoclave reactions.

A. Proton magnetic resonance spectra.

'H magnetic resonance spectra were recorded with a Varian spectrometer, Model HA-60 on neat liquids with an internal TMS standard.

B. Raman spectra.

Solid-state Raman spectra were obtained using a Coderg spectrometer, Type CPH 100 with a laser-source excitation wavelength of 514.5 nm.

C. Calorimetry.

The calorimeter used for the determination of heats of reaction in this work was a constant-temperature-environment (C.T.E.) or isoperibol calorimeter designed and constructed in this laboratory. Detailed accounts of the construction and operating procedures are available.[19, 20] The convention used in describing the apparatus in this text is as follows:

(i) The 'calorimeter-vessel' refers to the evacuated unsilvered Dewar vessel containing the temperature sensor, heater, stirrer, ampoule etc., in which the reactions are carried out (Figure 1.1).

(ii) The 'calorimeter' refers to the apparatus as a whole i.e. the ancillary electronic equipment and the thermostat-bath containing the two calorimeter-vessels.

The principle of operation of the calorimeter is that the thermal energy produced in a chemical reaction is compared with a measured amount of electrical energy required to produce a similar temperature in the solution. The experiment therefore consists of two parts:

(a) the measurement of the temperature change produced by a chemical reaction (the reaction period) and (b) the measurement of the temperature change and the amount of electrical energy required to produce a comparable

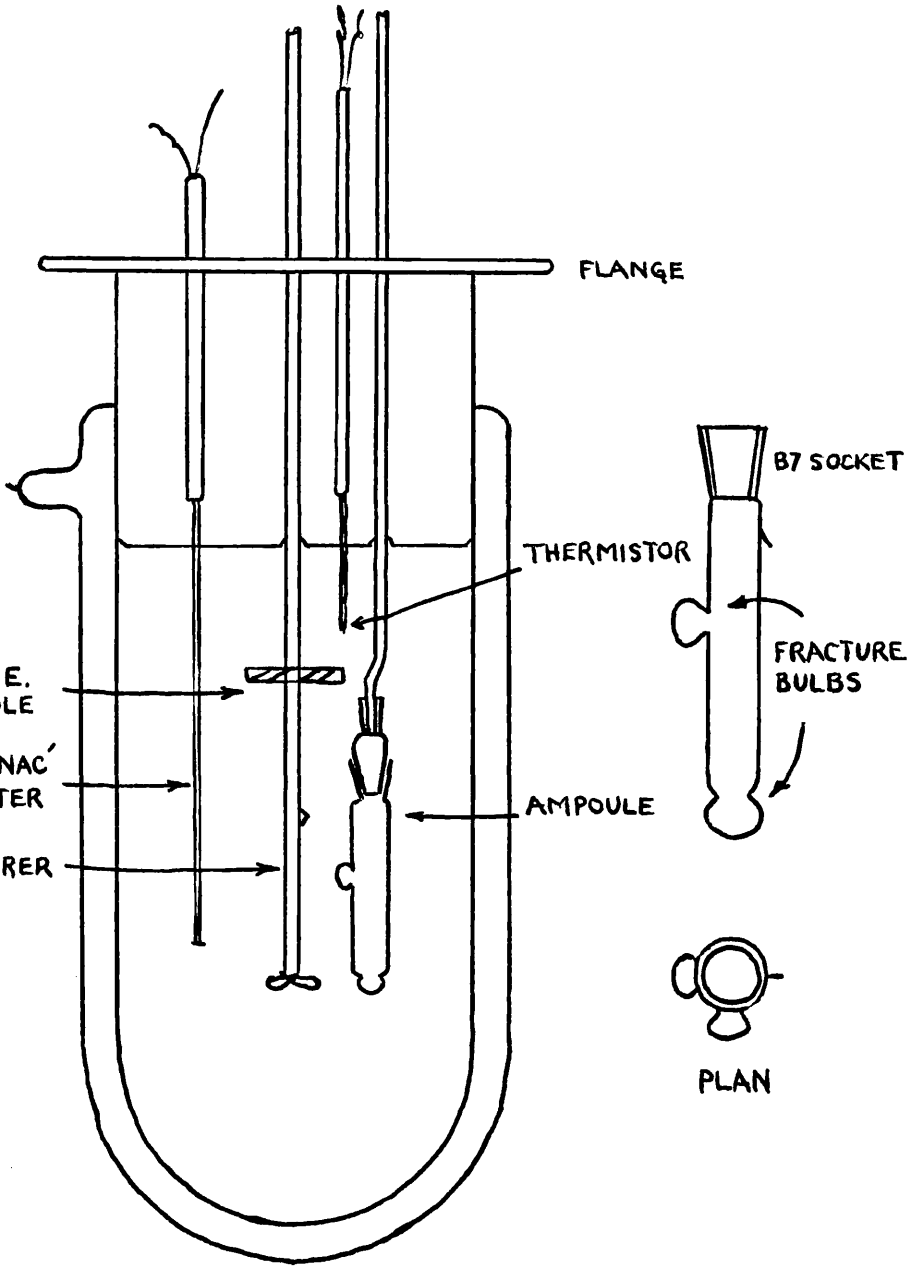

FLANGE
B7 SOCKET
THERMISTOR
FRACTURE BULBS
P.T.F.E. PADDLE
'TRONAC' HEATER
AMPOULE
STIRRER
PLAN

figure 1.1

temperature rise with that in (a), (the calibration period). Thermistors are used to detect and measure temperature changes and the temperature-resistance relationship is given by:

$$R = Ae^{B/T}$$

where R = resistance (Ω), T = temperature (K) and A, B are thermistor constants. The change in the thermistor resistance caused by the heat of a reaction is displayed on a linear chart-recorder and this provides a direct visual record of the temperature-time profile of the reaction. The compound whose heat of reaction is being determined is contained in an ampoule equipped with two fracture bulbs (Figure 1.1) and the reagent solution (200.0 cm^3), pre-equilibrated to ca. 298 K, is placed in the calorimeter-vessel. Each vessel is immersed in the water-thermostat bath maintained at 298.15 K $\pm$ 0.01 K and reactions and calibrations are started at a solution temperature of 298 K after thermal equilibration (ca. 1.5 h).

The accuracy and precision of the calorimeter is assessed using a test chemical reaction for which the enthalpy of reaction is accurately known. The neutralisation of tris-hydroxymethylaminomethane (THAM) in excess 0.1 mol. dm^{-3} hydrochloric acid is widely used; THAM is a non-hygroscopic crystalline solid which can be easily purified and analysed. The enthalpy of neutralisation has been measured at several thermochemical laboratories under rigorously controlled experimental conditions and the results are collected in Table 1.1.

TABLE 1.1

$$\text{Tham (c)} + n\text{HCl.N}H_2O = [\text{Tham } H^+ + Cl^-]n\text{-}1\text{HClN}H_2O$$

N	$-\Delta H$ /kJmol^{-1}
373 - 1120	29.736 ± 0.008 [21]
1138 - 1462	29.752 ± 0.008 [22]
1320 - 1390	29.757 ± 0.008 [23]
1170 - 1574	29.744 ± 0.006 [24]
1345	29.770 ± 0.029 [25]
1345	29.790 ± 0.029 [26]

In practice the weight of the compound whose standard heat of formation is being determined is adjusted such that the reaction generates a similar temperature rise in the calorimeter-vessel as does the test THAM reaction. This means that the calorimeter is never operated outside the limits of temperature change, calibration time etc., as found in the test-reaction. Under these conditions, the use of a test-reaction as an indication of overall accuracy in ΔH values of other chemical reactions is justified.

A number of modifications were made to the original design for the calorimeter-vessel[20] to improve performance and these are listed below:

(i) The stirring pattern within the liquid contained in the original vessel was found to be inadequate for reactions which gave products sparingly soluble in the reaction solution. An extra paddle, fabricated from polytetrafluoroethylene, was placed on the stirrer-shaft and this helped produce even agitation near the surface of the solution.

(ii) Thermistors are sensitive to changes in light intensity, to pressure changes and to mechanical shock; they must therefore be shielded and rigidly mounted. The thermistor support was reconstructed such that the tip of the thermistor was located ca. 3 cm below the surface of the solution thus minimising the effects of glass particles from broken ampoule bulbs. The sides of the glass thermostat-tank were covered using matt-black paper to reduce reflection of light and changes in light intensity during the course of an experiment.

(iii) Solid-state heaters (R-24 Tronac heater, TRONAC INC., OREM, PROVO, UTAH, U.S.A., nominal resistance 100Ω) were used to replace the laboratory-made wire-wound heaters. These are encapsulated in polytetrafluoroethylene tubing and have the advantage of small-size, low heat-capacity and hence rapid response. The heaters were operated to dissipate ca. 1 watt during calibration.

(iv) The ampoule holder and support were redesigned to allow easier fracture of the two ampoule bulbs. The positions of the fracture-bulbs glass blown on the ampoule wall were standardised (Figure 1.1).

The results for the enthalpy of neutralisation of THAM in excess 0.1 mol. dm^{-3} HCl before and after the modifications are shown in Table 1.2. B.D.H. 'Aristar' grade THAM (minimum purity 99.9%) was used for each determination. A significant improvement in accuracy and precision was noted after calorimetric modifications.

TABLE 1.2

Heat of neutralisation of THAM in excess

0.1 mol dm^{-3} HCl

Before modifications		After modifications	
N	$-\Delta H$ /kJ mol^{-1}	N	$-\Delta H$ /kJ mol^{-1}
1310	29.83	1275	29.79
1220	29.87	1301	29.79
1197	29.87	1365	29.75
1344	30.04	1189	29.79
1315	29.92	1340	29.79
1364	29.79	1260	29.75
1326	29.87	1265	29.83
1251	29.86	1305	29.83
1362	29.96	1200	29.75
		1319	29.79
mean = 29.89 ± 0.14		mean = 29.79 ± 0.08	

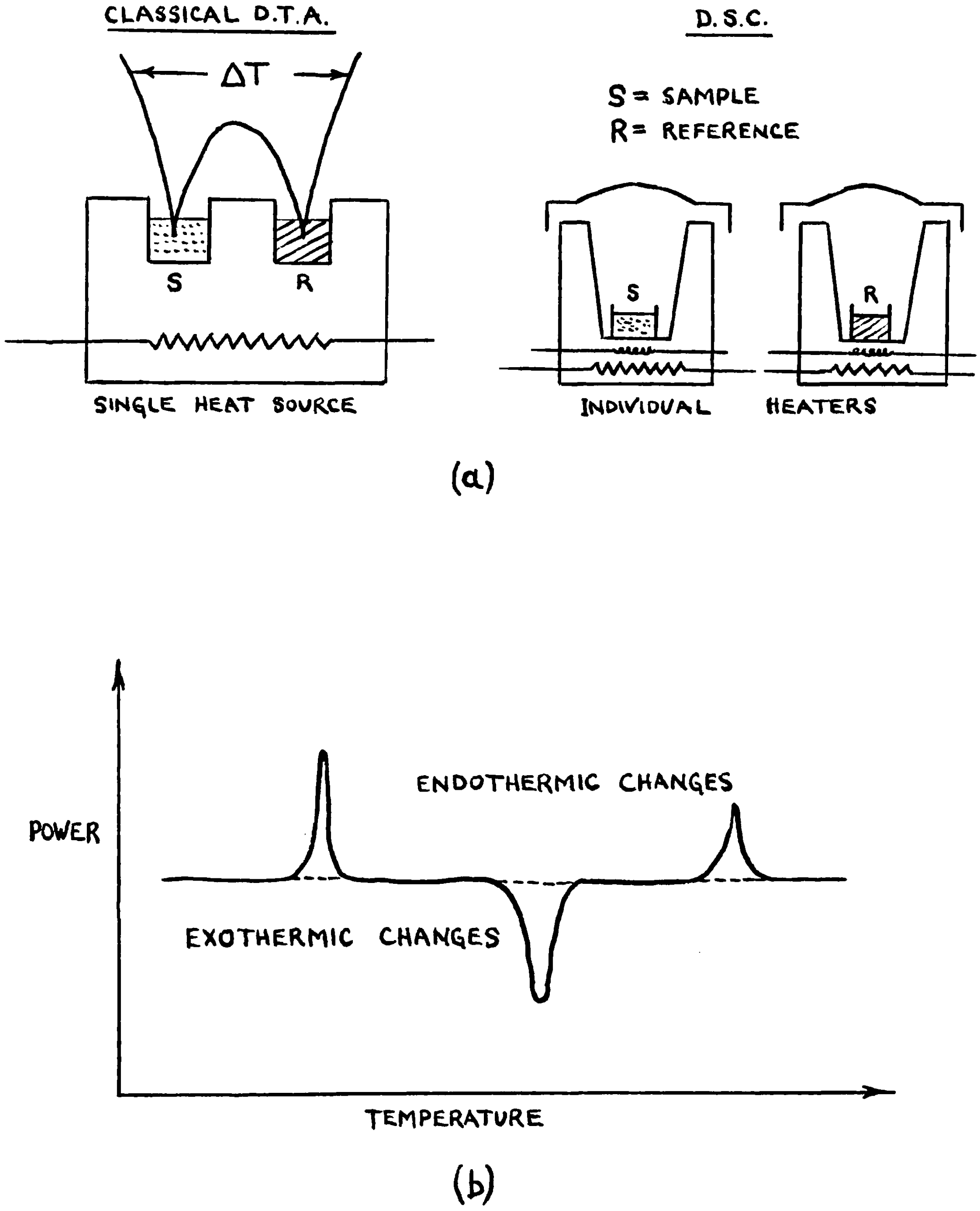
D. Precision resistance measurements.

Precision resistance values of the calorimeter heaters and heater-circuit resistors[20] are necessary to achieve accuracy in the derived standard heats of reaction. The resistances of two Tronac heaters, numbers 1 and 2, and three high-stability resistors comprising the heater circuit (nominal resistances 1 Ω, 10 Ω and 100 Ω respectively) were measured potentiometrically against a standardised resistor (NPL, grade 2 resistor, nominal value 10.000 ± 0.001 Ω, H.W. Sullivan Ltd.).

The value of the standard resistor was determined potentiometrically using a Class S resistor (10.00012 ± 0.00005 Ω, 293 K, Cambridge Instruments Ltd.) and the Tronac heaters were measured at 298 K in a stirred thermostat-bath to prevent local overheating and to simulate as near as possible the working conditions in the calorimeter-vessel. The determinations were made using a 4-Range High Precision Stabaumatic Potentiometer, Type 5545 (H. Tinsley & Co. Ltd.) and potential-drop values were measured to a precision of $\pm 3 \times 10^{-5}$ V.

E. Differential scanning calorimetry (D.S.C.).

D.S.C. is a technique which allows the direct measurement of enthalpies of transitions and has been used to determine the standard heat of fusion of para-tolyldichloroborane. (Perkin-Elmer D.S.C. 1B instrument). It can also be used to determine the heat capacities and purities of compounds. The technique is a development of 'classical' differential thermal analysis, D.T.A., and the basic difference between the two methods is shown in Figure 1.2. In D.S.C. the power to individual heaters located in the sample and reference holders is varied continuously in response to sample thermal effects to prevent the development of a differential temperature between sample and reference. The differential power provided is recorded as ordinate versus programmed temperature as abscissa. One of the numerous practical benefits of D.S.C. is that a peak area is a true electrical energy measurement, and does not depend on any of the thermal constants of the sample or apparatus, e.g. emissivity, thermal conductivity etc. Figure 1.2 shows a typical (idealised) output from a D.S.C. During an endothermic change, heat is automatically supplied to the sample in order to compensate for the heat loss associated


CLASSICAL D.T.A.
ΔT
S
R
SINGLE HEAT SOURCE
D.S.C.
S = SAMPLE
R = REFERENCE
S
R
INDIVIDUAL HEATERS
POWER
ENDOTHERMIC CHANGES
EXOTHERMIC CHANGES
TEMPERATURE

(a)

(b)

figure 1.2

with the endothermic change; the opposite applies in the case of an exothermic change. If a linear time-base recorder is used, peak areas represent the energy of the associated transitions and are theoretically independent of scanning speed, temperature, nature of sample or mode of operation (heating, cooling or isothermal). Calibration is made using a material of precisely known thermal characteristics, usually indium metal, and this provides the area-to-calories constant. Samples are contained in small aluminium metal pans equipped with lids for sealing (Figure 1.4).

The required heat of fusion of a sample is calculated from the general formula:

$$\Delta H^o_{fus} = \frac{M_1.\text{area (compound)}}{g_1 \text{ area (indium)}} . g_{In} . \frac{3261.85}{114.82}$$

(joule mol^{-1})

where M_1 = molecular weight of compound.

g_1 = weight of compound, g.

g_{In} = weight of In in calibration, g.

3261.85 = ΔH^o_{fus} In metal, joule mol^{-1}

114.82 = atomic weight In.

Peak areas are measured using a planimeter.

F. Measurement of enthalpies of vaporisation.

The two methods most frequently used are the direct calorimetric method, in which the amount of electrical energy needed to vaporise isothermally a measured quantity of a liquid is determined, and the indirect vapour-pressure method using a tensimeter. The latter method was used in this work and the standard heats of vaporisation of meta-tolyldichloroborane, mesityldichloroborane and tri(tertiary-butylperoxy)borane were derived from vapour-pressure measurements.

The apparatus (Figure 1.3) consisted of a strain-gauge (Bell and Howell, type 4-366 general purpose pressure transducer, Serial No. L34035) incorporated into a glass tube equipped with a greaseless joint for connexion to a vacuum line. The strain-gauge was sealed into the apparatus using 'Torrseal' resin (Varian Ltd.). The nominal 40 mV full range output (0 - ca. 500 Torr) was amplified to ca. 10V, giving 0.015V per Torr. The voltage was registered on a digital voltmeter (Marconi Ltd., TF 2660) with a precision of ± 1mV. The apparatus was immersed to the level of the top of the transducer in an oil-thermostat bath operating over the temperature range 298 K - 363 K and the temperature coefficient of the transducer response was determined in the form of a voltage versus temperature graph after evacuating the tube to 10^{-4} Torr, (i.e. effectively zero pressure). The graph was used to reduce all pressure measurements to 298.15 K. The corrected voltage output from the transducer was calibrated in terms of pressure by using water as a standard substance.

The heats of vaporisation over the temperature range used were calculated from the integrated form of the Clausius-Clapeyron equation:

$$\log_{10}(P/\mathrm{Torr}) = -\frac{\Delta H_{vap.}}{2.303R} \cdot \frac{1}{T} + \mathrm{const.}$$

It follows from the form of the equation that a plot of log P versus $\frac{1}{T}$ should give a straight line of slope = $-\Delta H_{vap.}/2.303R$. The value obtained by the above method refers to the mean temperature of the range over which measurements were taken. These values were 'corrected' to 298.15 K using an empirical equation[27]:

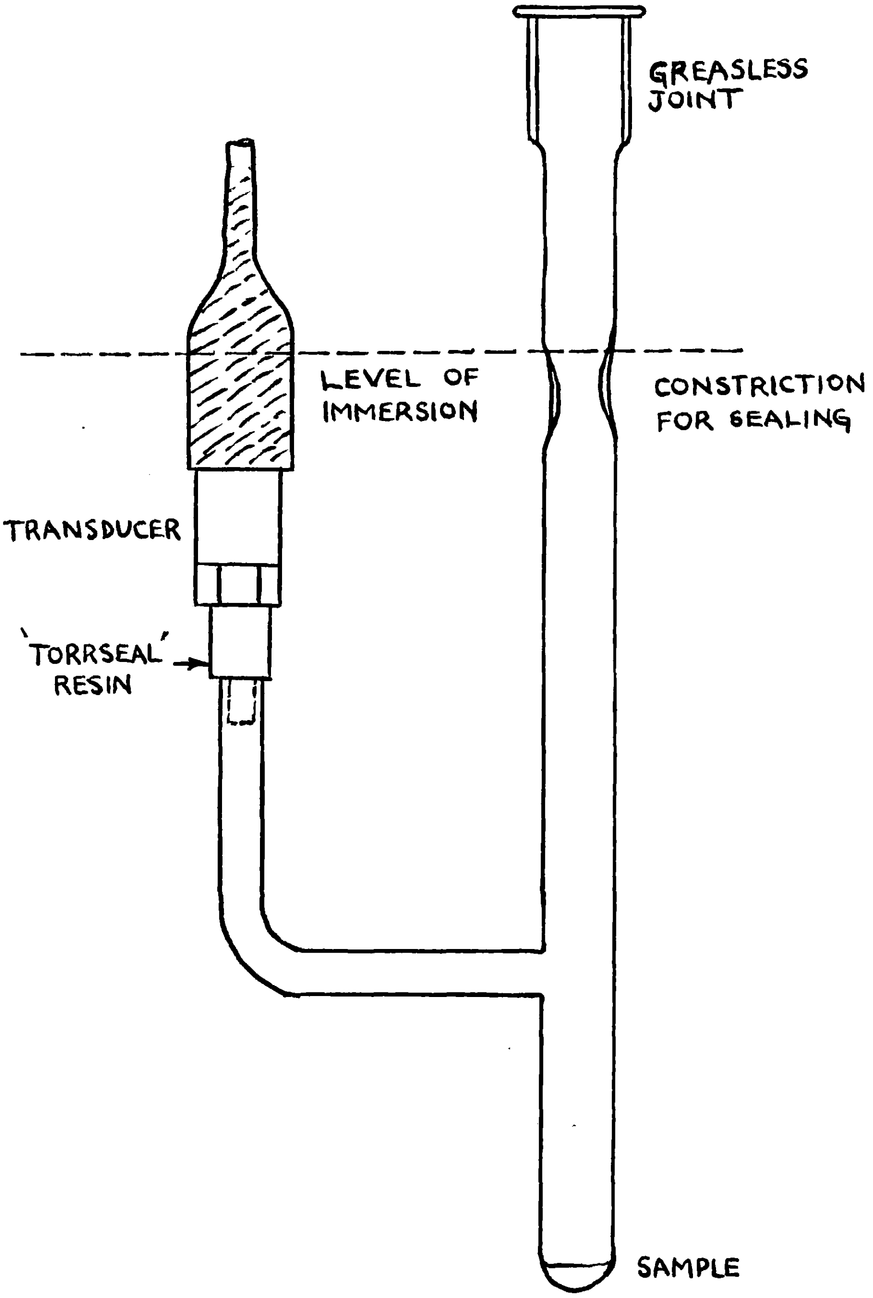

GREASLESS JOINT
LEVEL OF IMMERSION
CONSTRICTION FOR SEALING
TRANSDUCER
'TORRSEAL' RESIN
SAMPLE

figure 1.3

$$\frac{\Delta H_{\mathrm{vap.}}\ T/\mathrm{K}}{\Delta H_{\mathrm{vap.}}\ 298.15\ \mathrm{K}} = \left[\frac{1 - T/T_c}{1 - 298.15\ \mathrm{K}/T_c}\right]^{0.38}$$

where T/K = mean temperature

T_c/K = critical temperature.

The value of T_c for different compounds can be estimated.[28, 29] The boiling point temperature, which is required for this estimation, was obtained by extrapolation of the $\log_{10}(P/\mathrm{Torr})$ vs. $\frac{1}{T}$ graphs to 760 Torr vapour-pressure. The equations used to estimate T_c give values within 5% agreement of the experimental values.[29]

G. Purification of solvents and reagents.

I. Separation of t-butyl hydroperoxide from di t-butylperoxide in a commercial sample.

t is tertiary -

Commercial hydroperoxide (Koch-Light Co. Ltd.) contains ca. 30% di t-butylperoxide as an impurity. Fractional distillation under reduced pressure was used to separate the components.[30] An air fractionation-column (Quickfit, length 9 dm) was connected to a double-helix water-cooled condenser equipped with three collection flasks (100 cm³). Impure hydroperoxide (300 cm³), previously dried over molecular sieves, (4Å) was contained in a round-bottom flask connected to the column. The flask was heated carefully in a water-bath and the two fractions were collected under reduced pressure (Table 1.3). Complete separation was achieved under these conditions and 100% pure hydroperoxide was isolated.

TABLE 1.3

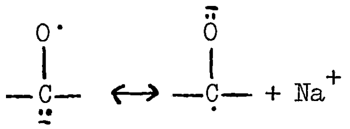
Separation of peroxides under reduced pressure

Peroxide	Water bath temperature/K	Distillation temperature/K	Pressure at manometer/Torr
di t-butylperoxide	337	311-321	50-35
t-butyl hydroperoxide	337	313	15

Ambient temperature = 295K

II. Dry tetrahydrofuran (THF) for Grignard reactions.[31]

Commercial THF (2000 cm^3, B.D.H. Chemicals Ltd) was refluxed over ca. 0.3 weight per cent of cuprous chloride for 0.5 h to destroy any peroxides, then distilled.[32] The solvent was transferred to a reflux apparatus connected to a dry-nitrogen supply and freshly cut pieces of sodium metal (ca. 10 g) and benzophenone (ca. 50 g) added. The solvent was gently refluxed until the whole of the solution became royal-blue coloured due to the benzophenone radical formed in the totally anhydrous solvent.



Anhydrous THF was distilled from the mixture and used immediately (peroxides will quickly build up in the absence of a stabiliser).

III. Dry chloroform.[33]

Chloroform (May & Baker Chemicals Ltd., containing ca. 1% ethyl alcohol) was shaken four times with an equal volume of distilled water in a separation funnel and then dried over anhydrous calcium chloride for 24 h. The purified solvent was finally dried over molecular sieves (4Å) for a further 24 h and stored in the dark.

IV. Nitrobenzene.

Nitrobenzene (Koch-Light Ltd.) was dried and stored over molecular sieves (4Å) and used without further treatment.

H. Handling of moisture sensitive compounds.

All of the materials studied in this work are highly moisture sensitive and had to be handled in an efficient 'dry-box'. Initial failure of some experiments with a final purified product was traced to manipulation in an insufficiently dry atmosphere and hence great care in ensuring high-efficiency in drying was subsequently taken. Many types of dry-boxes have been described in the literature.[34, 36] A 'Mecaplex' dry-box of perspex construction, was filled with nitrogen gas and desiccated using phosphorus pentoxide. An equilibrium value for the relative humidity of $<10\%$ was routinely achieved; the relative efficiency of P_2O_5 as a desiccant is shown in Table 1.4.

Samples of the compounds for analysis, calorimetry, D.S.C., tensimetry, Raman spectroscopy and proton resonance spectroscopy were loaded in the dry-box as detailed below. The various techniques are shown in Figure 1.4.

TABLE 1.4

Common desiccants with their approximate gas-drying efficiencies.[37]

Desiccant	Residual water (mg/1000 cm^3)
Efficient trap at 77 K	10^{-23}
CaH_2	$< 10^{-5}$
Efficient trap at 173 K	1×10^{-5}
P_2O_5	2×10^{-5}
$Mg(ClO_4)_2$	5×10^{-4}
Efficient trap at 195 K	5×10^{-4}
BaO	7×10^{-4}
Molecular sieves	0.001
Silica gel; active Al_2O_3; KOH	$\approx$ 0.002
$CaSO_4$	0.005
CaO; 96% H_2SO_4	$\approx$ 0.01
$CaCl_2$	$\approx$ 0.2

Analysis

(a) Solids which were to be analysed by volumetric estimation of a hydrolysate were transferred to a polythene sample tube equipped with a tight fitting cap. After re-weighing, the cap was almost removed from the tube such that subsequent shaking in a flask with the reagent would dislodge it completely.

(b) Liquids were transferred to a calorimeter ampoule using a small glass pipette and the ampoule sealed with a lightly greased cone of the appropriate size. Reaction was initiated by fracturing the ampoule bulbs under the reagent solution.

Calorimetry

(a) Solids were loaded into an ampoule using a small glass-funnel and care was taken to ensure that no solid was deposited above the top fracture-bulb.

(b) Liquids were loaded using a 'Agla' glass-needle attached to a Luer-fitting syringe. Again no liquid was deposited above the upper fracture-bulb.

D.S.C.

Untreated aluminium D.S.C. sample pans (Volatile sample pan, part No. 219 - 0062) were loaded using an 'Agla' glass-needle (compound heated above transition) and the lids were secured in the dry-box using a special press.

Tensimetry

The tensimeter was evacuated to ca. 10^{-3} Torr and filled with dry nitrogen. The arm of the tensimeter was stoppered using a greaseless cone sealed at one end, and the tensimeter transferred to the dry-box. The stopper was removed and the apparatus allowed to finally dry for at least 0.5 h before loading.

Raman samples

Raman sample tubes made from capillary tubes sealed at one end were dried in an oven at 393 K and cooled in a desiccator. The tubes were left in the dry-box for several hours before loading.

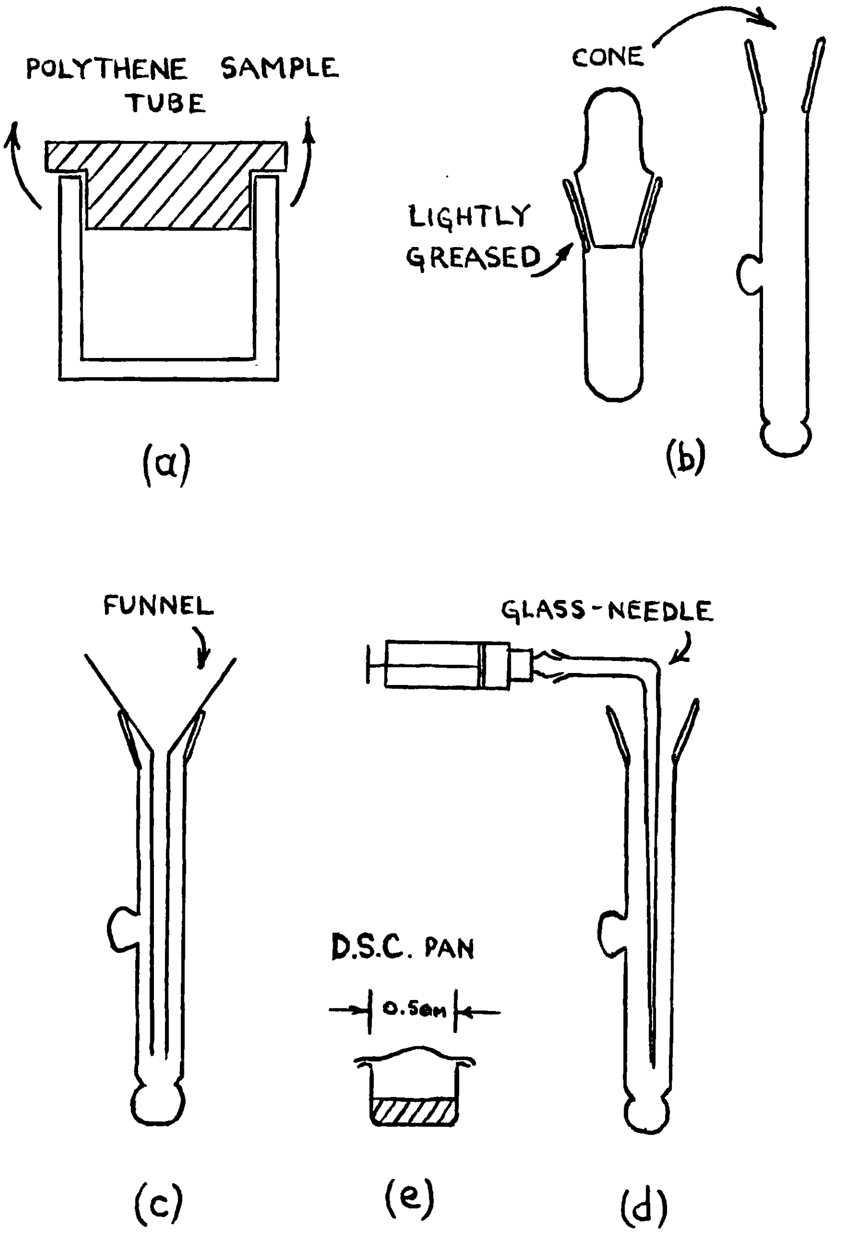

POLYTHENE SAMPLE TUBE
CONE
LIGHTLY GREASED
(a)
(b)
FUNNEL
GLASS-NEEDLE
D.S.C. PAN
0.5cm
(c)
(e)
(d)

figure 1.4

^{1}H N.M.R. samples

Standard N.M.R. tubes were dried in an oven at 393 K, cooled and desiccated in the dry-box for 0.5 h before filling.

I. Autoclave reactions.

A high-pressure reaction bomb (A Parr-High pressure Autoclave, Series 4652, 500 cm^3 capacity) was used for the synthesis of rubidium and caesium tetrachloroborates. The reagents (BCl_3, alkali-metal chloride and nitrobenzene) were contained in a spherical borosilicate glass ampoule (nominal capacity 80 cm^3) equipped with a neck for sealing. A pressure-equalising fluid was used in the autoclave; iso-pentane was selected for this reaction from vapour-pressure data.[38] A neoprene-rubber 'O' ring was used to replace the Nimonic alloy ring supplied with the apparatus since the metal seal was found to leak considerably at 363 K.

A procedure (employing the same principle as above) for high-pressure temperature (573 K) reactions with PCl_5 in glass-ampoules but using nitrogen-gas as the pressure equaliser has been reported.[39]

CHAPTER II

Synthesis and Analysis of Compounds

I. Tri(tertiary-butylperoxy)borane.

II. Tolyldichloroboranes.

III. Rubidium and caesium tetrachloroborates.

I. Tri(tertiary-butylperoxy)borane.

The compound was prepared in good yield by the reaction of boron trichloride and tertiary-butyl hydroperoxide[40]:

$$3\text{t-BuOOH} + \text{BCl}_3 \xrightarrow[298\ \text{K}]{\text{n-pentane}} (\text{t-BuOO})_3\text{B} + 3\text{HCl} \qquad \ldots \qquad (2.1)$$

where t-Bu is tertiary-butyl. The apparatus used[40] is shown in Figure 2.1. The usual precautions were taken in handling peroxides.[41]

Procedure.

The apparatus was connected at B to a vacuum line provided with a tap to a dry-nitrogen supply. Purified hydroperoxide (16 g) with an equal volume of pentane (reagent grade) was placed in the apparatus at A, cooled to 273 K and stirred using a magnetic-follower (polytetrafluoroethylene). The cold finger (at position C) was charged with solid carbon-dioxide/acetone mixture and BCl_3 (7.0 g) was allowed to distil into the reaction mixture through tap D.

The contents of A were allowed to warm to ca. 298 K and stirred for 2 h, after which the refigerant in the cold-finger was removed. Pentane and any residual hydroperoxide were removed from the reaction product at 1 Torr pressure and finally at 10^{-1} Torr pressure.

The cold finger was then placed in position F, and the product distilled into the receiver G at 10^{-4} Torr from a bath at ca. 343 K. The distilled material (m.p. 285 - 288 K) was recrystallied from pentane at 193 K three times in a dry-box. Purified samples were stored at room temperature under dry nitrogen.

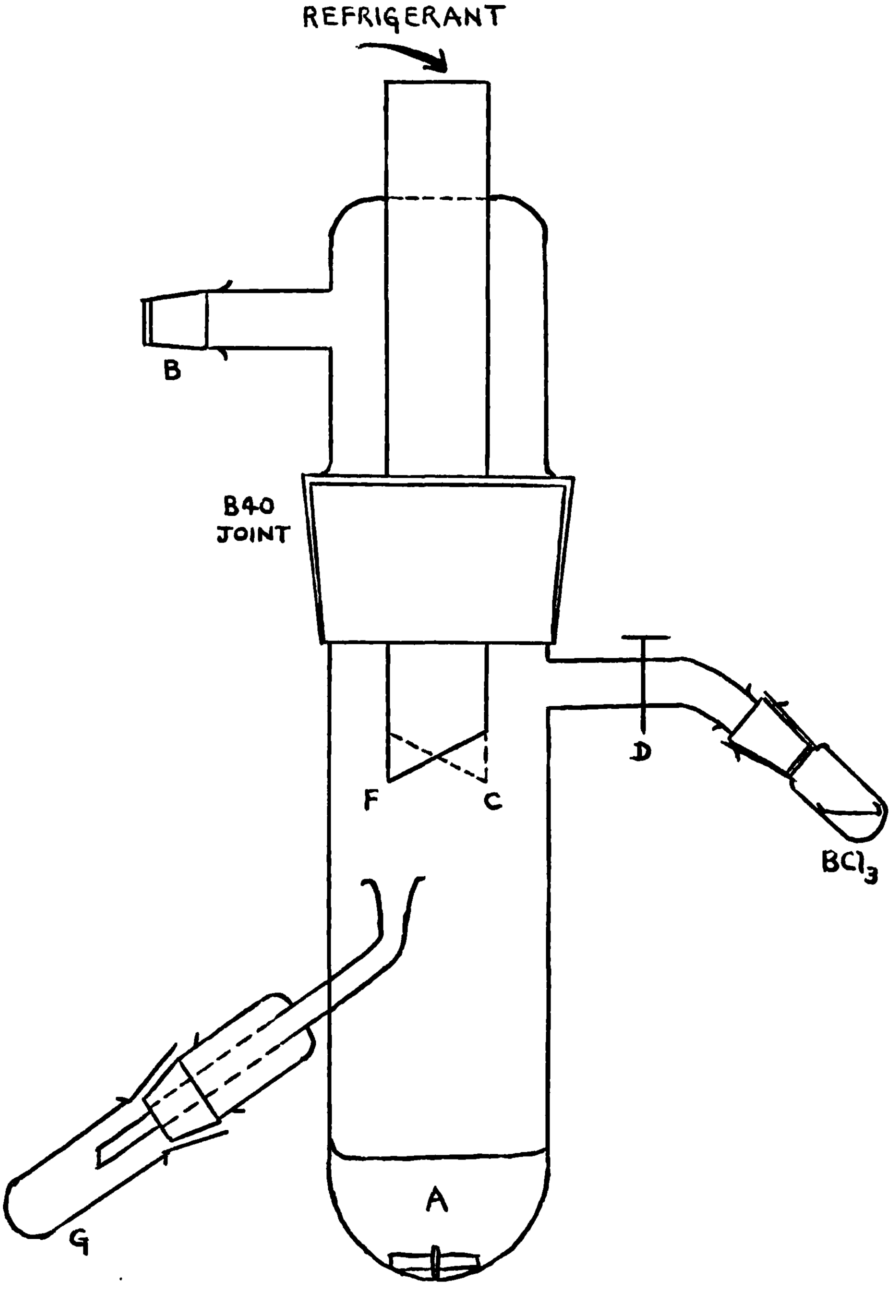


figure 2.1

Analysis

$(t\text{-BuOO})_3B$ reacts quantitatively with water to produce orthoboric acid and the parent alkyl hydroperoxide[42]:

$$(t\text{-BuOO})_3 + 3H_2O \longrightarrow 3t\text{-BuOOH} + B(OH)_3 \qquad \ldots \qquad (2.2)$$

A suitable volumetric technique for the determination of alkyl hydroperoxides involves reduction of the peroxide by ferrous ion in acid aqueous solution[43]:

$$t\text{-BuOOH} + Fe^{2+} \xrightarrow[\text{solution}]{\text{acid}} t\text{-BuO}^{\bullet} + Fe^{3+} + OH^{-} \qquad \ldots \qquad (2.3)$$

In this method, excess standard Fe^{2+} solution is run into an aqueous solution of the hydroperoxide; the excess of ferrous-ion is then determined with standard potassium permanganate solution. The t-butoxy radical generated in the initial oxidation process can react by two different routes:

$$t\text{-BuO}^{\bullet} + Fe^{2+} + H^{+} \longrightarrow t\text{-BuOH} + Fe^{3+} \qquad \ldots \qquad (2.4)$$

and $$t\text{-BuO}^{\bullet} \longrightarrow (CH_3)_2CO + CH_3^{\bullet} \qquad \ldots \qquad (2.5)$$

When ferrous-ion solution is run into a solution of the hydroperoxide, reaction (2.4) is inhibited as the hydroperoxide is in excess and the radical produced in (2.3) disproportionates as shown (2.5).[44]
A stoichiometry of hydroperoxide to ferrous-ion of exactly 1:1 is observed under these conditions.

Boron was titrated as boric acid in the presence of mannitol using a standard volumetric procedure[45]; no explanation for the slightly high results was found. The analytical results are shown in Table 2.1.

TABLE 2.1

Analysis of tri(tertiary-butylperoxy)borane

Determination	Batch	% required	% found
Peroxidic oxygen	A	34.5	34.6
	B	34.5	34.5_5
	C	34.5	34.5
Boron content	A	3.90	4.05
	B	3.90	4.08
	C	3.90	4.20

II. Tolyldichloroboranes.

The aryldichloroboranes were synthesised by established procedures[46,47,48] according to the reactions (2.6) and (2.7):

$$\mathrm{ArBr} \xrightarrow{\mathrm{Mg/THF}} \mathrm{ArMgBr} \xrightarrow[\text{reflux}]{\mathrm{HgCl_2THF}} \mathrm{ArHgCl} \qquad \ldots \qquad (2.6)$$

$$\mathrm{ArHgCl} \xrightarrow[\text{reflux}]{\mathrm{BCl_3/benzene}} \mathrm{ArBCl_2} \qquad \ldots \qquad (2.7)$$

where Ar is ortho-tolyl, meta-tolyl, para-tolyl and mesityl.

Typical procedure

The arylhalide (0.5 mole) and magnesium (0.5 mole) were reacted together in a conventional Grignard type apparatus in THF (1.5 mole); no initiator was required. The solution of the arylmagnesium halide was then diluted to 500 cm^3 using THF.

$HgCl_2$ (0.5 mole) was dissolved in THF (400 cm^3) contained in a 2000 cm^3 flask (3-neck, round-bottom) fitted with a mechanical stirrer, a reflux condenser and a dropping funnel. The stirring was started and the mercuric chloride dissolved to give a clear solution; the arylmagnesium halide solution (0.5 mole/500 cm^3 THF) was then added dropwise. The mixture was allowed to reflux by the heat of the reaction and following the addition of all the reagent was stirred for a further 0.5 h and left to stand overnight.

The precipitate formed during the reaction was filtered and washed with THF; the filtrate, combined with washings, was evaporated on a water bath to leave a white solid. The solid was treated with 1 mol dm^{-3}HCl (700 cm^3) and the crude material collected in a No. 1 sintered glass funnel. The material was washed with dilute HCl and crystallised from THF. White crystals of the pure compound were dried at 353 K.

The dry arylmercuric chloride (0.5 mole), dry benzene (150 cm^3) and BCl_3 (0.5 mole) were mixed in a 250 cm^3 flask equipped with a 'cold-finger' condenser and a dry-nitrogen supply. The condenser was charged with solid carbon-dioxide/acetone mixture and the contents of the flask were gently refluxed for 4 h. Mercuric chloride produced during the reaction was filtered in a No. 1 sinter and the filtrate returned to a single-neck 250 cm flask. Benzene was evaporated from the product at 10 Torr pressure and the aryldichloroborane was fractionally distilled and collected in a 50 cm^3 flask. Boiling point data are collected in Table 2.2.

TABLE 2.2

Fractional distillation of aryldichloroboranes

Ar in $ArBCl_2$	Preparative b.p.	Literature b.p.
ortho-tolyl	362 K/10 Torr	361-364 K/10 Torr[47]
meta-tolyl	342-344 K/9 Torr	359-361 K/15 Torr[47]
para-tolyl	363 K/10 Torr	365 K/10 Torr[47]
mesityl	347/6 Torr	———

During the synthesis of the ortho-isomer contamination by meta-isomer from an isomerisation reaction has been noted.[49] Hence the isomeric purity of the samples was checked using proton magnetic resonance spectroscopy. Comparison of the intensity of the signal from the meta-isomer methyl protons (δ = 2.15 ppm) with the intensities of the signals from the ^{13}C satellites from the ortho-isomer methyl protons (δ = 2.44 ppm) revealed that the concentration of the meta-isomer in the ortho-isomer sample to be less than 0.5 mass per cent. No isomeric contamination could be detected in the sample of the para-isomer. The isomeric purity of the ortho-isomer was checked after calorimetry and no significant increase in impurity was found.

Analysis

Analysis for chloride[50] on hydrolysis and for boron[45] were by conventional procedures (Table 2.3).

TABLE 2.3

Analysis of tolyldichloroboranes

Ar in $ArBCl_2$	Chlorine % Required	Found	Boron % Required	Found
ortho-tolyl	41.02	41.1	6.25	6.25
meta-tolyl	41.02	40.8	6.25	6.26
para-tolyl	41.02	40.6	6.25	6.26
mesityl	35.29	35.4	5.38	5.35

III. Rubidium and caesium tetrachloroborates.

These compounds were prepared by reacting boron trichloride and the appropriate alkali-metal chloride in nitrobenzene under pressure[51]:

$$MCl(solution) + C_6H_5NO_2{\cdot}BCl_3 \rightleftharpoons MBCl_4 + C_6H_5NO_2 \quad \ldots \quad (2.8)$$

where M is Rb or Cs. The use of an autoclave is described in Chapter I, section I.

Procedure

Caesium chloride, 6.0 g (or rubidium chloride, 4.0 g) was loaded into a dry ampoule with nitrobenzene (50 cm^3) under dry-box conditions. The contents of the ampoule were cooled to 193 K and BCl_3 (20 cm^3) at 193 K added. The ampoule was sealed and allowed to warm to room temperature gradually. The autoclave was charged with the ampoule and iso-pentane (100 cm^3) then heated to 363 K for 4 h. After reaction the ampoule was cooled to 193 K before opening.

The contents of the ampoule were transferred to a conical flask using nitrobenzene (50 cm^3) under dry-box conditions and any insoluble material allowed to settle. The supernatant liquid was carefully decanted into a 1000 cm^3 conical flask containing dry chloroform (ca. 500 cm^3). The precipitated tetrachloroborate was allowed to settle and then collected on a No. 3 sinter. The isolated product was washed three times with portions of chloroform (20 cm^3) and vacuum dried at 20 Torr for 0.5 h (298 K).

The impure product was transferred to a conical flask containing nitrobenzene (100 cm^3) and BCl_3 (15 cm^3). Nitrobenzene was added in 50 cm^3 portions, shaking the flask between additions, until the whole of the tetrachloroborate had dissolved. The solution was allowed to stand for at least 1 h and the supernatant decanted from any insoluble material. The product was again precipitated by the addition of chloroform and collected on a No. 3 sinter. The purified material was washed several times with portions of chloroform (10 cm^3) to give a pure white product and finally vacuum dried on the sinter at 10^{-3} Torr for 2 h (308 K). The dry tetrachloroborate was stored under nitrogen on the sinter and all subsequent sampling of the product was made in a dry-box.

Analysis

The presence of the BCl_4^- group in each compound was confirmed from the observed vibrational frequencies in the Raman spectrum.[52]

Alkali-metal content: The gravimetric method using sodium tetraphenylboron as reagent was used.[53]

Total chloride content: The conventional Volhard method was used to determine the chloride content of a hydrolysed sample of the tetrachloroborate.[50]

Combined HCl and boron determination: The compounds hydrolyse according to the following equation:

$$MBCl_4 + 3H_2O \longrightarrow MCl + B(OH)_3 + 3HCl \qquad \ldots \qquad (2.9)$$

Hence, exactly 0.75 of the chlorine content as hydrochloric acid can be determined by titration with 0.1 mol dm^{-3} NaOH and similarly boron can be titrated as a strong monobasic acid after the addition of mannitol.[45] A temperature compensated Ingold electrode was used for the determination; standardisation to pH = 7.0 and 4.0 was made using buffer solutions.

The analytical results are collected in Table 2.4.

TABLE 2.4

Analysis of rubidium and caesium tetrachloroborates

Determination	% required	% found	purity (%)
$RbBCl_4$			
Rubidium content	35.90	35.95 : 36.02	100.2
Total chloride	59.56	59.50	99.9
Chloride via HCl	59.56	59.40	99.7
Boron content	4.54	4.55	100.13
Overall purity			100.0
$CsBCl_4$			
Caesium content	46.55	46.58 : 46.60	100.06
Total chloride	49.66	49.52	99.8
Chloride via HCl	49.66	49.63	99.9
Boron content	3.786	3.78	99.9
Overall purity			99.9

Although the above values would also be obtained for a mixture ($MCl + BCl_3$), the following evidence strongly supports the conclusion that the product contains the BCl_4^- anion.

(i) the vibrational frequencies noted for BCl_4^- in the Raman spectrum are very much different from those for BCl_3.[54]

(ii) the vapour-pressure of a mixture containing BCl_3 would be reasonably high (b.p. BCl_3, 28 K/760 Torr) and consequently during the final drying stage (10^{-4} Torr/308 K for 2 h) some loss of BCl_3 would be expected. The compound would therefore be deficient in both chlorine and boron.

Density determination: The density of each compound was determined in dry carbon tetrachloride at 298 K using a conventional specific gravity bottle. These densities are required for buoyancy corrections in calorimetric experiments. The results were $RbBCl_4(c) = 2.40$ g/cm^3 and $CsBCl_4(c) = 2.68$ g/cm^3.

CHAPTER III

The Thermochemistry of Tri(t-butylperoxy)borane and the Role of Organoperoxyboranes in Hydrocarbon Oxidation

Introduction

Experimental Results

Results

Discussion

Introduction

The action of boric acid to favour alcohol formation in the air-oxidation of hydrocarbons $[C_6 - C_{16}]$ has been known for many years, the earliest patent application date being 1928.[55] Hydrocarbon oxidation in the presence of boron compounds is a complex process sensitive to changes in many reaction variables. The standard procedure consists of passing air or dilute oxygen in a nitrogen stream through a suspension of boric acid in the heated substrate (438 - 448K).[56] The alcohol:ketone ratio is increased on addition of boric acid from 1-1.5, as is normally obtained, to 5-10 for many hydrocarbons.

Boron compounds are unique is this context in that it is the only element which directs the reaction successfully to increased alcoholic yields.[57] Although silicic and antimonic acids enhance the yields of alcohols during paraffin hydrocarbon autoxidations, they are less efficacious than are boron compounds (e.g. boric acid, metaboric acid, or pyroboric acid).[57] Considerable data are at hand to show that the presence of boron compounds does not change the essential free-radical chain reaction character of alkane autoxidations.[58] Induction periods are observed with and without boron present and the reaction is autocatalytic under both conditions.[59]

Various proposals[60] as to the role of boron compounds have been made and the most important of these are:-

(a) boron compounds (e.g. metaboric acid) serve to esterify the produced alcohol, ROH.

(b) the $>$ BOH group serves as a hydrogen atom source in the abstraction process $>\mathrm{BOH} + \mathrm{RO_2}^{\bullet} \longrightarrow\ >\mathrm{B{-}O}^{\bullet} + \mathrm{ROOH}$.

(c) boron compounds react with hydroperoxide formed during the oxidation to produce alcohol:

$$3ROOH + B(OR')_3 \rightleftharpoons B(OOR)_3 + 3R'OH.$$

(d) Peroxyboranes are formed as intermediates leading directly to the production of free alcohol or possibly directly to a boric acid ester, $(OBOR)_3$.

The question of the inclusion of peroxyboranes in the reaction sequence is of importance and has been suggested by several workers. It has been inferred that alkyl peroxyborates are the chief intermediates in alkane autoxidations and that they subsequently give rise to the boron compound ester.[61] Further, it has been proposed that the direct interaction of alkylperoxy radicals with the boron coreactant accounts for the inhibitory effect of boron compounds in hydrocarbon oxidations.[58] There is also evidence to show that orthoboric acid, metaboric acid and their esters catalyse the decomposition of hydroperoxides; the decomposition is directed towards alcohol formation, thereby possibly accounting for the enthanced selectivity in hydrocarbon oxidations in the presence of boric acid.[62] The question arises as to whether these reactions proceed to give a peroxyborane species with liberation of alcohol. It has been established that other acids such as dodecane dicarboxylic acid, arsenious oxide, trichloroacetic acid, phthalic anhydride and P_2O_5 do not direct the decomposition of hydroperoxides towards alcoholic products.[63] Apparently the Lewis acidity of trigonal boron uniquely allows boric acid and its esters to alter the normal course of the oxidation of many saturated aliphatic and alicyclic materials.

The feasibility of many of the proposed intermediates and reaction schemes would be clarified if thermodynamic data for compounds containing the organoperoxyborane grouping were available. Compounds selected for thermodynamic study should ideally exhibit the following properties:

(a) be easily purified

(b) be stable over a reasonable temperature range to allow $\Delta H^o_{vap.}$ to be measured and

(c) have a suitable quantitative chemical reaction at 298 K for calorimetry (and available ΔH^o_f ancillary data).

Of the organoperoxyboranes synthesised to date[64] only tri-t-butyl peroxyborane and tri-n-butylperoxyborane satisfy the above conditions. Tri-t-butylperoxyborane was selected and studied in detail. The standard heat of formation of t-BuOOH, (l) (produced in the calorimetric hydrolysis reaction) is in dispute, two different combustion calorimetry values having been reported in the literature. (Details in Appendix III).

It was therefore necessary to measure $\Delta H^o_f[\text{t-BuOOH, l}]$ independently and this was achieved using solution reaction calorimetry.

Experimental Results

I. Calorimetric results

(a) tri-t-butylperoxyborane, (l)

The aqueous hydrolysis of this peroxy compound proceeds rapidly and completely liberating the corresponding alkyl hydroperoxide.[65]

$$(\text{t-BuOO})_3\text{B,l} + (\text{N}+3)\text{H}_2\text{O,l} \twoheadrightarrow [3\text{t-BuOOH}+\text{B(OH)}_3]\text{N.H}_2\text{O(aq)}\ \ \Delta H, \quad \ldots \quad (3.1)$$

and the standard heat of formation is calculated from the equation:

$$\Delta H^o_f[(\text{t-BuOO})_3\text{B,l}] = 3.\Delta H^o_f[\text{t-BuOOH,NH}_2\text{O}] + \Delta H^o_f[\text{B(OH)}_3\text{,NH}_2\text{O}] - 3\Delta H^o_f[\text{H}_2\text{O,l}] \ -\Delta H \quad \ldots \quad (3.2)$$

Table 3.1 lists the results obtained for the hydrolysis of $(\text{t-BuOO})_3\text{B,l}$.

Table 3.1

Heats of hydrolysis of tri-t-butylperoxyborane, reaction 3.1

N	$-\Delta H$ /kJ mol^{-1}
2983	58.16
3483	58.99
2746	58.99
2344	58.99
3090	58.58
3069	58.99
2993	58.16
3243	58.16
3012	58.55
$<-\Delta H>$ =	58.58 ± 0.4

(b) t-butyl hydroperoxide, l. The calorimetric equations are described in Appendix III.

Table 3.2

Heat of reaction of t-BuOOH,(l) in 0.9 mol dm^{-3} ammonium ferrous sulphate solution, reactions 2.3 - 2.5

N	$-\Delta H$ /kJ mol^{-1}
17094	226.98
10384	225.94
9496	227.19
10582	226.77
$<-\Delta H>$ =	226.77 ± 1.26

Table 3.3

Ferric iron analyses of post-reaction solutions (from reactions in Table 3.2)

Weight t-BuOOH/g	% yield Fe^{3+}, based on a 2.0:1.0 ratio of Fe^{3+} to ROOH (Equations 2.3 - 2.5)
0.0587	92.1
0.0967	92.3
0.1061	92.0

The heat of solution of the hydroperoxide in aqueous orthoboric acid was determined; the final molar ratio of $B(OH)_3$ to ROOH was 3:1.

Table 3.4

Heat of solution of t-BuOOH(l) in aqueous orthoboric acid

N	$-\Delta H$ (kJ mol^{-1})
1038	9.54
1010	9.50
1028	9.46
1021	9.62
1010	9.50
984	9.54
972	9.46
990	9.54
$\langle -\Delta H \rangle$ =	9.52 ± 0.04

II. Tensimetry (Chapter I, F)

The heat of vaporisation of water was calculated from the calibration graph and the result was found to be in satisfactory agreement with literature values. $\Delta H^{o}_{vap} = 44.14 \pm 0.4$ kJ mol^{-1}; lit. value = 43.88 kJ mol^{-1}. The results for the peroxyborane are set out in Table 3.5.

Table 3.5

Vapour-pressure measurements for $(t\text{-BuOO})_3B$,(l)

Temperature/K	Reading/V	Correction/V	Corrected/V reading	Pressure/Torr
328.15	−0.230	+0.280	+0.050	28.4
338.15	+0.612	+0.378	+0.990	70.8
343.15	+1.213	+0.410	+1.623	111.5
346.15	+1.883	+0.440	+2.323	148.5

Results

I. Standard heats of formation

The following standard heats of formation were calculated using the appropriate ΔH value and the ancillary data in Table 3.6.

(a) $\Delta H^{o}_{f}[(t\text{-BuOO})_3B,l] = -1066.1 \pm 5.0$ kJ mol^{-1}

(b) $\Delta H^{o}_{f}[(t\text{-BuOO})_3B,g] = -974.0 \pm 5.7$ kJ mol^{-1} (from (d) below)

(c) $\Delta H^{o}_{f}[t\text{-BuOOH},l] = -293.3 \pm 4.1$ kJ mol^{-1} (Appendix III)

(d) The enthalpy of vaporisation of $(t\text{-BuOO})_3B$,l (92.1 ± 2.1 kJ mol^{-1}) was calculated from the experimental data in Table 3.5. These data are represented in the form $\log_{10}P/\text{Torr} = a - \frac{b}{T/K}$ where a (= 15.18) and b (= 4.508×10^{-3}) were obtained from a least-squares analysis.

Table 3.6

Ancillary thermochemical data

Compound (state)	$-\Delta H_f^o$/kJ mol^{-1}
H_2O (l)	285.83 ± 0.008^{67}
$B(OH)_3$, $3090H_2O$, aq.	1072.40^{68}
t-BuOOH(l)	293.72 ± 5.0^{69}
t-BuOOH, $1000H_2O$, aq.	303.21 ± 5.0 ^{69} and this work
OH^-, aq. molality=1	230.0^{68}
Fe^{2+}, aq. molality=1	89.12^{68}
Fe^{3+}, aq. molality=1	48.53^{68}
t-BuOH, (l)	359.20 ± 0.8^{70}
t-BuOH, $8188H_2O$, aq.	376.52 ± 0.8^{71}
$(CH_3)_2CO$ (l)	248.0^{72}
$(CH_3)_2CO$, $10000H_2O$, aq.	260.5^{72}
C_2H_6(g)	84.7^{72}

II. Bond-energy terms

(a) E(BO-OR) in t-butyl peroxyborane

The calculation utilises the following hypothetical dissociation:

$$(n\text{-BuO})_3B, g \longrightarrow B(O^\bullet)_3, g + 3.n\text{-Bu}^\bullet, g$$

This permits ΔH_f^o $B(O^\bullet)_3$ to be calculated from:

$$\Delta H = \Delta H_f^o[B(O^\bullet)_3 g] + 3\Delta H_f^o[n\text{-Bu}, g] - \Delta H_f^o[(n\text{-BuO})_3B g]$$

Assuming $\Delta H = 3.D(\text{n-Bu-OH})$ and using $D(\text{n-Bu-OH}) = 380.7 \pm 8.4$,[73] $\Delta H_f^o[\text{n-Bu}^\bullet,g] = 71.1 \pm 8.4$[73] and $\Delta H_f^o[(\text{n-BuO})_3B,g]$, (= -1145.2 ± 2.5[72]) $\Delta H_f^o[B(O^\bullet)_3,g]$ is calculated to be -216.3 kJ mol^{-1}.

Inserting this figure into the thermochemical equation for the corresponding peroxyborane dissociation:

$$(\text{t-BuOO})_3B,g \longrightarrow B(O^\bullet)_3,g + 3.\text{t-BuO}^\bullet,g$$

and using $\Delta H_f^o[\text{t-BuO}^\bullet, g] = -90.37$[74], $\Delta H_f^o[\text{peroxyborane}, g]$, we have $E(\text{BO-OR}) = 162.3 \pm 12$ kJ mol^{-1}.

(b) E(B-OOR) in t-butyl peroxyborane

The following equation was used:

$(\text{t-BuOO})_3B,g \longrightarrow B,g + 3\text{t-BuOO}^\bullet, g$, where $\Delta H = 3.E(\text{B-OOR})$.
Using $\Delta H_f^o[B,g] = 555.6 \pm 16.7$,[17] $\Delta H_f^o[\text{t-BuOO}^\bullet,g] = -80.3 \pm 8.3$[74] and $\Delta H_f^o[\text{peroxyborane}, g]$, E(B-OOR) was calculated to be 429.3 ± 19 kJ mol^{-1}. The high error is due mainly to the uncertainty in $\Delta H_f^o[B,g]$.

The corresponding data for the normal-butyl derivative was estimated using Benson's group additivity scheme[75] (Appendix I for details) for $\Delta H_f^o[(\text{n-BuOO})_3\,B,g]$ as follows:

The t-BuO group was calculated from:

$$\begin{array}{lcr} 3C(H_3)(C) & = & -126.5 \\ C(O)(C_3) & = & -27.6 \\ O(O)(C) & = & -18.8 \\ \hline & & -172.9 \end{array}$$

The unique group, O(O)(B) can be calculated using the measured value of $\Delta H_f^o[(\text{t-BuOO})_3B,g]$ thus:

$$3.O(O)(B) = \Delta H_f^o[(\text{t-BuOO})_3B,g] - 3.\Delta H_f^o[\text{t-BuOO},g] = -455.2 \text{ kJ mol}^{-1}$$

The normal -BuO group was calculated using the scheme:

$C(H_3)(C) = -42.2$
$2.C(H_2)(C_2) = -41.2$
$C(H_2(C)(O) = -33.5$
$O(O)(C) = -18.8$

-135.7

therefore, the required standard heat of formation can be calculated from:

$$\Delta H_f^o[(n\text{-BuOO})_3B,g] = 3.\Delta H_f^o[n\text{-BuO},g] + 3\Delta H_f^o O(O)(B)$$

$$= -862.3 \pm 9 \text{ kJ mol}^{-1}$$

(c) E(BO-OR) in n-butyl peroxyborane

The following hypothetical dissociation was used:

$$(n\text{-BuOO})_3\ B,g \longrightarrow B(O^{\bullet})_3,g + 3.n\text{-BuO}^{\bullet},g$$

therefore $3E(BO\text{-}OR) = \Delta H = \Delta H_f^o[B(O^{\bullet})_3,g] + 3H_f^o[n\text{-BuO}^{\bullet},g]-\Delta H_f^o[(n\text{-BuOO})_3B,g]$

Using the estimated value of ΔH_f^o[peroxyborane,g] above and $\Delta H_f^o[n\text{-BuO}^{\bullet},g]$ = -55.7, E(BO-OR) = 159.4 ± 14 kJ mol^{-1}.

(d) E(B-OOR) in n-butyl peroxyborane

This calculation requires $\Delta H_f^o[n\text{-BuOO}^{\bullet},g]$ which is itself derived from $\Delta H_f^o[n\text{-BuOOH},g]$; accordingly these values were calculated using the group additivity scheme.

$\Delta H_f^o[n\text{-BuOOH},g] = 1.n\text{-BuO group} + O(H)(O) = -203.7 \pm 4 \text{ kJ mol}^{-1}$
$(O(H)(O) = -68.07$[75]$\text{kJ mol}^{-1})$

Considering the dissociation: $n\text{-BuOOH} \longrightarrow n\text{-BuOO}^{\bullet} + H^{\bullet}$, it is assumed that $D(ROO\text{-}H) = D(HOO\text{-}H)$[76] $= 376.6 \pm 8 \text{ kJ mol}^{-1}$.

Therefore: $\Delta H = \Delta H_f^o[n\text{-BuOO}^{\bullet},g] + \Delta H_f^o[H^{\bullet},g] - \Delta H_f^o[n\text{-BuOOH},g]$

$\Delta H_f^o\ [n\text{-BuOO}^{\bullet},g]$ was calculated to be -44.8 kJ mol^{-1}

Hence $3.E(B{-}OR) = \Delta H = \Delta H^o_f(B,g] + 3.\Delta H^o_f[n\text{-}BuOO^{\bullet},g] - \Delta H^o_f[(n\text{-}BuOO)_3B,g]$

$E(B{-}OOR) = 436.0 \pm 20$ kJ mol^{-1}. Again the high error is principally due to the $\Delta H^o_f[B,g]$ uncertainty. The results of the bond-energy calculations are presented in Table 3.9 (Discussion).

The various standard heats of formation determined are collected below in Table 3.7.

Table 3.7

Heats of formation of some peroxyboranes and hydroperoxides

Compound	ΔH^o_f (l)/kJ mol^{-1}	ΔH^o(l→ g)/kJ mol^{-1}	ΔH^o_f(g)/kJ mol^{-1}
t-butyl peroxyborane	-1066.1±5.0	92.1±2.1	-974.0±5.4 (Exper.)
n-butyl peroxyborane	-	-	-862.3±9 (Calc.)
t-butyl hydroperoxide	-293.3±4.1	47.74±0.16[69]	-245.6±4.2 (Exper.)
n-butyl hydroperoxide	-	-	-203.7±4 (Calc.)

The difference in the thermodynamic stability of the normal- and tertiary-butylperoxyboranes and hydroperoxides, measured in terms of ΔH^o_f, conforms to a trend noted in other normal-butyl and tertiary-butyl isomers (Table 3.8).

Table 3.8

ΔH_f^o values for n-butyl and t-butyl isomers of some organic compounds[72]

Compound(g)	$-\Delta H_f^o$/kJ mol^{-1}
t-butanol	312.5
n-butanol	275.3
di-t-butyl ether	364.4
di-n-butyl ether	333.9
t-butylamine	120.9
n-butylamine	95.0

Discussion

Although a large body of experimental information is available on saturated hydrocarbon autoxidation in the absence of boron compounds, relatively little has been done towards mechanism elucidation of oxidations with boron coreactants/catalysts present. However, various workers have reported their experimental findings of the characteristics of alkane oxidation in the presence of boric acid[60] and these are listed below:-

(i) Autoxidation is a free-radical chain reaction having zero-order overall kinetics.

(ii) Boron compounds inhibit the overall reaction rate.

(iii) Hydroperoxide levels during autoxidation are lower in the presence of boron compounds than in their absence.

(iv) The hydrocarbon skeletal structure is preserved in the product alcohol i.e. RH $\longrightarrow$ ROH.

(v) The relative reactivity of various positions in a hydrocarbon undergoing oxidation is tertiary carbon > secondary C > primary C.

(vi) The alcohol is isolated from the oxidate in the form of a boron ester.

(vii) Water has a deleterious effect on oxidations in the presence of boron coreactants.

(viii) Boron compounds are unique in directing the course of an oxidation towards an alcoholic product.

It is first necessary to examine some aspects of boron chemistry in detail before formulating a mechanism. The relevant areas of boron chemistry to be considered are listed below:-

I. Thermodynamic study of the peroxyborane grouping, $>$BOOR.

II. Thermal decomposition of some peroxyboranes in hydrocarbon solution.

III. Autoxidation of boron compounds.

IV. Decomposition of hydroperoxides in the presence of boron compounds.

V. Mechanism of hydrocarbon autoxidations.

I. Thermodynamic study of the peroxyborane grouping

The results of the bond-energy term calculations are summarised in Table 3.9.

Table 3.9

Bond-energy terms in $(ROO)_3B$(g)

R	E(BO-OR)/kJ mol^{-1}	E(B-OOR)/kJ mol^{-1}
t-butyl	162.3±12	429.3±19
n-butyl	159.4±14	436.0±21

These values are realistic in magnitude and are compared with bond-dissociation energies (BDE) and bond-energy terms (E) from similar compounds (Table 3.10).

Table 3.10

Selected BDE and E values

Bond	BDE or E/kJ mol^{-1}
D(t-BuO-OBu^t)	156.9[75]
D(t-BuO-OH)	179.9[75]
D(HO-OH)	213.4[75]
E(B-O), esters	460.2[77]

It is likely that E(R-OOB$<$) is similar to E(R-OOH),[75] 292.9 kJ mol^{-1} and this strongly indicates that the weakest bond in an alkyl peroxyborane is the peroxy linkage. Homolytic cleavage of the oxygen-oxygen bond in both tri n-butyl and tri t-butyl peroxyborane is indicated by their catalysis of the polymerisation of styrene and methyl methacrylate.[65]

II. Thermal decomposition of some peroxyboranes in hydrocarbon solution

The decomposition of a series of peroxyboranes in hydrocarbon solution at temperature above 403K have been studied kinetically.[78,79,80] A typical reaction sequence[78] [for $(t\text{-}BuOO)_3B$ in n-nonane(SH)] is shown overleaf:-

$(t\text{-BuOO})_3B \longrightarrow (t\text{-BuOO})_2BO^{\bullet} + t\text{-BuO}^{\bullet}$ ... (3.3)

$(t\text{-BuOO})_2BO^{\bullet}+SH \longrightarrow (t\text{-BuOO})_2BOH + S^{\bullet}$ ... (3.4)

$(t\text{-BuOO})_3B + S^{\bullet} \longrightarrow (t\text{-BuOO})_2BOS + t\text{-BuO}^{\bullet}$ ... (3.5)

$t\text{-BuO}^{\bullet} + SH \longrightarrow t\text{-BuOH} + S^{\bullet}$ ... (3.6)

$t\text{-BuO}^{\bullet} \longrightarrow (CH_3)_2CO + CH_3^{\bullet}$ ... (3.7)

$CH_3^{\bullet} + SH \longrightarrow CH_4 + S^{\bullet}$ ... (3.8)

$2S^{\bullet} \longrightarrow S\text{-}S$ ... (3.9)

The activation energies of the spontaneous reaction (3.3) and the induced decomposition (3.5) were calculated for each of the peroxyboranes studied and the results are presented in Table 3.11.

Table 3.11

Activation energies (E_{ACT}) for steps (3.3) and (3.5) in the decomposition of some peroxyboranes in n-nonane solution (at temperatures > 403K)

Peroxyborane	E_{ACT}(Spont.3.3)/kJ mol^{-1}	E_{ACT}(induced,3.5)/ kJ mol^{-1}	Order of reaction
$(t\text{-BuOO})_3B$	136.4	174.0	1st
$(t\text{-BuOO})_2B.OBu^{-n}$	125.5	131.8	1st
$t\text{-BuOO}.B(OBu\text{-}n)_2$	125.5	104.6	1st
$t\text{-BuOO}.B(OMe)_2$	121.3		2nd
$(t\text{-BuOO})_2BOH$	117.1		1st

Tests in which t-butyl peroxide was added to the initial solution (reactions 3.6) were carried out with the aim of confirming the effect of the induced decomposition reactions (reaction 3.5 above); a considerable acceleration of the decomposition of the peroxyborane in n-nonane solution was observed. For both the di- and tri-peroxyboranes, E(spontaneous) $<$ E (induced) while the converse effect is noted for the monoperoxyborane; similar results have been observed for decompositions of t-butylperoxytriethylsilicon in n-decane.[81] The interpretation of these facts is that decompositions involving two or more peroxy groupings proceed via a different mechanism to that in which only one peroxy group is present. The character and yield of the compounds formed in all the decompositions is consistent with a free-radical reaction mechanism.

It is significant that the values of E_{ACT}(spont.) and E_{ACT}(induced) for tri(tert-butylperoxy)borane are similar in magntitude to the E(BO-OR) bond-energy terms obtained in this work, accepting the various approximations involved. This would also strongly indicate that the activation energies of the various peroxyborane decompositions[78,79,80] can be taken to be close to the BDE's of the initial homolytic cleavage reaction (reaction 3.3 etc). This, of course, assumes that reactions are in the ideal gas states, that the radicals are formed in their ground states and that the activation energy for the reverse reaction is zero.

The rate constants for the process $ROOBR_2 \rightarrow RO^{\bullet} + {}^{\bullet}OBR_2$, have been measured and are $1.1 \times 10^{-5}s^{-1}$ for R = n-butyl, $3.8 \times 10^{-4}s^{-1}$ for R = sec-butyl and $5.2 \times 10^{-4}s^{-1}$ for R = exo 2-norbornyl (all at 303K).[82]

III. Autoxidation of boron compounds

Detailed studies[82] of the oxidation of boron compounds have showed that the process follows a free-radical chain mechanism and not a polar mechanism as was first assumed.[83,84] The following steps have been proposed:[82]

Initiation: $\longrightarrow \; R^{\bullet}$ ... (3.10)

Propagation: $R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$ ... (3.11)

$RO_2^{\bullet} + BR \xrightarrow{k_p} ROOB + R^{\bullet}$ (3.12)

Termination: $2RO_2^{\bullet} \xrightarrow[k_b]{} \text{inactive products}$ (3.13)

In the early stages of the reaction initiation is by the direct reaction between the borane and oxygen, but as the reaction proceeds, the unimolecular decomposition of the alkylperoxyborane, or its bimolecular reaction with alkylborane become more important. The propagation rate constants for some organoboron compounds at 303K are in the range $k_p = 10^4 - 10^6 \text{ mol}^{-1}\text{s}^{-1}$. Comparing the rate constants for radical displacement on boron by peroxy radical with rate constants for hydrogen-atom abstraction by these radicals, it is shown that the former displacement is clearly among the most rapid reactions of peroxy radicals known. For example, in the kinetic study of the reaction of an alkylperoxy-radical at B in tri-alkylboranes, the rate was shown to be 10^7 times faster than the similar reaction of hydrogen with toluene.

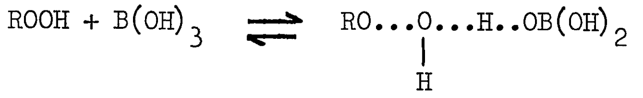
The high rate of autoxidation of many organoboron compounds compared with hydrocarbons can therefore be accounted for by the relative propagation rate constants of the two reactions.

Reactions such as $RO^{\bullet} + MR' \longrightarrow ROM + R'^{\bullet}$ (RM = organometallic compound) have also been studied.[85] These are very fast reactions ($k = 10^5 - 10^7 \text{ mol}^{-1}\text{s}^{-1}$) and are characterised by low activation energies ($0 - 20 \text{ kJ mol}^{-1}$).

IV. Decomposition of hydroperoxides in the presence of boron compounds

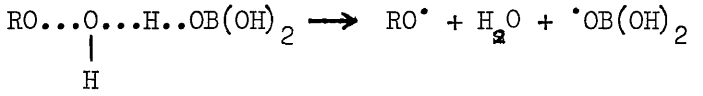
There is evidence to show that orthoboric acid, metaboric acid and their esters catalyse the decomposition of hydroperoxides and that the decomposition is directed towards alcohol formation.[86] The decreases in hydroperoxide concentration during autoxidation can be considerable and in some instances may be halved.[63,87]

A number of mechanisms have been proposed to account for this action and one scheme[88] involves an initial association between hydroperoxide and boric acid:



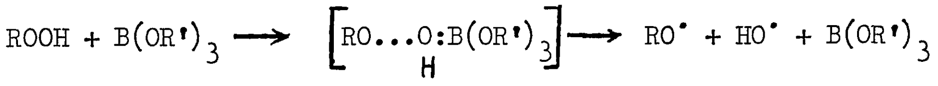
$$ROOH + B(OH)_3 \rightleftharpoons RO\ldots\underset{\overset{|}{H}}{O}\ldots H..OB(OH)_2 \qquad \ldots (3.14)$$

homolytic decomposition of this complex is envisaged to give alkoxy radicals which sequentially abstract hydrogen from the hydrocarbon to produce alcohol:



$$RO\ldots\underset{\overset{|}{H}}{O}\ldots H..OB(OH)_2 \longrightarrow RO^{\bullet} + H_2O + {}^{\bullet}OB(OH)_2 \quad .. (3.15)$$

Some workers[89] have found that boric acid esters are about as effective as boric acid in directing n-paraffin oxidations towards alcohol. A series of esters (n-propyl to n-cetyl) was found to give selectivity for alcohol even at concentrations equivalent to only 0.2% boric acid. A mechanism not involving hydrogen bonding was proposed:



$$ROOH + B(OR')_3 \longrightarrow \left[RO\ldots\underset{H}{O}{:}B(OR')_3\right] \longrightarrow RO^{\bullet} + HO^{\bullet} + B(OR')_3 \quad \ldots (3.16)$$

The production of alcohol via reactions such as:

$$3ROOH + B(OR')_3 \rightleftharpoons B(OOR)_3 + 3R'OH \qquad \ldots (3.17)$$

is unlikely in that such equilibria are known to lie largely on the left.[90] A further possibility is that interaction of hydroperoxide with the boron coreactant could lead directly to the boric acid ester, without any free alcohol being formed. This proposal received some support from the experimental evidence that no free alcohol was detected in the oxidate from cyclododecane.[63]

V. Mechanism of hydrocarbon autoxidation

The stages of hydrocarbon oxidation are examined below as to how boron compounds might influence the course of autoxidation at each step. Non-catalysed oxidation of hydrocarbons[91,92,93] in the liquid phase may be considered to proceed as follows[94]:

$$RH \xrightarrow{O_2} R^\bullet \text{ (chain initiation)} \qquad \ldots \quad (3.18)$$

$$\left.\begin{array}{ll} R^\bullet + O_2 \longrightarrow RO_2^\bullet & \quad \ldots \quad (3.19) \\ RO_2^\bullet + RH \longrightarrow ROOH + R^\bullet & \quad \ldots \quad (3.20) \end{array}\right\} \begin{array}{l}\text{chain}\\ \text{propagation}\end{array}$$

$$ROOH \longrightarrow RO^\bullet + {}^\bullet OH \text{ (chain-branching)} \qquad \ldots \quad (3.21)$$

$$\left.\begin{array}{l} R^\bullet + R^\bullet \longrightarrow R\text{-}R \\ RO_2^\bullet + R^\bullet \longrightarrow ROOR \\ RO_2^\bullet + RO_2^\bullet \longrightarrow ROH + RCOR + O_2 \end{array}\right\} \begin{array}{l}\text{chain}\\ \text{termination}\end{array} \qquad \ldots \quad (3.22)$$

Radicals $R^\bullet$, can also be formed termolecularly:

$$2RH + O_2 \longrightarrow R^\bullet + H_2O_2 + R^\bullet \qquad \ldots \quad (3.23)$$

The rate of reaction (3.19) is some $10^4 - 10^7$ times that of reaction (3.20) and this means that the overall rate-determining propagation step is the abstraction of a hydrogen atom by a peroxy radical to give hydroperoxide molecule. Other reactions which are thought to take place as the hydroperoxide level builds up are:

$$2ROOH \longrightarrow RO^\bullet + RO_2^\bullet + H_2O \qquad \ldots \quad (3.24)$$

and

$$ROOH + RH \longrightarrow RO^\bullet + R^\bullet + H_2O \qquad \ldots \quad (3.25)$$

VI. Mechanism

The primary information provided by the present thermochemical study of the peroxyborane grouping is the close similarity in properties between peroxyboranes and organic peroxides. Substantially all of the unusual features of peroxide reactivity can be associated with the fact that the

O–O bond can be easily broken and can undergo reactions of several kinds. The C–OOR bond-strength in many organic peroxides is of the order 300 kJ mol^{-1} and hence one characteristic of these peroxides is the presence of a relatively weak O–O bond ($\approx$ 170 kJ mol^{-1}) flanked by two generally stronger C–OOR bonds (in hydroperoxides one of these is a OO–H bond). This trend is evident in the peroxyboranes except that the B–OOR bond-strength (Table 3.10) is somewhat higher than the corresponding C–OOR bond-strength.

It would be inappropriate to attempt a full explanation of the role of boron coreactants in oxidation processes solely on the basis of the determined "peroxide" properties of peroxyboranes. However, some general conclusions may be drawn and the various aspects of boron chemistry summarised in Sections II to IV can be combined with the known stages of hydrocarbon autoxidation (Section V) to provide a basis for mechanism elucidation. The following reaction scheme is proposed; $B(OH)_3$ is a typical coreactant/catalyst and RH is the hydrocarbon undergoing oxidation ($T = 440K$).

Initiation reactions:

$$RH + O_2 \longrightarrow \text{radicals i.e. } R^{\bullet} \qquad \ldots \qquad (3.26)$$

Propagation reactions:

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \qquad \ldots \qquad (3.27)$$

$$\left\{\begin{array}{ll} RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} & \qquad \ldots \qquad (3.28) \\ RO_2^{\bullet} + B(OH)_3 \longrightarrow ROOB(OH)_2 + {}^{\bullet}OH & \qquad \ldots \qquad (3.29) \end{array}\right.$$

$$ROOB(OH)_2 \longrightarrow RO^{\bullet} + {}^{\bullet}OB(OH)_2 \qquad \ldots \qquad (3.30)$$

$$RH + {}^{\bullet}OB(OH)_2 \longrightarrow HOB(OH)_2 + R^{\bullet} \qquad \ldots \qquad (3.31)$$

$$ROOB(OH)_2 + R^{\bullet} \longrightarrow ROB(OH)_2 + {}^{\bullet}OR \qquad \ldots \qquad (3.32)$$

reactions involving the $^{\bullet}OR$ radical:

$$RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet} \quad \ldots \quad (3.33)$$

$$RO^{\bullet} + B(OH)_3 \longrightarrow ROB(OH)_2 + {}^{\bullet}OH \quad \ldots \quad (3.34)$$

Termination reactions:

$$RO^{\bullet} \longrightarrow \text{non-radical product + a radical } (Y^{\bullet}) \quad (3.35)$$

($Y^{\bullet}$ is usually a small radical CH_3, C_2H_5 etc.)

$$Y^{\bullet} + Y^{\bullet} \longrightarrow Y\text{–}Y \quad \ldots \quad (3.36)$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R\text{–}R \quad \ldots \quad (3.37)$$

$$RO_2^{\bullet} + RO_2^{\bullet} \longrightarrow \text{non-radical products} \quad \ldots \quad (3.38)$$

The main feature of this mechanism is the competition between the boron coreactant and RH for reaction with $RO_2^{\bullet}$ radicals (3.28 and 3.29). Similar reactions occur with $RO^{\bullet}$ (3.33 and 3.34). The sequence involving peroxyboranes (or radicals generated from them) are detailed in 3.30 (spontaneous decomposition), 3.31 and 3.32 (induced decomposition). Expected characteristics of the proposed mechanism (3.26 – 3.38) would be general inhibition of reaction (disruption of the chain-propagation step 3.28) and attendant low hydroperoxide levels. Both of these features are noted experimentally. The inhibitory influence of boron compounds has been observed in some closely related free-radical processes, e.g. boron and boric acid inhibit the air oxidation of graphite at a level of 0.1 mole %.[95]

Of the proposals (a–d, Introduction), it would seem unlikely that (a), (b) or (c) alone could account for the effect of boron compounds in hydrocarbon autoxidations. Simple esterification processes (a) are highly unlikely and there is reasonable evidence to show that the BOH group does not serve as a hydrogen atom source.[96] Reaction (c) is equally unlikely to be operative (Section IV).

While the experimental observations (i-viii, Discussion) are consistent with the above mechanism, it is clear that alternative mechanisms may also satisfy these observations. Hence this work provides a plausible but not unequivocal mechanism for hydrocarbon autoxidation in the presence of boron containing coreactant/catalysts.

CHAPTER IV

The Thermochemistry of Mesityldichloroborane, Ortho-, Meta-, and Para-Tolyldichloroboranes, and the Boron-to-Carbon Bond Strength.

Introduction

Experimental Results

Results

Discussion

Introduction

The occurrence of π character in carbon-boron bonds has frequently been postulated to explain the properties of certain organoboron compounds. Chemical and spectroscopic evidence for (C-B) π bonding has been reviewed.[97] An analysis of the available data suggests that much of the evidence is circumstantial and most of the data taken individually are inconclusive.[98]

Thermochemical studies[99,100] of $C_6H_5BX_2$(I), $(C_6H_5)_2BX$(II), $(C_6H_5)_3B$(III) and (cyclo-$C_6H_{11})_3B$(IV), where X = Cl, Br, showed the order of boron-carbon bond strength, E, in these molecules to be $E(I) > E(II) > E(III) \gg E(IV)$. The marked enhancement of the boron-carbon (aromatic) bond energy compared with the boron-carbon (aliphatic) bond energy was discussed in terms of pπ -pπ bonding. The successive decrease in E on replacement of halogen by phenyl in the series $(C_6H_5)_{3-n}BX_n$ (n = 0,1,2) was rationalised by proposing an increased steric interaction causing the phenyl groups to be twisted out-of-plane relative to the boron atom with concomitant reduction in resonance stabilisation.[99] Support for the above conclusion comes from a spectroscopic study of all the phenylhaloboranes of the type, $(C_6H_5)_{3-n}BX_n$, (n = 1,2 and X = F, Cl, Br, I). The same study also shows that the structure of $C_6H_5BF_2$ and of $(C_6H_5)_2BF$ are distinctly different from those of the other halides.[101]

Several methyl substituted aryldichloroboranes and aryldifluoroboranes have been studied using dipole moment measurements, N.M.R., I.R., and U.V. spectroscopy[102] and the conclusion drawn that the majority of data indicated the presence of considerable carbon-boron π bonding.

Molecular orbital calculations of the π electronic structures of $C_6H_5BCl_2$[103] and $(C_6H_5)_2BCl$[104] show that the electron density on boron mainly originates from the halogen orbitals and that the contribution from the phenyl ring(s) is small.

The present thermochemical study on mesityldichloroborane, ortho-, meta-, and para-tolyldichloroboranes investigates the steric and electronic influence of the methyl substituent(s) in the aromatic ring on E(B-C). Results of previous studies[99,100] indicate that in the case of these molecules, methyl groups positioned ortho to the $-BCl_2$ group should cause a decrease in E(B-C) whilst para-methyl groups should cause little change (relative to E(B-C) in phenyldichloroborane).

Experimental Results

I. Calorimetry

Generally arylboron compounds readily deboronate to aromatic hydroxy compounds and orthoboric acid with hydrogen peroxide in a basic medium[105,106,107], and this reaction (4.1) was used to determine the standard heats of formation of the arylhaloboranes. The calorimetric fluid used was an aqueous solution 0.1 mol dm^{-3} with respect to H_2O_2 and 1.00 mol dm^{-3} with respect to NaOH (this mixture designated aqueous excess base and abbreviated a.e.b.)

$$\mathrm{ArBCl_2(l) + [H_2O_2 + 2NaOH]a.e.b. = [ArOH + B(OH)_3 + 2NaCl]a.e.b.} \qquad (4.1)$$

and therefore:

$$\Delta H_f^o[\mathrm{ArBCl_2,l}] = \Delta H_f^o[\mathrm{ArOH,a.e.b.}] + \Delta H_f^o[\mathrm{B(OH)_3,a.e.b.}] + 2\Delta H_f^o[\mathrm{NaCl,a.e.b.}]$$
$$-2\Delta H_f^o[\mathrm{NaOH,a.e.b.}] - \Delta H_f^o[\mathrm{H_2O_2,a.e.b.}] - \Delta H \quad \ldots \quad (4.2)$$

Quantities of the aryldichloroboranes were chosen such that both peroxide and base were in excess. The para-isomer was studied at 303.15 K where the sample is liquid and no correction of the results to 298.15 K was made.

Table 4.1

Enthalpies of reaction for equation 4.1

N	$-\Delta H$/kJ mol^{-1}	N	$-\Delta H$/kJ mol^{-1}
Ar = O-$CH_3.C_6H_4$(l) (ortho-tolyl)		Ar = p-$CH_3.C_6H_4$(l)* (para-tolyl)	
28812	720.9	25431	686.2
23760	723.4	20269	677.8
35540	724.2	32499	679.9
23269	720.0	24028	687.0
42414	715.5	28115	685.3
28182	715.0	26159	686.2
25671	722.2	28879	678.2
30727	716.7	20508	675.7
30341	716.3	30054	674.9
29230	718.4		
32387	720.9	* at 303.15 K	
$\langle -\Delta H \rangle = 719.4 \pm 1.9$		$\langle -\Delta H \rangle = 681.2 \pm 3.3$	
Ar = m-$CH_3.C_6H_4$(l) (meta-tolyl)		Ar = 2,4,6,$(CH_3)_3C_6H_2$(l) (mesityl)	
27847	714.6	30861	686.2
28490	706.7	29317	692.4
28785	706.7	28490	692.9
28503	719.2	27708	687.8
23540	718.0	24801	689.9
26205	705.4	29709	684.5
23741	715.0	29010	687.0
23588	713.8	24857	687.8
		24857	690.8
$\langle -\Delta H \rangle = 712.5 \pm 3.8$		$\langle -\Delta H \rangle = 688.7 \pm 1.9$	

The enthalpies of mixing of the products in all of the calorimetric reactions were assumed to be zero and the enthalpies of solution of H_2O_2, NaCl and NaOH in a.e.b. were assumed to be equal to the corresponding values in water. The thermal effect of the catalysis of the decomposition of hydrogen peroxide by base is known to be negligible. The enthalpies of reaction (equation 4.1) are given in Table 4.1; the enthalpies of neutralisation of mesityldichloroborane and meta-tolyldichloroborane were determined in the same calorimeter. (Table 4.2).

Table 4.2

Enthalpies of neutralisation for ArOH(c or l) + a.e.b. = [ArOH,a.e.b.]

N	$-\Delta H/\mathrm{kJ\ mol^{-1}}$	N	$-\Delta H/\mathrm{kJ\ mol^{-1}}$
Ar = m $-CH_3.C_6H_4$(l)		Ar = 2,4,6$(CH_3)_3.C_2H_6$(c)	
1348	28.5	1372	13.4
1515	28.7	1247	13.4
958	28.7	1182	12.6
829	28.7	1162	13.0
$\langle -\Delta H \rangle = 28.7 \pm 0.1$		$\langle -\Delta H \rangle = 13.0 \pm 0.4$	

II. Tensimetry

The enthalpies of vaporisation of meta-tolyldichloroborane and mesityldichloroborane were determined using the procedure described in Chapter I, F and Chapter III (in experimental results section). The measurements are set out in Table 4.3.

Table 4.3

Vapour-pressure measurements of $ArBCl_2(l)$

Temperature K	Reading V	Correction V	Corrected reading V	Pressure Torr
Ar = meta-tolyl				
343.15	+0.310	+0.410	+0.720	64.6
348.15	+0.664	+0.455	+1.119	85.0
353.15	+1.114	+0.485	+1.599	110.5
358.15	+1.657	+0.512	+2.163	140.5
Ar = mesityl				
338.15	-0.363	+0.378	+0.015	26.5
348.15	-0.114	+0.455	+0.331	43.0
358.15	+0.320	+0.512	+0.832	69.5

III Differential scanning calorimetry (D.S.C.)

The enthalpy of fusion of para-tolyldichloroborane (mp 300.15 K) was determined and calculated as described in Chapter I, E. Three separate samples were run and the average area of several scans from each sample was used in the calculation of results. The enthalpy of fusion was found to be 4.39 $\pm$ 0.13 kJ mol^{-1}, where the uncertainty interval quoted is the range of the determinations and includes a calibration error.

IV N.M.R. spectra

^{1}H n.m.r. spectra of ortho-tolyldichloroborane and para-tolyldichloroborane used in the determination of the meta-isomer concentration (Chapter II, II) are shown in Figure 4.1.

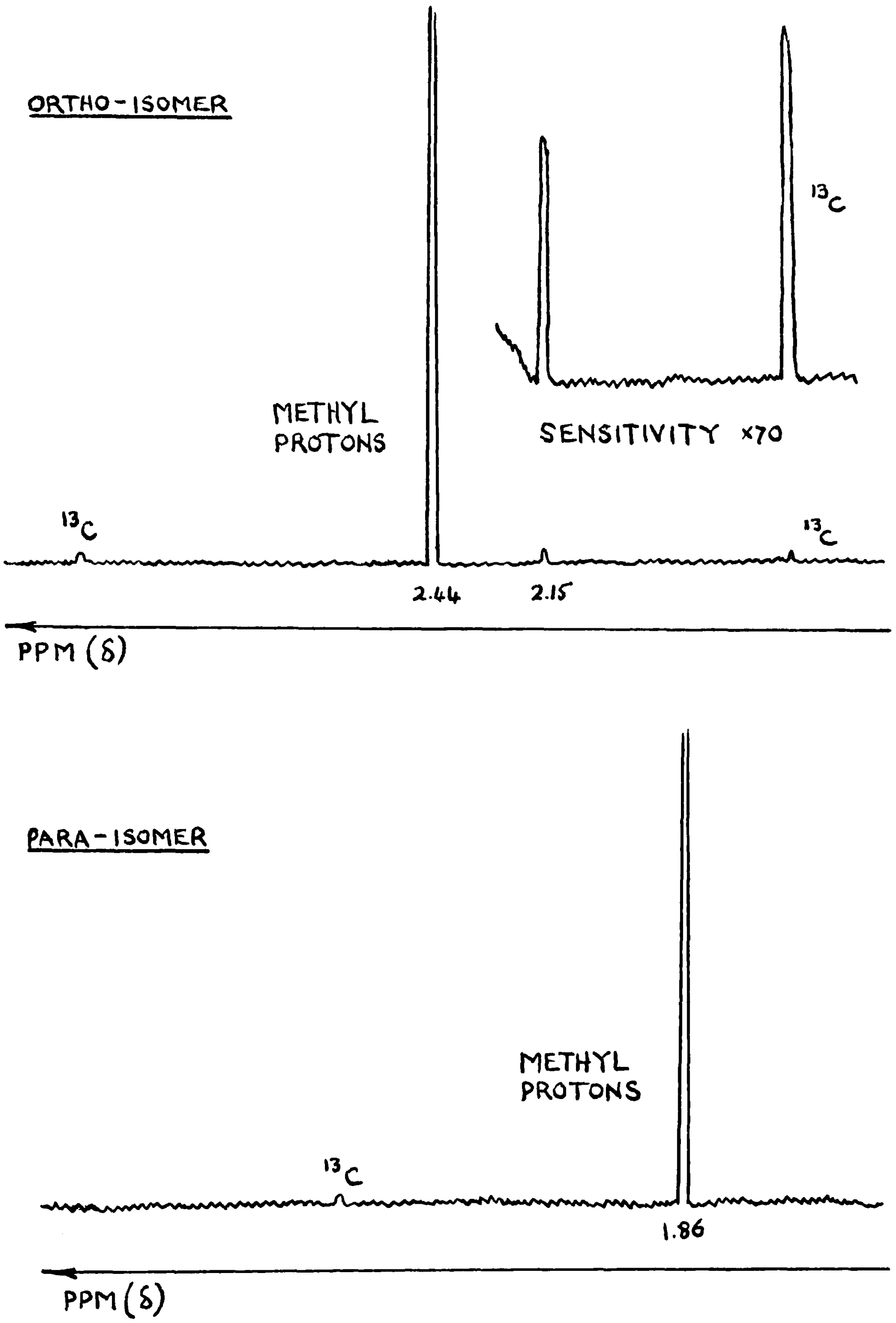

ORTHO-ISOMER
^{13}C
METHYL PROTONS
SENSITIVITY ×70
^{13}C
^{13}C
2.44
2.15
PPM (δ)
PARA-ISOMER
METHYL PROTONS
^{13}C
1.86
PPM (δ)

figure 4.1

Results

I Standard heats of formation

The following standard heats of formation were calculated using equation 4.2, the appropriate $-\Delta H$ value (Table 4.1) and the ancillary data in Table 4.5. The term (ΔH_f^o[NaCl, a.e.b.] $-\Delta H_f^o$[NaOH, a.e.b.] reduces to (ΔH_f^o[Cl^-,aq.] $-\Delta H_f^o$[OH^-,aq.] and the value for ΔH_f^o[$B(OH)_3$,c] is the mean of two reliable determinations.[108,109]

Table 4.4

Standard enthalpies of formation of $ArBCl_2(l)$

Compound	$-\Delta H_f^o$/kJ mol^{-1}
$o-CH_3.C_6H_4.BCl_2(l)$	300.7 ± 2.5
$m-CH_3.C_6H_4.BCl_2(l)$	309.8 ± 4.1
$p-CH_3.C_6H_4.BCl_2(l)$	334.8 ± 3.6
$2,4,6,(CH_3)_3C_6H_2.BCl_2(l)$	395.8 ± 4.8

Table 4.5

Ancillary thermochemical data

Compound (state)	$-\Delta H_f^o$/kJ mol^{-1}
$B(OH)_3(c)$	1094.0 ± 0.8[108] and 1095.0 ± 1.3[109] mean = 1094.5 ± 1.2
$B(OH)_3$,a.e.b.	1116.5 ± 1.2[110]
[Cl^-, aq − OH^-,aq]	-62.83[111]
H_2O_2,aq	191.2[111]
$o-CH_3.C_6H_4.BCl_2$,a.e.b.	220.5 ± 1.1[112,113]
$m-CH_3.C_6H_4.BCl_2$,a.e.b.	222.7 ± 1.1[112], this work.
$p-CH_3.C_6H_4BCl_2$, a.e.b.	216.4 ± 0.9[112,113]
$2,4,6,(CH_3)_3.C_6H_2.BCl_2$,a.e.b.	284.9 ± 4.2[113], this work.

The enthalpies of vaporisation of m-$CH_3.C_6H_4.BCl_2$ and 2,4,6,$(CH_3)_3C_6H_2.BCl_2$ were calculated from the data in Table 4.3. These data are represented in the form $\log_{10}P/\text{Torr} = a - \frac{b}{T/K}$, where a and b were obtained from a least-squares analysis. For meta-tolyldichloroborane a = 9.90 and b = 2.776 x 10^{-3} and for mesityldichloroborane a = 8.91 and b = 2.533 x 10^{-3}. The enthalpies of vaporisation of the four aryldichloroboranes are collected in Table 4.6.

Table 4.6

Enthalpies of vaporisation of $ArBCl_2(l)$

Compound	$\Delta H^o_{vap.}/\text{kJ mol}^{-1}$
o-$CH_3.C_6H_4.BCl_2$	46.9 ± 0.9^{113}
m-$CH_3.C_6H_4.BCl_2$	55.2 ± 2.6
p-$CH_3.C_6H_4.BCl_2$	40.7 ± 1.3^{113}
2,4,6$(CH_3)_3C_6H_2.BCl_2$	51.5 ± 2.6

The enthalpies of formation of the aryldichloroboranes in the gaseous state were calculated from the respective enthalpies of formation and transition; these are collected in Table 4.7.

Table 4.7

Enthalpies of formation and transition of $ArBCl_2$ (kJ mol^{-1})

Compound	$\Delta H_f^o(c)$	$\Delta H_f^o(c \rightarrow l)$	$\Delta H_f^o(l)$	$\Delta H_f^o(l \rightarrow g)$	$\Delta H_f^o(g)$
$o-CH_3.C_6H_4.BCl_2$	-		-300.7 ± 2.5	46.9 ± 0.9	-253.8 ± 2.7
$m-CH_3.C_6H_4.BCl_2$	-		-309.8 ± 4.1	55.2 ± 2.6	-254.6 ± 4.7
$p-CH_3C_6H_4.BCl_2$	-339.2 ± 3.6	$4.39 \pm 0.13^*$	-334.8 ± 3.6	40.7 ± 1.3	-294.1 ± 3.8
$2,4,6,(CH_3)_3C_6H_4\ BCl_2$	-		-395.8 ± 4.8	51.5 ± 2.6	-344.3 ± 5.3

*mp 300.15 K

II. Bond-energy terms

The boron-carbon bond energy in the arylhalogenoboranes, $ArBCl_2$, is defined in equations 4.3 and 4.4:

$$ArBCl_2(g) = Ar(g) + B(g) + 2Cl(g) \quad \ldots \quad \Delta H \quad \ldots \qquad (4.3)$$

$$\text{where } \Delta H = 2E(B\text{-}Cl) + E(B\text{-}C) \quad \ldots \qquad (4.4)$$

The difference in the bond energies for the ortho- and para- isomers is given in equations 4.5, 4.6 and 4.7 below:

$$E(B\text{-}C)_p - E(B\text{-}C)_o = \Delta H \text{ (para isomer)} - \Delta H \text{ (ortho isomer)} \qquad (4.5)$$

$$= \Delta H_f^o[o\text{-}CH_3.C_6H_4.BCl_2,g] - \Delta H_f^o[p\text{-}CH_3.C_6H_4.BCl_2,g]$$

$$+ (\Delta H_f^o[p\text{-}CH_3.C_6H_4.,g] - \Delta H_f^o[o\text{-}CH_3.C_6H_4.,g]) \quad \ldots \qquad (4.6)$$

$$\approx \Delta H_f^o[o\text{-}CH_3.C_6H_4BCl_2,g] - \Delta H_f^o[p\text{-}CH_3C_6H_4.BCl_2,g] \quad \ldots \qquad (4.7)$$

Equating the term in parentheses in (4.6) to zero is equivalent to equating the carbon-to-ortho hydrogen bond dissociation energy to the carbon-to-para hydrogen bond dissociation energy in toluene. There is no direct evidence[114,115] to support this above assumption, but it is likely that the steric effect of a methyl group on an ortho-hydrogen is small and that the difference in the electronic effect of the methyl group on the ortho- and para- hydrogens is similarly small. The assumption is probably valid to within $\pm$ 4 kJ mol^{-1}. $E(B\text{-}C)_p - E(B\text{-}C)_o$ = 40.3 $\pm$ 4.7 kJ mol^{-1} and using similar assumptions as above for the meta-isomer, $E(B\text{-}C)_p - E(B\text{-}C)_m = 39.7 \pm 5.3$ kJ mol^{-1}.

In order to derive explicit values for the boron-carbon bond energies rather than their difference, it is necessary to estimate $\Delta H_f^o[CH_3.C_6H_4\cdot,g]$. If the assumption is made that $D(C_6H_5\text{-}H) \approx D(CH_3.C_6H_4\text{-}H)$, this function is readily obtained from equation 4.8:

$$\Delta H_f^o[CH_3.C_6H_4\cdot,g] = D(C_6H_5\text{-}H)^{116} - \Delta H_f^o[H,g]^{117} + \Delta H_f^o[CH_3.C_6H_5,g]^{111} \quad \ldots (4.8).$$

In support of this second assumption, gas-phase kinetic studies[118] indicate $D(CF_3.C_6H_4\text{-}H) = 456 \pm 10$ kJ mol^{-1}, a figure close to the accepted value[116] for $D(C_6H_5\text{-}H) = 460 \pm 8$ kJ mol^{-1}. It is probable that $-CF_3$ will have a more marked influence on the ring C-H bond energies than $-CH_3$ so the assumption is most likely valid to within the difference between $D(CF_3.C_6H_4\text{-}H)$ and $D(C_6H_5\text{-}H)$, i.e. $\pm$ 4 kJ mol^{-1}. $\Delta H_f^o[2,4,6,(CH_3)_3.C_6H_3,g]$ is not available and the standard enthalpy of formation of $2,4,6(CH_3)_3C_6H_2\cdot(g)$ was estimated as indicated below (4.9):

$$\Delta H_f^o[2,4,6(CH_3)_3C_6H_2\cdot,g] = \Delta H_f^o[2,4,6(CH_3)_3C_6H_2.OH,g]^{113} - \Delta H_f^o[OH,g]^{111} + E(C_{Ar}\text{-}OH)^{116,119} \quad \ldots (4.9).$$

Ancillary data required to calculate E(B-C) in $ArBCl_2$ (equation 4.10) is contained in Table 4.8.

Table 4.8

Ancillary thermochemical data

Species	ΔH_f^o/kJ mol^{-1}
$o\text{-}CH_3.C_6H_4.(g)$	292 ± 8
$m\text{-}CH_3.C_6H_4.(g)$	292 ± 8
$p\text{-}CH_3.C_6H_4.(g)$	292 ± 8
$2,4,6,(CH_3)_3C_6H_2.(g)$	231 ± 10
B (g)	555.6 ± 16.7[120]
Cl (g)	121.0 ± 0.1 [120]
E(B-Cl)	440.1[120]

The required bond-energies were calculated using

$$E(B\text{-}C) = \Delta H_f^o[Ar,g] + \Delta H_f^o[B,g] + 2\Delta H_f^o[Cl,g] - 2E(B\text{-}Cl) - \Delta H_f^o[ArBCl_2,g] \quad ...(4.10)$$

Table 4.9

Boron-carbon bond energies in $ArBCl_2$ (eqn. 4.10)

Compound	E(B-C)*/kJ mol^{-1}
$o\text{-}CH_3.C_6H_4.BCl_2$	463 ± 10
$m\text{-}CH_3.C_6H_4.BCl_2$	463 ± 10
$p\text{-}CH_3.C_6H_4.BCl_2$	504 ± 10
$2,4,6,(CH_3)_3C_6H_2.BCl_2$	491 ± 12

* The major part of the error in these values is from $\Delta H_f^o[B,g]$ and ΔH_f^o[aryl radical, g]; the differences between appropriate values will lead to error cancellation.

A mass spectroscopic study of photoionisation yields from B_2Cl_4 and BCl_3 gives $\Delta H_f^o[BCl_2\cdot,g] = -61 \pm 5$ kJ mol^{-1}. Using this result it is possible to calculate bond dissocation energies in the aryldichloroboranes which do not include the implicit assumption of bond-energy transferability as do the bond-energy calculations described above. The same trends are observed in the bond dissociation energy results although the absolute magnitudes differ. (Table 4.10).

Table 4.10

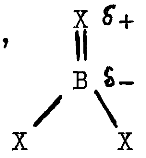
Bond dissociation energies in $ArBCl_2$

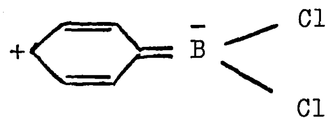
Compound	$D(Aryl-BCl_2)/kJ\ mol^{-1}$
$o-CH_3.C_6H_4.BCl_2$	485 ± 10
$m-CH_3.C_6H_4.BCl_2$	485 ± 10
$p-CH_3.C_6H_4.BCl_2$	525 ± 10
$2,4,6,(CH_3)_3.C_6H_2,BCl_2$	514 ± 12

Discussion

In order to discuss the significance of the above derived bond energies, it is necessary to examine the nature of the B-C bond in detail, and in particular, the question of B-C π bonding.

I. Bonding considerations

Boron trihalides, which may be considered the parent molecules for the arylhaloboranes, are known to have a planar structure, (D_{3L}) in the gaseous phase, and the observed bond lengths in each halide differ significantly from the sum of the covalent single-bond radii. Several different kinds of experimental evidence[98] support the "partial double-bond character" in the boron-halogen bond and this simple generalisation assists in the correlation of a broad spectrum of properties. Accordingly, the trihalide molecule may be considered to have a structure,  with the partial double-bond and single-bonds resonating among the three equivalent positions, the extent of $p\pi$-$p\pi$ donation depending, inter alia, X.

It is reasonable to assume that similar $p\pi$ - $p\pi$ bonding will occur in the aryldichloroboranes. The extant literature[122-125] suggests that although $p\pi$-$p\pi$ donation probably occurs in the boron-halogen bond in the aryldichloroboranes, the main contribution to electron density on the electrophilic boron atom comes from $p\pi$-$p\pi$ bonding in the boron-carbon bond. A commoner form is the quinoid type structure, , and the contribution of these structures is supported by the large dipole moment in $C_6H_5BCl_2$[126] (3.07D).

The proton magnetic resonance of all phenylhaloboranes[101] are typical of a monosubstituted benzene ring in which substituents are electron withdrawing. Two groups of peaks are observed, the area of which integrates to a low field/high field ratio of 2/3. The two less shielded protons are those in the ortho-position to the dihaloborane group. For methyl substituted boranes,[102] the shift of the ortho-protons show a dependence on the position of the second substituent in the ring giving an order of increasing δH values, meta < para < ortho (where 'meta', 'para' and 'ortho' refer to the position of the second substituent). A similar correlation for the meta/para proton multiplets gives an order of increasing δH values, para < ortho < meta. The methyl proton resonances are positioned in order of increasing electron density (decreasing δH) as $o\text{-}CH_3.C_6H_4.BCl_2 < p\text{-}CH_3.C_6H_4.BCl_2 < m\text{-}CH_3.C_6H_4.BCl_2$.

In summary, the nature of the bonding in the aryldichloroboranes is that boron-carbon π bonding will be important and the extent of this bonding will be a function of the electron withdrawing or electron-releasing properties of the aryl ring.

II. Bond-energies in related molecules and ^{11}B n.m.r. spectra

Data are available[99,100] for the boron-carbon bond energy in triphenylborane, tricyclohexylborane, diphenylchloroborane and phenyldichloroborane. Table 4.11 lists updated values from reference 127.

Table 4.11

Boron-carbon bond energies in $(C_6H_5)_{3-n}BCl_n$ (n=0,1,2) and tri(cyclohexyl)borane

Compound	E(B-C)/kJ mol^{-1}
$C_6H_5.BCl_2$	508 ± 10*
$(C_6H_5)_2BCl$	485 ± 10*
$(C_6H_5)_3B$	462 ± 10
$(c\text{-}C_6H_{11})_3B$	370 ± 12

* evaluated assuming that E(B-Cl) in these molecules is equal to E(B-Cl) in BCl_3.

Two noteworthy features of these data are firstly, the wide divergence of the boron-carbon (aliphatic) bond-energy from the boron-carbon(aromatic) bond-energy and secondly, the reduction in the bond-energy with successive phenyl group substitution. These data will be discussed in conjunction with the results for the aryldichloroboranes.

The ^{11}B resonances of some boron compounds[128] are compared in Table 4.12.

Table 4.12

^{11}B chemical shifts in some boron compounds

Compound	^{11}B/ppm	Compound	^{11}B/ppm	Compound	^{11}B/ppm
$(CH_3)_3B$	-86.2	$(C_2H_5)_3B$	-86.5	$(C_6H_5)_3B$	-60 ± 4
$(CH_3)_2BCl$	-77.2	$(C_2H_5)_2BCl$	-78.0	$(C_6H_5)_2BCl$	-61.0
CH_3BCl_2	-62.3	$C_2H_5BCl_2$	-63.4	$C_6H_5BCl_2$	-54.8
BCl_3	-45.6	BCl_3	-45.6	BCl_3	-45.6

$$\delta = \frac{H_B - H_r}{H_r} \times 10^6, \quad BF_3: O(C_2H_5)_2, \quad \delta = 0$$

Of interest is the effect of the phenyl groups in triphenylborane compared with triethylborane and trimethylborane; the resonance effect of the phenyl groups permits greater shielding and a shift to higher field.

<u>Bond-energies in the arylhaloboranes</u>

For brevity the available data are tabulated in Table 4.13.

Table 4.13

Summary of bond-energy values (kJ mol^{-1})

Compound	E(B–C)	Compound	E(B–C)
o-$CH_3.C_6H_4.BCl_2$	463±10	$C_6H_5.BCl_2$	508±10
m-$CH_3.C_6H_4.BCl_2$	463±10	$(C_6H_5)_2BCl$	485±10
p-$CH_3.C_6H_4.BCl_2$	504±10	$(C_6H_5)_3B$	462±10
2,4,6,$(CH_3)_3C_6H_2.BCl_2$	491±12	(c-$C_6H_{11})_3B$	370±12

These data show that the difference in bond-energies in the methyl substituted aryldichloroboranes lie approximately in the range observed for phenyldichloroborane and the progressively substituted phenylhaloboranes. The wide divergence of the boron-carbon (aliphatic) and the boron-carbon (aromatic) bond-energies similarly applies. Bond-length shortening is observed in boron-carbon (aromatic) bonds, e.g. B–C in $C_6H_5BCl_2$[122] = 0.152 nm and in $(CH_3)_3B$,[129] = 0.156 nm; this correlates with the above bond-energy data. It is tacitly assumed that the boron-halogen bond strength remains constant in the phenylhaloboranes and the aryldihaloboranes and that the observed variation in E(B–C) is due to the influence of the aromatic moiety. This is probably justified as the B–Cl bond length varies little with environment,[130] e.g. in BCl_3, 0.173 ± 0.002 nm and $C_6H_5BCl_2$, 0.172 ± 0.003 nm.

The difference between the boron-carbon bond energy in p-$CH_3.C_6H_4.BCl_2$ and $C_6H_5BCl_2$ is 4 kJ mol^{-1} which is within experimental error and so is not significant. Accepting the validity of the assumptions discussed above and the transferability of the B–Cl bond-energy from BCl_3 to $ArBCl_2$, this implies that the electronic effect of a para-methyl substituent on the B–C bond-energy in the aryldichloroboranes is negligible. Phenyldichloroborane is planar by electron-diffraction[122] and by analogy the structure of $p\text{-}CH_3.C_6H_4.BCl_2$ would probably also be planar. At most, the effect of a para-methyl group would be to augment the B–C bond-energy slightly through hyperconjugation.[97]

The B–C bond-energy in the ortho-isomer is some 40 kJ mol^{-1} less than both $p\text{-}CH_3.C_6H_4.BCl_2$ and $C_6H_5.BCl_2$; this is significant and reflects the steric effect of an ortho-methyl substituent. Spectroscopic evidence indicates that in diphenylhaloboranes,[101] the two phenyl groups are twisted out-of-plane relative to the C_2B skeleton and this would reduce ring-ring steric interaction at the expense of resonance stabilisation. Further, there is evidence that in triphenylborane the three phenyl rings are twisted $\approx 45^{\circ}$ from the C_3B plane[131] and this would lessen resonance stabilisation more so. The E(B–C) values for $(C_6H_5)_2BCl$ and $(C_6H_5)_3B$ of 485 and 462 kJ mol^{-1} respectively reflect these trends. Similarly, it is probable that in ortho-$CH_3.C_6H_4.BCl_2$, the $-BCl_2$ group is twisted out of the ring plane to minimise steric interaction resulting in loss of $p\pi - p\pi$ character in the B–C bond.

In mesityldichloroborane there are two methyl groups flanking the dichloroborane group. However, the steric effect of the 'second' methyl group would not be added to that of the first inasmuch that rotation of the $-BCl_2$ group away from the plane of symmetry (ring plane) would result in an equivalent 'space' being formed to accommodate this group. The observed increase from 463 to 491 kJ mol^{-1} (i.e. from ortho-tolyl to mesityl-dichloroborane) could arise from the input of electron density into the B-C bond from the 'second' methyl group relative to the hydrogen atom in the ortho-isomer. The para-methyl group would not be expected to influence the boron-carbon bond energy.

The proportionately low value of E(B-C) in the meta-isomer indicates that the meta-methyl group inhibits the stabilisation of the quinoid structure describing the aryldihaloboranes to the extent that the B-C bond strength approaches that in $(C_6H_5)_3B$ where there is minimum resonance stabilisation.

Indirect evidence for the nature of the bonding in arylhaloboranes comes from the study of $C_6H_5BF_2$ and $(C_6H_5)_2BF$.[101] Additionally, ^1H n.m.r. evidence[102] supports the picture that a fluorine atom may more easily π-bond to boron than a chlorine atom. Thus, the boron atom requires less electron density to be abstracted from the aryl ring in the fluoroboranes than in the chloroboranes to satisfy its electrophilic character.

Mass spectral data[101] indicates that in phenyldifluoroborane the boron-carbon bond is readily cleaved and the $-BF_2$ group is left intact. In contrast, the spectrum of phenyldichloroborane indicates ready loss of HCl from the parent molecule. An analogous situation is noted in the spectrum of phenyldibromoborane (E(B-C)[99] = 494 kJ mol^{-1}, cf. E(B-C) in $C_6H_5BCl_2$ = 508 kJ mol^{-1}).

Many examples of bond weakening have been attributed to steric effects[119] but the magnitudes have only been a few kJ, hardly enough to distinguish them from zero point energy corrections or other small effects. However, in this study the differences noted are somewhat larger (between 15 and 46 kJ mol^{-}) and therefore reflect more accurately changes in the B-C bond strength between isomers.

CHAPTER V

The Synthesis and Some Thermodynamic Functions of Rubidium and Caesium Tetrachloroborates

Introduction

Experimental Results

Results

Discussion

Introduction

In contrast to the ready preparation of tetrafluoroborates, the corresponding tetrachloroborates have proved difficult to isolate and were not characterised until 1957 when pyridinium tetrachloroborate was prepared.[132] Subsequently, autoclave syntheses[133] at 773 K of M^IBCl_4 (M = Cs, Rb and K) from MCl and BCl_3 provided clear evidence of the existence of alkali-metal salts although the purity of the products obtained was low $\approx$90 per cent. This synthetic route was modified later[51] by inclusion of a nitrobenzene solvent when smooth reactions proceeded at $\approx$ 373 K. The maximum purity of $CsBCl_4$ isolated using this procedure was 97.5 per cent but the potassium salt was considerably less pure. Sodium chloride was quantitatively recovered, without even visible alteration of crystalline size,[133] from a $NaCl-BCl_3$ sealed-tube reaction at 773 K, similarly, sodium chloride was precipitated by chloroform from a nitrobenzene:boron trichloride mixture.[51]

The formation of chloroborates only by alkali-metal ions of low polarising power and the extreme hydrolytic instability suggest that the stability of the chloroborate lattice is marginal. Approximate measurements of the dissociation pressures of potassium, rubidium and caesium tetrachloroborates indicate that these chloroborates are more prone towards dissociation than the corresponding fluoroborates.[133] The thermochemical interest in the tetrachloroborates lies in the determination of the lattice energies of the alkali-metal salts and the standard enthalpy of formation of $[BCl_4^-,g]$. This ion occurs in several compounds whose thermodynamic properties are largely unknown, e.g. $[PCl_4^+][BCl_4^-]$,$[PCl_3Br^+][BCl_4^-]$.

This section describes the calorimetry of analytically pure samples of rubidium and caesium tetrachloroborates prepared using a modified synthetic procedure (Chapter II, section III). Some derived thermodynamic functions of each of the salts are discussed. The mechanism of formation of the alkali-metal tetrachloroborates has been studied using ^{36}Cl as a radio tracer. It was concluded[134] from reactions between BCl_3 and labelled $M^{36}Cl$, that exchange occurred between ionised solute and BCl_3, i.e.

$$^{36}Cl^- + BCl_3 \leftrightarrows BCl_3{}^{36}Cl^-$$

rather than by:

$$M^{36}Cl + BCl_3 \leftrightarrows MCl + BCl_2{}^{36}Cl.$$

Studies of halogen exchange in nitrobenzene solutions using ^{11}B n.m.r. as probe,[135] revealed that rapid halogen exchange occurred between the boron trihalide:nitrobenzene complex and the ionised metal salt:

$$BX_3.\phi NO_2 + X^- \leftrightarrows BX_4{}^- + \phi NO_2$$

where X = Cl, Br and $\phi = C_6H_5$. This was observed for both BCl_3 complexed with Cl^- and BBr_3 complexed with Br^-; in addition, exchange of $BBr_3.\phi NO_2$ with chloride ion produced all possible ion combinations rapidly.

Experimental Results

The alkali-metal tetrachloroborates hydrolyse rapidly[133] according to:

$$MBCl_4(c) + (N + 3)H_2O(l) = [MCl + B(OH)_3 + 3HCl]N.H_2O(soln.) \quad \ldots \quad (5.1)$$

The calorimetric fluid used was single distilled water and the enthalpies of reaction (5.1) are collected in Table 5.1. The mole ratios, N, from equation 5.1 include a buoyancy correction for sample mass.

Table 5.1

Heats of hydrolysis of Rb and Cs tetrachloroborates

N	$-\Delta H(M{=}Rb)/kJ\ mol^{-1}$	N	$-\Delta H(M{=}Cs)/kJ\ mol^{-1}$
11167	211.4	9721	197.9
14374	212.6	7754	198.9
14411	209.8	10394	199.0
9078	210.0	9004	199.7
9747	209.2	7068	200.0
9842	208.7	9815	199.0
12237	211.0	10725	199.0
7559	208.9		
9004	209.2		
10203	210.2		
$\langle -\Delta H\rangle = 210.1 \pm 0.8$		$\langle -\Delta H\rangle = 199.1 \pm 0.6$	

Results

The standard enthalpies of formation were calculated from equation (5.2) using the ancillary data in Table 5.2; the enthalpies of mixing of the products was assumed to be zero. Ignoring the thermal effect of the different extent of dilution of the products introduces a maximum error of 0.1 kJ mol^{-1}.

Table 5.2

Ancillary thermochemical data

Species	$-\Delta H_f^o$/kJ mol^{-1}
RbCl,10000 H_2O	418.08 ± 0.15 [67,136]
CsCl,10000 H_2O	425.12 ± 0.15 [67,136]
HCl,3300 H_2O	116.82 ± 0.08 [137]
$B(OH)_3$,10000 H_2O	1072.53 ± 1.3 [68]
$H_2O(l)$	285.83 ± 0.04 [137]

Hence, $\Delta H_f^o[RbBCl_4,c] = -923.5 \pm 1.6$ kJ mol^{-1}

and $\Delta H_f^o[CsBCl_4,c] = -941.4 \pm 1.4$ kJ mol^{-1}.

Discussion

Heats of formation of two salts with a common anion may be used,[138] in combination with readily available ancillary data, to determine a 'thermochemical radius' for that anion. This permits estimation of the lattice energies of salts containing that anion via a derived equation[138,139] (Kapustinskii's equation). This method of estimation is only useful when crystallographic dimensions are not available and hence a more refined calculation[138] of the lattice energy is not possible.

Thus:

$$U_o = \frac{287.2V2 + 2-}{r_c + r_a} \left[1 - \frac{0.345}{r_c+r_a}\right] 4.184 \text{ kJ mol}^{-1} \qquad (5.3)$$

where V = number of ions per molecule, Z+ and Z- are the cationic and anionic charges respectively, and r_c and r_a are the cationic and anionic radii (the equation is written for r_c and r_a in Å). For a uni-univalent salt equation (5.3) becomes,

$$U_o = \frac{574.4}{r_c+r_c}\left[1 - \frac{0.345}{r_c+r_a}\right] 4.184 \text{ kJ mol}^{-1} \quad \ldots \quad (5.4)$$

therefore, only a knowledge of r_c and r_a is needed to estimate lattice energies. In considering the tetrachloroborates, the ionic radii of the alkali-metal cations are known and hence a 'thermochemical radius' may be ascribed to the complex anion, BCl_4^-, by the method described in Appendix IV (Yatsimirskii's method[140]).

Consider two salts M_1BCl_4 and M_2BCl_4.

$$M_1BCl_4(c) \longrightarrow M_1^+(g) + BCl_4^-(g) \quad \ldots \quad U_1 + 2RT \quad \ldots \quad (5.5)$$

and $$M_2BCl_4(c) \longrightarrow M_2^+(g) + BCl_4^-(g) \quad \ldots \quad U_2 + 2RT \quad \ldots \quad (5.6)$$

$$\therefore \quad U_1 - U_2 = \Delta H_f^o M_1^+(g) - \Delta H_f^o M_2^+(g) - \Delta H_f^o M_1BCl_4(c) + \Delta H_f^o M_2BCl_4(c) \quad (5.7)$$

From equation (5.4) it follows that:

$$U_1-U_2 = C\left[\frac{1}{(r_{M_1^+} + r_{BCl_4^-})}\; 1 - \frac{0.345}{(r_{M_1^+} + r_{BCl_4^-})} - \frac{0.345}{(r_{M_2^+} + r_{BCl_4^-})}\; 1 - \frac{0.345}{(r_{M_2^+} + r_{BCl_4^-})}\right] \quad \ldots \quad (5.8)$$

To solve for $r_{BCl_4^-}$, equation (5.8) reduces to:

$$\begin{aligned} 0 = {} & r^4+2r^3(m_1+m_2) + r^2[m_1^2+m_2^2+4m_1m_2 + c(m_1-m_2)] \\ & + r[2m_1^2m_2+2m_1m_2^2+c(m_1^2-m_2^2) - 0.69C(m_1-m_2)] \\ & + [m_1^2m_2^2+c(m_1^2m_2-m_2^2m_1) + 0.345c(m_2^2-m_1^2)] \end{aligned} \quad \ldots \quad (5.9)$$

where m_1 and m_2 equal $r_{M_1}+$ and $r_{M_2}+$ respectively, the ionic radii of cations, $r = r_{BCl_4^-}$ which is the 'thermochemical radius' of the anion, and

$c = \frac{574.4}{U_1-U_2}$. By calculating U_1-U_2 from equation (5.7) the 'thermochemical radius' of the BCl_4^- ion can be found from equation (5.9). The input data required for the calculation of $r_{BCl_4^-}$ are listed in Tables 5.3 and 5.4.

Table 5.3

Thermochemical input data

Compound, species	ΔH_f^o/kJ mol^{-1}	ionic radius/nm
$Rb^+(g)$	487.8 ± 4	0.148[141]
$Cs^+(g)$	458.5 ± 4	0.169[141]
$RbBCl_4(c)$	-923.5 ± 1.6	
$CsBCl_4(c)$	-941.4 ± 1.4	

Table 5.4

Thermochemical data for $Rb^+(g)$ and $Cs^+(g)$

Species	ΔH_{sub}/kJ mol^{-1}	I.P./eV	ΔH_f^o/kJ mol^{-1}
Rb(g)	79.5 ± 4[142]	4.176[144]	487.8 ± 4*
Cs(g)	76.7 ± 4[143]	3.893[144]	458.5 ± 4*

* See Appendix IV for conversion of I.P. (at 0 K) to ΔH_f^o at 298.15 K.

One main source of error in the calculation of $r_{BCl_4^-}$ arises in $\Delta H_f^o Rb^+(g)$ and $\Delta H_f^o Cs^+(g)$ which themselves arise from the uncertainty in the heats of sublimation of Rb and Cs. Hence the resulting thermochemical radius has a large error; $r_{BCl_4^-} = 0.45 \pm 0.145$ nm.

From covalent bond lengths and van der Waal's radii, the radii of circumscribing spheres for BCl_4^- and BF_4^- may be estimated as 0.35 and 0.28 nm respectively, (Table 5.5).

Table 5.5

Calculation of circumscribing radii

Bond, radius	length/nm
B-F (sp^3,B)	0.142[145]
B-Cl(sp^3,B)	0.183[146]
F(van der Waals)	0.135[141]
Cl(van der Waals)	0.180[141]

It has been demonstrated[147] that for a series of ions of similar structure (e.g. in the tetrahedral ions, MnO_4^-, BF_4^-, $SO_4^=$,$CrO_4^=$, and $MoO_4^=$) that the ratio of the 'thermochemical radius' and the radius of the circumscribed sphere is virtually constant. An updated value for the thermochemical radius for BF_4^- is 0.24 nm (calculated using ΔH_f^o values for group I tetrafluoroborates[148]) and this gives $\frac{\text{thermochemical radius}}{\text{circumscribing radius}} = \frac{0.24}{0.28} = 0.85$. Using this value to calculate the radius forBCl$_4^-$, i.e. thermochemical radius = 0.85 x 0.35, which gives 0.31 nm, it becomes evident that the lower limit of 0.30 nm as calculated using the present thermochemical data is the most realistic value to use in subsequent calculations.

Substituting this radius (0.30 nm) in equation (5.4), the following lattice energy estimates result:

$U_o[RbBCl_4,c] = 494 \text{ kJ mol}^{-1}$

and $U_o[CsBCl_4,c] = 473 \text{ kJ mol}^{-1}$

The enthalpy of formation of the gaseous tetrachloroborate anion can now be calculated:

$$MBCl_4(c) \longrightarrow M^+(g) + BCl_4^-(g) \quad \ldots \quad U_o+2RT \quad \ldots \qquad (5.10)$$

amd therefore,

$$\Delta H_f^o[BCl_4^-,g] = U_o + 2RT - \Delta H_f^o(M^+,g] + \Delta H_f^o[MBCl_4,c] \qquad (5.11)$$

From (5.11), $\Delta H_f^o[BCl_4^-,g] \approx -921$ kJ mol, which is the average value for M = Rb and Cs. This is compared with the value of $\Delta H_f[BF_4^-,g] = -1807 \text{ kJ mol}^{-1}$, calculated using 0.24 nm for the thermochemical radius of BF_4^- in Kapustinskii's equation and enthalpy of formation[148] data for $LiBF_4$, $NaBF_4$ and KBF_4.

From a knowledge of the thermochemical radius of BCl_4^- and $\Delta H_f^o[BCl_4^-,g]$, the lattice energy and enthalpy of formation of salts containing the tetrachloroborate anion can be estimated using equations (5.4) and (5.11). The results of these calculations are shown in Table 5.6 together with the ancillary data used.

Table 5.6

Lattice energies and enthalpies of formation of other tetrachloroborate compounds

Compound	ionic radius/nm N^+	$\Delta H_f^o[M,^+g]^{149}$ kJ mol^{-1}	$U_o[MBCl_4,c]$ kJ mol^{-1}	$-\Delta H_f^o[MBCl_4,c]$ kJ mol^{-1}
$LiBCl_4$	0.06	687.4	604	815
$NaBCl_4$	0.95	610.4	555	870
$KBCl_4$	0.133	514.6	511	922
NH_4BCl_4	0.144	619.2	499	805

The sensitivity of lattice enthalpies to choice of anion radius is ca. 70 kJ $mol^{-1}nm^{-1}$.

The thermodynamic instability of the tetrachloroborates compared with the tetrafluoroborates may not be readily deduced from the relative magnitudes of the lattice energies [$U_o[RbBF_4] \approx 569$ kJ mol^{-1} and $U_o[CsBF_4] \approx 543$ kJ mol^{-1} via Kapustinskii's equation[138]], although the gas phase enthalpies of formation of the complex ions is significant. However, if the dissociation enthalpies for the reactions:

$$\begin{aligned} M^IBCl_4(c) &\leftrightarrows M^ICl(c) + BCl_3(g) \\ M^IBF_4(c) &\leftrightarrows M^IF(c) + BF_3(g) \end{aligned} \qquad \ldots \qquad (5.12)$$

are calculated for the alkali-metal salts, a clear demonstration of thermodynamic stability results, (Table 5.7).

Table 5.7

Dissociation enthalpies for M^IBX_4 (M^I = alkali metal, X = F, Cl), reactions 5.12

Compound	$\Delta H^o(X{=}Cl)/kJ\ mol^{-1}$	$\Delta H^o(X{=}F)/kJ\ mol^{-1}$
$LiBX_4$	31‡	111*
$NaBX_4$	57‡	151*
KBX_4	80‡	199*
$RbBX_4$	91	209†
$CsBX_4$	106	214†

‡ $\Delta H_f^o[MBCl_4, c]$ from Table 5.6.

* $\Delta H_f^o[MBF_4, c]$ from ref. 148.

† Calculated from $U_o[MBF_4, c]^{138}$ and $\Delta H_f^o[BF_4^-, g] = -1807\ kJ\ mol^{-1}$.

The relative stability is further demonstrated in the magnitudes of the dissociation pressures in the reaction:

$$M^IBX_4(c) \longrightarrow M^IX(c) + BX_3(g, p_{BX_3}) \quad \ldots \quad (5.13)$$

M = Rb or Cs and X = F or Cl.

Table 5.8

Dissociation pressures for reaction (5.13)

Compound	p_{BX_3} (333 K)/Torr
$RbBCl_4$	20*
$RbBF_4$	5×10^{-11} ‡
$CsBCl_4$	4.0*
$CsBF_4$	5×10^{-11} ‡

* reference 150, ‡ extrapolated values from ref. 151.

The values for $\Delta H_f^o[BCl_4^-,g]$ and $\Delta H_f^o[BF_4^-,g]$ allow the enthalpy changes in the gas-phase formation of the complex ions to be estimated:

$$BX_3(g) + X^-(g) \leftrightarrows BX_4^-(g) \qquad \ldots \qquad (5.14)$$

Thus for X = Cl, ΔH^o = -272 kJ mol^{-1} and for X = F, ΔH^o = -393 kJ mol^{-1}, this moderate difference in values indicates the relative stability of the two complex ions in the gas phase with respect to dissociation to BX_3.

In a study[145] of the acceptor properties, reorganisation energies, and π-bonding in boron and aluminium halides, reorganisation energies were evaluated and were defined as the energies required to destroy the π-bonding plus any energy change (+ve or −ve) which occurs as a result of changing from sp^2 to sp^3 orbitals for the metal atom. The following reactions were considered:

$$BF_4^-(g) \leftrightarrows BF_3(g) + F^-(g),\ \Delta H_1 \qquad \ldots \qquad (5.15)$$

$$BF_4^-(g) \leftrightarrows BF_3^*(g) + F^-(g),\Delta H_2 \qquad \ldots \qquad (5.16)$$

$$BF_4^-(g) \leftrightarrows B^*(g) + 3F^*(g) + F^-(g),\ \Delta H_3 \qquad \ldots \qquad (5.17)$$

B^* and F^* refer to the species arising from BF_3^*.

It is clear that $\Delta H_2 - \Delta H_1$ is just the reorganisation energy, the reorganised BF_3 molecule being denoted by BF_3^*. It is argued that ΔH_2 $\frac{1}{4}\Delta H_3$ since ΔH_2 represents (approximately) the enthalpy change when one B–F link in BF_4^- is broken and all of the resonance stabilisation gained by delocalising the negative charge over the ion is lost. $\frac{1}{4}\Delta H_3$ represents the average enthalpy change for breaking one B–F link plus one-fourth of the resonance (charge delocalisation) stabilisation energy of BF_4^-. Clearly, it is assumed here that the energy to break one bond in (5.16) (excluding the resonance effect) is the same as $\frac{1}{4}$ of the total bond-breaking energy (again excluding the resonance effect) in (5.17). Accepting this assumption it follows that:

$$\frac{1}{4}\Delta H_3 - \Delta H_1 > E_{reorg} \qquad \ldots \qquad (5.18)$$

where E_{reorg} = the reorganisation energy.

Corresponding reactions and considerations apply in the case of $BCl_4^-(g)$. Using the derived value for $\Delta H_f^o[BCl_4^-,g]$ in this work and an updated value for $\Delta H_f^o[BF_4^-,g]$, reorganisation are calculated according to equations (5.15 - 5.17). The results are tabulated (Table 5.9) along with the original calculated values using simple MO theory.[145]

Table 5.9

Reorganisation energies in some boron halides/kJ mol^{-1}

Halide	ΔH_1	ΔH_3	$E_{reorg.}$(this work)	E_{reorg}(calc)[145]
BF_3	394	2300	<180	202
BCl_3	268	1593	<130	127
BBr_3	-	-	-	110

APPENDIX I

Estimation of Thermodynamic Properties by Additivity Rules

Several thermodynamic functions H, S, Cp etc., have been shown to obey, with varying accuracy additivity rules. The basis of a general approach to the construction of additivity rules[152,153] is set out in Table AI.1. RNR and SNS are molecules, containing the groups (or atoms) R and S respectively, attached to a common molecular framework N_1 and Φ is a molecular property.

Table AI.1

Additivity rules for the estimation of molecular properties

Rule	Statement
Limiting law.	RNR + SNS $\leftrightharpoons$ 2SNR. For this disproportionation, $\Delta \Phi \longrightarrow 0$ as the separation between R and S becomes large compared to their own dimensions.
Zero-order approximation; Additivity of atomic properties.	$R_2 + S_2 \leftrightharpoons 2RS$. The molecular framework N permitted to vanish; net changes in molecular properties vanish except for statistical contributions.*
First-order approximation; Additivity of bond properties.	Permit the molecular framework N to become a single atom (such as O, S) or a partially substituted atom (such as CH_2, NH, CO).
Second-order approximation; Additivity of group properties.	This approximation is obtained with the increase in size of the molecular framework N to two atoms or to structural elements having distances of about 0.3 - 0.5 nm between attached groups.

[*] This is not accurate in terms of the statement of the rule since ring compounds such as aromatics, alicyclics, cannot be made to undergo disproportionation without breaking the ring at two points. Thus for the additivity rule, such structures must be considered as irreducible entities whose properties are not to be expected to be additive in the atoms composing their structures.

The second order approximation has been further developed; consider the disproportionation equation:

$Cl{-}CH_2.CH_2{-}Cl + H{-}CH_2.CH_2{-}H \leftrightarrows 2.H{-}CH_2.CH_2{-}Cl$ ... (I.1)

and

$H{-}CH_2.O{-}H + CH_3{-}CH_2.O{-}CH_3 \leftrightarrows CH_3{-}CH_2.O{-}H + H{-}CH_2.O{-}CH_3$ ... (I.2)

It is observed that the change in group substitution takes place on adjacent atoms rather than on the same atom as in the previous (1st) approximation. The disproportionation thus leaves unchanged the nearest neighbours of the atom or group being interchanged. In (I.1) the Cl atoms are bound to carbon atoms having 2H atoms and 1C atom as neighbouring ligands and this relationship is preserved in the disproportionation. If a group is defined as a polyvalent atom together with its ligands, then it can be shown that this second-order approximation is equivalent to the rule of additivity of group properties. As in the previous case, ring systems and unsaturated centres are preserved in disproportionations and so must be considered as irreducible, structural entities. This rule of additivity of group properties is restricted to the class of compounds containing at least two polyvalent atoms (i.e. two groups).

The group additivity property may be illustrated with the compounds from the series $C_2X_nY_{6-n}$. There are 7 compounds having different formulas in this series and 3 isomers; a total of 10 compounds. 6 distinct frameworks about which to construct disproportionation equations can be selected from this series. These are:

3 symmetrical nuclei: $-(C_2X_4)-$, $-(CXY{-}CXY)-$, $-(C_2Y_4)-$.
and 3 unsymmetrical nuclei: $-(CX_2.CY_2)-$, $-(CX_2.CXY)-$, $-(CY_2.CXY)-$.

A total of 6 disproportionation equations using the above nuclei can be written, e.g.

(Sym) $X(C_2X_4)X+Y(C_2X_4)Y \leftrightarrows 2X(C_2X_4)Y$ ... (I.3)

(Unsym) $X(CX_2.CY_2)X + Y(CX_2.CY_2)Y \leftrightarrows X(CX_2.CY_2)Y + Y(CX_2.CY_2)X$ (I.4)

Thus there will be 6 relations of additivity for the properties of the 10 compounds and so only 4 of the compounds can be independent of the rest. Further inspection shows that these correspond to the 4 groups contained in the series:

$C-(C)(X)_3$; $C-(C)(Y)_3$; $C-(C)(X)(Y)_2$; $C-(C)(X)_2(Y)$.

If we are given the properties of any 4 compounds in the series in each of which is contained at least one of these groups, then it is possible through the 6 disproportionation equations to deduce the properties of all others. While this may be done through the use of such equations, the group additivity property leads to the direct method of writing the properties of a compound as the sum of the properties of its groups. Thus, $(C_2X_6) = 2[C-(C)(X)_3]$ while $CX_3.CY_3 = [C-(C)(X)_3] + [C-(C)(Y)_3]$, etc.

Groups are obtained from measured data. For example, in the case of ΔH_f^o for dimethyl peroxide $2[C-(O)(H)_3] + 2[O-(O)(C)] = -125.5$, so that the sum of the $\Delta H_f^o[C-(O)(H)_3]$ and $[O-(O)(C)]$ groups is -62.8. Pairs of groups are awkward to handle, so the convention adopted is that all $[C-(X)(H)_3]$ are assigned the same value. The heat of formation $[C-(X)(H)_3]$ is -42.3, giving $[O-(O)(C)] = -20.5$. The group $[O-(O)(H)]$ is obtained directly from hydrogen peroxide, $2[O-(O)(H)] = -136.0$, that is $[O-(O)(H)] = -68.2$. We now have the values of the groups necessary to calculate the heat of formation of methyl hydroperoxide. The result is

$[C-(O)(H)_3] + [O-(O)(C)] + [O-(O)(H)] = -42.3 -20.5 -68.2 = -130.9$ kJ mol^{-1}, which is, of course, identical to that obtained by the simple disproportionation reaction:

$$CH_3OOCH_3 + HOOH \leftrightharpoons 2CH_3OOH \qquad \ldots \qquad (I.5)$$

Aside from their obvious use in calculating thermodynamic properties, the additivity rules can be extremely useful in many auxiliary contexts as well. One immediate use is in the checking of data for self-consistency; also in a series of homologous or related compounds the rules can be used to check errors either in the data or in calculations.

A very important use of the laws of bond or atom additivity is in deriving heats of reaction from the measurement of equilibrium constants at a single temperature. The usual method of measuring K (equilibrium) at two different temperatures in order to calculate ΔH may be either difficult, impractical because of a side reaction, or very inaccurate. In such cases a relatively poor measurement of K(eq) together with estimates of ΔS from either the rules of atom or bond additivity may give a value of ΔH with good precision. Thus, since $\Delta H = \Delta G - T\Delta S = -RT \ln K_{eq} + T\Delta S$, a measure of K_{eq} to ± 20% will introduce an error in ΔH of only ± 1.6 kJ at 400 K, and ± 3.2 kJ at 800 K. An estimate of ΔS to ± 8 kJ mol^{-1}K will represent ± 3.2 kJ in ΔH at 400 K and only ± 6.5 kJ at 800 K.

Finally, disproportionation equations may be used directly to predict heats of reaction among a related series of compounds where other thermodynamic data are lacking and the heats of reaction of a few members of the series are known.

APPENDIX II

Computer Analysis of Thermochemical Data

CATCH Tables

This Appendix lists standard enthalpies of formation of some organoboron and inorganic boron compounds derived from a set of enthalpies of reaction compiled at Royal Holloway College and processed by Dr. J.B. Pedley at the School of Molecular Sciences, University of Sussex.

In the method described,[154] standard enthalpies of reaction are punched on to cards, and a computer generates tables of self-consistent standard enthalpies of formation of the substances involved. Computers can obviously be used for storage and routine up-dating of standard enthalpies of formation as new data becomes available. Thus even though there may still be doubt concerning the absolute reliability of a given standard enthalpy of formation, it is possible to ensure that all data is at all times mutually consistent and up-to-date. The conventional typesetting and proof reading of tables which include numerical data is very tedious and subject to error. The use of automatic typesetting techniques operated directly by the computer virtually eliminates this source of error.

The method of analysis is as follows:
The standard enthalpy, ΔH^o_j of a reaction at 298.15 K is given by the equation:

$$\Delta H^o_j = \sum_i \nu_{ij} \quad \Delta H^o_{fi} \qquad \ldots \qquad (II.1)$$

where ν_{ij} is the stoichiometric number (positive for products, negative for reactants) of the substances i in the reaction j and ΔH^o_{fi} is the standard enthalpy of formation of i.

Some of the simultaneous equations are overdetermined and the standard enthalpies of formation can be obtained by the method of least squares by use of the equations:

$$\sum_i \Delta H^o_{fi} \sum_j {}_{ij} W_j^2 \nu_{kj} = \sum_j \Delta H^o_j W_j^2 \nu_{kj} \qquad \ldots \qquad (II.2)$$

where i and k denote substances and j the corresponding reactions. The weighting factors W_j are set equal to the reciprocals of the uncertainty intervals. When the enthalpy of formation of a substance k is determined from only one reaction, equations (II.2) reduce to a single equation:

$$\nu_{kj} \Delta H^o_{fk} = \Delta H^o_j - \sum_i \Delta H^o_{fi} \nu_{ij} \qquad (II.3)$$

where $\sum_i$ denotes summation over all substances except k.

The residuals Δ_j associated with each of the interdependent reactions are computed from the expression:

$$\Delta_j = \Delta H^o_j - \sum_i \nu_{ij} \Delta H^o_{fi} \qquad \ldots \qquad (II.4)$$

The values of Δ_j indicate the compatibility of the interdependent enthalpies of reaction.

The output consists of the empirical formulae of the compounds, their names, their molecular weights, the reactions in which they occur and the derived standard enthalpies of formation at 298.15 K. These are followed by a list of substances, other than boron compounds, which appear in the list of reactions. These enthalpies of formation of these compounds are taken from results of other compilations[111, 136] or are key values.[117] The compiled enthalpies of reaction are listed numerically along with their respective 'residuals', that is, the differences between the experimental value of the standard enthalpy of reaction and that calculated from the derived standard enthalpies of formation of the species in the reaction. The uncertainties (errors) on the standard enthalpies of formation are calculated by the usual square root of sum of squares rule from the uncertainty of the reaction and the standard deviation and stoichiometric coefficients of the other species in the reaction.

The following symbols are used to indicate the states of the substances involved.

(C)	crystalline solid
(L)	liquid
(G)	gaseous
(Am)	glassy or amorphous
(A)	completely dissociated species at infinite aqueous dilution
(AO)	undissociated species at infinite aqueous dilution

For solutions which are not infinitely dilute, the number of moles of water associated with one mole of solute is indicated in brackets, eg (1000 H_2O).

Elements in their standard reference states are indicated by the symbols (CS), (LS) and (GS) and these, with the hydrogen ion at infinite dilution and the gaseous electron, are defined to have zero enthalpy of formation.

The literature search for results on substances containing boron was not exhaustive, nor was the assignment of reliability unambiguous. Nevertheless, the tables represent values which are mutually self-consistent and it is a trivial matter to incorporate new values and recalculate the standard enthalpies of formation.

COMPOUND	FORMULA WEIGHT	ΔH_f° kcal mol^{-1}	ERROR kcal mol^{-1}	ΔH_f° kJ mol^{-1}	REACTIONS FOR ΔH_f°
B 1(CS)	10.810	0.000	0.000	0.000	0
B 1 (C 1 H 3) 3(L)	55.915	-34,168	0,981	-142,958	1 2
B 1 (C 1 H 3) 3(G)	55.915	-29,339	0,981	-122,754	3
B 1 (C 2 H 5) 3(L)	97,996	-45,328	0,700	-189,653	4 5 6
B 1 (C 2 H 5) 3(G)	97,996	-36,528	0,704	-152,834	7
C 8 H17 B 1(L)	124,034	-46,625	0,447	-195,078	8 9
B 1 (C 3 H 7) 3(L1)	140.077	-66,397	0,762	-277,804	10 11 12
B 1 (C 3 H 7) 3(G1)	140.077	-56,397	0,821	-235,964	13
B 1 (C 3 H 7) 3(L2)	140.077	-70,157	0,662	-293,537	14 15 16
B 1 (C 3 H 7) 3(G2)	140.077	-60,157	0,728	-251,697	17
B 1 C10 H21(L)	152.088	-67,313	0,625	-281,638	18
B 1 (C 4 H 9) 3(L1)	182.158	-83,925	0,447	-351,141	19 20 21 22
B 1 (C 4 H 9) 3(G1)	182.158	-69,125	0,671	-289,218	23
B 1 (C 4 H 9) 3(L2)	182.158	-89,177	0,352	-373,118	24 25 26 27
B 1 (C 4 H 9) 3(G2)	182.158	-75,377	2,031	-315,379	28
B 1 (C 4 H 9) 3(L3)	182.158	-78,283	1,000	-327,536	29
B 1 (C 4 H 9) 3(G3)	182.158	-63,983	1,414	-267,705	30
B 1 (C 1 H 2 C 4 H 9) 3(L)	224.239	-104,376	0,508	-453,446	31 32 33
B 1 (C 1 H 2 C 4 H 9) 3(G)	224.239	-91,176	0,777	-381,481	34

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B 1 ( C 6 H 5 ) 3(C )                   242,128     11,522   1,667     48,208  35
B 1 ( C 6 H 5 ) 3(G )                   242,128     31,022   1,740    129,796  36
( C 6 H11 ) 3 B 1(C )                   260,272   -114,628   2,500   -479,604  37
( C 6 H11 ) 3 B 1(G )                   260,272    -95,128   2,693   -398,016  38
( C 6 H13 ) 3 B 1(L )                   266,320   -116,277   0,271   -486,503  39  40
( C 6 H13 ) 3 B 1(G )                   266,320    -95,077   0,764   -397,804  41
( C 7 H15 ) 3 B 1(L )                   308,401   -133,010   0,238   -556,514  42
( C 7 H15 ) 3 B 1(G )                   308,401   -108,610   0,753   -454,424  43
( C 8 H17 ) 3 B 1(L1)                   350,482   -150,500   0,278   -629,692  44
( C 8 H17 ) 3 B 1(G1)                   350,482   -122,900   0,766   -514,214  45
( C 8 H17 ) 3 B 1(L2)                   350,482   -140,800   0,333   -589,107  46
( C 8 H17 ) 3 B 1(G2)                   350,482   -114,200   2,028   -477,813  47
B10 C 2 H12(C1)                         144,218    -40,747   1,667   -170,485  48
B10 C 2 H12(C2)                         144,218    -57,647   1,667   -241,195  49
B10 C 2 H12(C3)                         144,218    -74,447   1,667   -311,486  50
B 1 H 3 C 1 O 1(G )                      41,844    -26,042   0,135   -108,960  51
B 1 H 1 ( O 1 C 1 H 3 ) 2(L )            73,887   -144,473   0,270   -604,475  52
B 1 H 1 ( O 1 C 1 H 3 ) 2(G )            73,887   -138,333   1,036   -578,785  53
B 1 ( O 1 C 1 H 3 ) 3(L )               103,913   -223,038   0,127   -933,191  54
B 1 ( O 1 C 1 H 3 ) 3(G )               103,913   -214,738   0,516   -898,464  55
C 5 H11 O 1 B 1(L )                      97,952    -93,362   0,360   -390,626  56  57
C 6 H 5 B 1 ( O 1 H 1 ) 2(C )           121,931   -172,098   0,213   -720,058  58
C 6 H 5 B 1 ( O 1 H 1 ) 2(A )           121,931   -168,898   0,235   -706,669  59
( C 3 H 7 O 1 ) 2 B 1 H 1(L )           129,995   -182,379   0,202   -763,075  61  62
B 1 ( O 1 C 2 H 5 ) 3(L )               145,994   -250,503   0,132  -1048,105  63
B 1 ( O 1 C 2 H 5 ) 3(G )               145,994   -240,003   0,512  -1004,173  64
( C 4 H 9 ) 2 B 1 O 1 H 1(L )           142,049   -146,340   0,915   -612,287  65  66
( C 4 H 9 ) 2 B 1 O 1 H 1(G )           142,049   -131,340   2,200   -549,527  67
C 9 H21 O 1 B 1(L )                     156,076   -131,950   0,373   -552,077  68  69
B 1 ( O 1 C 3 H 7 ) 3(L )               188,075   -269,553   0,132  -1127,810  70
B 1 ( O 1 C 3 H 7 ) 3(G )               188,075   -257,753   1,009  -1078,439  71
C12 H11 O 1 B 1(L )                     182,029    -77,249   0,837   -323,210  72
C12 H27 O 1 B 1(L )                     198,157   -156,488   0,447   -654,746  73  74
C12 H27 O 2 B 1(L )                     214,157   -227,248   1,118   -950,806  75  76
B 1 ( O 1 C 4 H 9 ) 3(L )               230,156   -286,745   0,129  -1199,741  77  78
B 1 ( O 1 C 4 H 9 ) 3(G )               230,156   -274,245   1,008  -1147,441  79
( C 1 H 3 O 1 ) 4 B 2(L )               145,758   -278,880   0,625  -1166,834  80
( C 1 H 3 O 1 ) 4 B 2(G )               145,758   -268,200   0,626  -1122,149  81
C16 H36 O 1 B 2(L )                     266,083   -212,899   0,830   -890,769  82  83
( C12 H10 ) 2 B 2 O 1(C )               346,043    -84,058   0,714   -351,698  84
( C 6 H 5 B 1 O 1 ) 3(C )               311,746   -301,431   1,000  -1261,186  85
( C 6 H 5 B 1 O 1 ) 3(G )               311,746   -269,931   2,236  -1129,390  86
( C 1 H 3 ) 2 C 1 ( B 2 H 6 ) 2(G )     101,405    -28,570   0,526   -119,537  87
B10 C 2 H11 C 1 O 1 O 1 H 1(C1)         188,228   -129,598   2,500   -542,238  88
B10 C 2 H11 C 1 O 1 O 1 H 1(C2)         188,228   -157,598   2,500   -659,390  89
B10 C 2 H11 C 1 O 1 O 1 H 1(C3)         188,228   -149,798   2,500   -626,755  90
C 1 H 3 B 1 F 2(G )                      63,842    -61,800  10,000   -258,571  91
C 1 H 2 C 1 H 1 B 1 F 2(G )              75,853     49,000   3,333    205,016  92
C 2 H 5 B 1 F 2(G )                      77,849    -76,000   3,333   -317,984  93
C 3 H 7 B 1 F 2(G )                      91,896    -81,000   3,333   -338,904  94
( C 1 H 3 ) 2 O 1 B 1 F 3(L )           113,875   -337,592   0,311  -1412,485  95
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( C 1 H 3 ) 2 O 1 B 1 F 3(G )          113.875  -328,792  0,238  -1375,666  96
( C 2 H 5 ) 2 O 1 B 1 F 3(L )          141.929  -354,262  0,311  -1482,232  97
( C 2 H 5 ) 2 O 1 B 1 F 3(G )          141.929  -343,562  0,238  -1437,463  98
C 6 H 5 B 1CL 2(L )                    158.822   -71,664  0,384   -299,842  60
C 6 H 5 B 1CL 2(G )                    158.822   -60,364  0,554   -252,563  99
( C 4 H 9 ) 2 B 1CL 1(L )              160.495   -99,371  0,921   -415,769 100
( C 4 H 9 ) 2 B 1CL 1(G )              160.495   -87,371  0,969   -365,561 101
( C 6 H 5 ) 2 B 1CL 1(L )              200.475   -31,550  0,853   -132,005 102
( C 6 H 5 ) 2 B 1CL 1(G )              200.475   -21,650  0,972    -90,584 103
C 2 H 4 O 2CL 1 B 1(L )                106.316  -180,516  0,625   -755,279 104
( C 1 H 3 O 1 ) 2 B 1CL 1(L )          108.332  -186,306  0,233   -779,504 105
( C 1 H 3 O 1 ) 2 B 1CL 1(G )          108.332  -178,106  0,382   -745,196 106
C 2 H 5 O 1 B 1CL 2(L )                126.777  -157,387  0,833   -658,507 107
C 2 H 5 O 1 B 1CL 2(G )                126.777  -148,987  0,857   -623,362 108
C 1 H 3 C 1 O 1CL 1 B 1CL 3(L )        195.667  -168,388  0,152   -704,535 109
C 3 H 6 O 2CL 1 B 1(L )                120.343  -191,066  0,323   -799,420 110
( C 2 H 5 O 1 ) 2 B 1CL 1(L )          136.386  -205,403  0,714   -859,406 111
( C 2 H 5 O 1 ) 2 B 1CL 1(G )          136.386  -196,103  0,742   -820,495 112
C 6 H 5 B 1BR 2(L )                    247.724   -41,310  0,384   -172,841 113
C 6 H 5 B 1BR 2(G )                    247.724   -30,810  0,630   -128,909 114
( C 4 H 9 ) 2 B 1BR 1(L )              204.946   -84,893  0,657   -355,193  21  65
( C 4 H 9 ) 2 B 1BR 1(G )              204.946   -72,393  0,724   -302,893 115
( C 6 H 5 ) 2 B 1BR 1(L )              244.926   -15,896  0,927    -66,509 116
( C 6 H 5 ) 2 B 1BR 1(G )              244.926    -1,496  1,054     -6,260 117
( C 4 H 9 ) 2 B 1 I 1(L )              251.947   -66,825  1,021   -279,596  22  66
( C 4 H 9 ) 2 B 1 I 1(G )              251.947   -53,825  1,178   -225,204 118
( C 1 H 3 ) 2 S 1 B 1 H 3(L )           75.964   -20,310  0,260    -84,977 119
( C 1 H 3 ) 2 S 1 B 1 H 3(G )           75.964   -10,210  0,167    -42,719 120
( C 1 H 3 S 1 ) 3 B 1(L )              152.095   -49,815  0,323   -208,426 121
( C 1 H 3 S 1 ) 3 B 1(G )              152.095   -36,915  0,380   -154,452 122
( C 2 H 5 ) 2 S 1 B 1 H 3(G )          104.018   -21,610  0,167    -90,416 123
( C 2 H 5 S 1 ) 3 B 1(L )              194.176   -81,405  0,417   -340,599 124
( C 2 H 5 S 1 ) 3 B 1(G )              194.176   -66,705  0,651   -279,094 125
C 8 H 9 S 2 B 1(L )                    180.090   -32,208  0,553   -134,758 126
C 9 H11 S 2 B 1(L )                    194.117   -36,788  0,633   -153,921 127
( C 3 H 7 S 1 ) 3 B 1(L )              236.257  -100,285  0,625   -419,592 128
( C 3 H 7 S 1 ) 3 B 1(G )              236.257   -79,485  0,800   -332,565 129
( C 4 H 9 S 1 ) 3 B 1(L )              278.338  -116,675  0,323   -488,168 130
( C 4 H 9 S 1 ) 3 B 1(G )              278.338   -93,775  0,595   -392,355 131
( C 5 H11 S 1 ) 3 B 1(L )              320.419  -135,225  0,233   -565,781 132
( C 5 H11 S 1 ) 3 B 1(G )              320.419  -110,225  0,551   -461,181 133
( C 6 H 5 S 1 ) 3 B 1(C )              338.308    16,285  0,323     68,136 134
( C 6 H 5 S 1 ) 3 B 1(G )              338.308    46,285  1,698    193,656 135
C 2 H 4 S 2CL 1 B 1(L )                138.437   -65,688  0,417   -274,839 136
C 3 H 6 S 2CL 1 B 1(L1)                152.464   -72,668  0,417   -304,043 137
C 3 H 6 S 2CL 1 B 1(L2)                152.464   -71,968  0,417   -301,114 138
B 1 H 3 N 1 H 2 C 1 H 3(C )             44.892   -20,920  0,238    -87,529 139
( C 1 H 3 ) 3 N 1 B 1 H 3(G1)           72.946   -19,747  0,263    -82,621 140
( C 1 H 3 ) 3 B 1 N 1 H 3(G2)           72.946   -67,519  1,021   -282,499 141
( C 1 H 3 ) 3 B 1 N 1 H 3(G2)           72.946   -53,719  1,001   -224,760 142
B 1 ( C 1 H 3 ) 3 N 1 H 2 C 1 H 3(C )   86.973   -52,939  1,021   -221,496 143
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B 1 ( C 1 H 3 ) 3 N 1 H 2 C 1 H 3(G )           86,973    -41,239   1,001   -172,543 144
( C 1 H 3 ) 4 N 1 B 1 H 4(C )                   88,989    -38,087   2,500   -159,354 145
( C 1 H 3 ) 4 N 1 B 1 H 4(A )                   88,989    -32,587   2,502   -136,342 146
( C 1 H 3 ) 3 N 1 B 1 ( C 1 H 3 ) 3(C1)        115,027    -66,109   1,021   -276,599 147
( C 1 H 3 ) 3 N 1 B 1 ( C 1 H 3 ) 3(G1)        115,027    -52,109   1,001   -218,023 148
( C 2 H 5 ) 3 N 1 B 1 H 3(L2)                  115,027    -44,428   0,417   -185,886 149
( C 2 H 5 ) 3 N 1 B 1 H 3(G2)                  115,027    -29,928   0,462   -125,218 150
( C 1 H 3 ) 6 N 3 B 1(L )                      143,040    -69,610   0,323   -291,248 151
( C 1 H 3 ) 6 N 3 B 1(G )                      143,040    -58,410   0,380   -244,387 152
C 7 H20 N 1 B 1(C )                            129,054    -78,899   1,021   -330,113 153
C 7 H20 N 1 B 1(G )                            129,054    -62,599   1,001   -261,914 154
( C 4 H 9 ) 2 B 1 N 1 H 2(L1)                  141,065    -88,354   0,625   -369,671 156
( C 4 H 9 ) 2 B 1 N 1 H 2(L2)                  141,065    -90,054   0,625   -376,784 157
( C 4 H 9 ) 2 B 1 N 1 H 1 C 4 H 9(L )          197,173   -108,494   0,559   -453,939 158 159
C 4 H 9 B 1 ( N 1 H 1 C 4 H 9 ) 2(L )          212,187   -120,175   2,500   -502,812 160
B 1 ( N 1 H 1 C 4 H 9 ) 3(L1)                  227,202   -141,532   0,833   -592,172 161
B 1 ( N 1 H 1 C 4 H 9 ) 3(L2)                  227,202   -110,733   0,833   -463,305 162
( C 1 H 3 ) 2 N 1 B 2 H 5(L )                   70,737    -28,286   0,714   -118,349 163
( C 1 H 3 ) 2 N 1 B 2 H 5(G )                   70,737    -21,396   0,716    -89,521 164
B 1 ( O 1 C 1 H 3 ) 3 N 1 H 3(C )              120,944   -254,118   0,553  -1063,230 165
B 1 C 9 N 1 O 1 H22(L )                        171,091   -146,119   0,500   -611,364 166
( C 1 H 3 ) 3 N 1 B 1 F 3(G )                  126,917   -303,972   0,238  -1271,819 167
( C 1 H 3 ) 2 N 1 B 1CL 2(L )                  125,793   -104,652   0,833   -437,864 168
( C 1 H 3 ) 2 N 1 B 1CL 2(G )                  125,793    -95,752   0,887   -400,626 169
( C 1 H 3 ) 4 N 2 B 1CL 1(L )                  134,416    -89,747   0,833   -375,501 170
( C 1 H 3 ) 4 N 2 B 1CL 1(G )                  134,416    -79,747   0,972   -333,661 171
( C 1 H 3 ) 3 P 1 B 1 ( C 1 H 3 ) 3(C )        131,994    -81,239   1,006   -339,903 172
( C 1 H 3 ) 3 P 1 B 1 ( C 1 H 3 ) 3(G )        131,994    -67,739   0,986   -283,419 173
B 1 F 3 P 1 ( C 1 H 3 ) 3(C )                  143,886   -327,002   0,257  -1368,176 174
B 1 F 3 P 1 ( C 1 H 3 ) 3(G )                  143,884   -312,202   0,161  -1306,253 175
( C 1 H 3 ) 3AS 1 B 1 ( C 1 H 3 ) 3(C )        175,942    -49,239   1,001   -206,015 176
B 1 F 3AS 1 ( C 1 H 3 ) 3(C )                  187,832   -291,502   0,238  -1219,644 177
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COMPOUNDS FROM OTHER SECTIONS

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O 2(GS)                                         31,999      0,000   0,000      0,000
H 2 O 1(L )                                     18,015    -68,315   0,000   -285,830
H 2(GS)                                          2,016      0,000   0,000      0,000
H 2 O 2(L )                                     34,015    -44,880   0,000   -187,778
H 2 O 2(AO)                                     34,015    -45,690   0,000   -191,167
H 1 F 1(3,0H2O)                                 20,006    -76,735   0,070   -321,059
H 1CL 1(1500 H2O)                               36,461    -39,848   0,001   -166,724
H 1CL 1(2000 H2O)                               36,461    -39,859   0,001   -166,770
H 1CL 1(5000 H2O)                               36,461    -39,886   0,001   -166,883
H 1CL 1(G )                                     36,461    -22,063   0,003    -92,312
H 1CL 1(4000 H2O)                               36,461    -39,879   0,001   -166,854
H 1CL 1(3000 H2O)                               36,461    -39,873   0,001   -166,829
H 1CL 1(A )                                     36,461    -39,933   0,001   -167,080
H 1CL 1(50 H2O)                                 36,461    -39,502   0,001   -165,276
H 1BR 1(G )                                     80,912     -8,695   0,001    -36,380
H 1BR 1(7000 H2O)                               80,912    -29,002   0,001   -121,344
H 1BR 1(2000 H2O)                               80,912    -28,971   0,001   -121,215
H 1BR 1(1500 H2O)                               80,912    -28,962   0,001   -121,177
H 1 I 1(G )                                    127,913      6,300   0,001     26,359
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H 1 I 1(7000 H2O)                    127.913   -11.566   0.004    -56.760
N 1 H 3(G )                           17.031   -10.980   0.003    -45.940
N 2(GS)                               28.013     0.000   0.000      0.000
C 1 O 2(G )                           44.010   -94.051   0.000   -393.509
C 2 H 4(G )                           28.054    12.450   0.000     52.091
C 1(CS)                               12.011     0.000   0.000      0.000
C 4 H10(G )                           58.124   -30.360   0.000   -127.026
C 4 H 8(G )                           56.108    -4.260   0.000    -17.824
C 6 H 5 O 1 H 1(C )                   94.113   -39.450   0.000   -165.059
C 6 H11 O 1 H 1(L )                  100.161   -83.200   0.000   -348.109
C 6 H12(L )                           84.162   -17.290   0.000    -72.341
C 7 H14(L )                           98.189   -23.330   0.000    -97.613
C 8 H16(L1)                          112.216   -29.110   0.000   -121.796
C 8 H16(L2)                          112.216   -29.110   0.000   -121.796
C 1 O 1(G )                           28.010   -26.417   0.000   -110.529
C 1 H 3 O 1 H 1(A )                   32.042   -58.749   0.000   -245.806
C 1 H 3 O 1 H 1(L )                   32.042   -57.010   0.000   -238.530
( C 1 H 3 ) 2 C 1 O 1(L )             58.080   -59.270   0.000   -247.986
C 3 H 7 O 1 H 1(L2)                   60.096   -76.020   0.000   -318.068
C 2 H 5 O 1 H 1(L )                   46.069   -66.420   0.000   -277.901
C 3 H 7 O 1 H 1(L1)                   60.096   -72.510   0.000   -303.382
C 4 H 9 O 1 H 1(L )                   74.123   -78.290   0.000   -327.565
C 1 H 3 O 1 H 1(25000H2O)             32.042   -58.749   0.000   -245.806
( C 1 H 3 ) 2 O 1(G2)                 46.069   -43.990   0.000   -184.054
C 1 H 3(G )                           15.035    33.200   0.000    138.909
C 1 H 2 C 1 H 1(G )                   27.046   160.000   0.000    669.440
C 2 H 5(G )                           29.062    25.000   0.000    104.600
C 3 H 7(G )                           43.089    15.000   0.000     62.760
( C 2 H 5 ) 2 O 1(G2)                 74.123   -60.260   0.000   -252.128
H 1 O 1 C 1 H 2 C 1 H 2 O 1 H 1(L )   62.069  -108.730   0.000   -454.926
C 2 H 5 O 1 H 1(3500 H2O)             46.069   -68.900   0.000   -288.278
C 1 H 3 C 1 O 1CL 1(L )               78.498   -65.600   0.000   -274.470
C 3 H 6 O 2(L )                       76.096  -119.580   0.000   -500.323
C 2 H 5 O 1 H 1(2500 H2O)             46.069   -68.900   0.000   -288.278
( C 1 H 3 ) 2 S 1(G2)                 62.130    -8.890   0.000    -37.196
C 1 H 3 S 1 H 1(G )                   48.103    -5.400   0.000    -22.594
( C 2 H 5 ) 2 S 1(G2)                 90.184   -19.890   0.000    -83.220
C 2 H 5 S 1 H 1(L )                   62.130   -17.530   0.000    -73.346
H 1 S 1 C 1 H 2 C 1 H 2 S 1 H 1(L )   94.190   -12.840   0.000    -53.723
H 1 S 1 ( C 1 H 2 ) 3 S 1 H 1(L1)    108.217   -18.820   0.000    -72.743
C 3 H 7 S 1 H 1(L )                   76.157   -23.790   0.000    -99.537
C 4 H 9 S 1 H 1(L )                   90.184   -29.720   0.000   -124.348
C 5 H11 S 1 H 1(L )                  104.211   -36.070   0.000   -150.917
C 6 H 5 S 1 H 1(L )                  110.174    15.300   0.000     64.015
C 3 H 8 S 2(L2)                      108.217   -18.820   0.000    -78.743
C 1 H 3 N 1 H 2(G )                   31.058     5.500   0.000     23.012
( C 1 H 3 ) 3 N 1(G )                 59.112    -5.670   0.000    -23.723
( C 1 H 3 ) 2 N 1 H 2CL 1(50 H2O)     81.546   -68.567   0.000   -286.884
( C 2 H 5 ) 2 N 1 H 1(G )             73.139   -17.160   0.000    -71.797
( C 1 H 3 ) 2 N 1 H 1(G )             45.085    -4.660   0.000    -19.497
( C 1 H 3 ) 2 N 1 H 2CL 1(4000 H2O)   81.546   -68.645   0.000   -287.211
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( C 1 H 3 ) 3 P 1(G )                  76,079    -22,500   0,000    -94,140
( C 1 H 3 ) 3AS 1(G )                 120,027      2,800   0,000     11,715
B 2 O 3(AM)                            69,618   -299,637   0,236  -1253,681
H 3 B 1 O 3(C )                        61,832   -261,568   0,117  -1094,401
B 2 H 6(G )                            27,668      9,360   0,264     39,162
B 1(CS)                                10,810      0,000   0,000      0,000
B 2 O 3(C )                            69,618   -303,996   0,235  -1271,919
H 3 B 1 O 3(AO)                        61,832   -256,160   0,117  -1071,773
H 3 B 1 O 3(25030H2O)                  61,832   -256,167   0,117  -1071,803
B 1 F 2(G )                            48,807      0,000   0,000      0,000
B 1 F 3(G )                            67,805   -271,502   0,127  -1135,964
H 3 B 1 O 3(3500 H2O)                  61,832   -256,174   0,117  -1071,832
B 1CL 3(L )                           117,169   -102,108   0,144   -427,220
H 3 B 1 O 3(2500 H2O)                  61,832   -256,175   0,117  -1071,836
( C 1 H 3 ) 3 N 1 B 1 H 3(C1)          72,946    -33,347   0,167   -139,524
H 1 B 1 O 2(C3)                        43,817   -188,520   0,000   -788,768
H 1 B 1 F 4(A )                        87,812   -376,354   0,162  -1574,665
H 3 B 1 O 3(4000 H2O)                  61,832   -256,173   0,117  -1071,828
NA 1 O 1 H 1(C )                       39,997   -101,990   0,000   -426,726
NA 1CL 1(C )                           58,443    -98,232   0,000   -411,003
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REACTIONS

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                                                                                          ΔH°     ERROR
                                                                                           kcal mol-1   REF.

1   2 B 1 ( C 1 H 3 ) 3(L ) +12 O 2(GS) = 1 B 2 O 3(AM) + 6 C 1 O 2(G ) + 9 H 2 O 1(L )     -1410,400  2,00064/14
                                                                                          RESIDUAL   0,045
    2 B 1 ( C 1 H 3 ) 3(L ) +12 O 2(GS) = 1 B 2 O 3(AM) + 6 C 1 O 2(G ) + 9 H 2 O 1(L )     -1410,600  5,000 49/3
                                                                                          RESIDUAL  -0,357

2   1 B 1 ( C 1 H 3 ) 3(L ) + 6 O 2(GS) = 1 H 3 B 1 O 3(C ) + 3 C 1 O 2(G ) + 3 H 2 O 1(L )   -714,500  5,40061/12
                                                                                          RESIDUAL  -0,002

3   1 B 1 ( C 1 H 3 ) 3(L ) = 1 B 1 ( C 1 H 3 ) 3(G )                                          4,830  0,02061/12
                                                                                          RESIDUAL   0,001
    1 B 1 ( C 1 H 3 ) 3(L ) = 1 B 1 ( C 1 H 3 ) 3(G )                                          4,800  0,100 63/6
                                                                                          RESIDUAL  -0,029

4   2 B 1 ( C 2 H 5 ) 3(L ) +21 O 2(GS) = 1 B 2 O 3(AM) +12 C 1 O 2(G ) +15 H 2 O 1(L )     -2360,200  2,00064/15
                                                                                          RESIDUAL   2,118

5   2 B 1 ( C 2 H 5 ) 3(L ) +21 O 2(GS) = 2 H 3 B 1 O 3(C ) +12 C 1 O 2(G ) +12 H 2 O 1(L )  -2378,400  7,20061/12
                                                                                          RESIDUAL   2,472

6   1 B 2 H 6(G ) + 6 C 2 H 4(G ) = 2 B 1 ( C 2 H 5 ) 3(L )                                 -172,500  2,100 63/8
                                                                                          RESIDUAL   2,216

7   1 B 1 ( C 2 H 5 ) 3(L ) = 1 B 1 ( C 2 H 5 ) 3(G )                                          8,800  0,10061/12
    1 B 1 ( C 2 H 5 ) 3(L ) = 1 B 1 ( C 2 H 5 ) 3(G )                                          8,800  0,100 63/8

8  16 C 1(CS) +17 H 2(GS) + 2 B 1(CS) = 2 C 8 H17 B 1(L )                                     -92,800  2,200 66/5
                                                                                          RESIDUAL   0,450

9   2 C 8 H17 B 1(L ) +26 O 2(GS) = 2 H 3 B 1 O 3(C ) +16 C 1 O 2(G ) +14 H 2 O 1(L )      -2891,000  1,000 72/2
                                                                                          RESIDUAL   0,112

10  2 B 1 ( C 3 H 7 ) 3(L1) +30 O 2(GS) = 1 B 2 O 3(AM) +18 C 1 O 2(G ) +21 H 2 O 1(L )     -3294,400  2,00064/15
                                                                                          RESIDUAL  -0,024

11  2 B 1 ( C 3 H 7 ) 3(L1) +30 O 2(GS) = 1 B 2 O 3(C ) +18 C 1 O 2(G ) +21 H 2 O 1(L )     -3298,800  3,100 63/9
                                                                                          RESIDUAL  -0,065

12  2 B 1 ( C 3 H 7 ) 3(L1) +30 O 2(GS) = 2 H 3 B 1 O 3(C ) +18 C 1 O 2(G ) +18 H 2 O 1(L )  -3312,800  3,100 72/2
                                                                                          RESIDUAL   0,130

13  1 B 1 ( C 3 H 7 ) 3(L1) = 1 B 1 ( C 3 H 7 ) 3(G1)                                        10,000  0,500 66/7

14  2 B 1 ( C 3 H 7 ) 3(L2) +30 O 2(GS) = 1 B 2 O 3(AM) +18 C 1 O 2(G ) +21 H 2 O 1(L )     -3287,000  2,00064/15
                                                                                          RESIDUAL  -0.144
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15   2 B 1 ( C 3 H 7 ) 3(L2) +30 O 2(GS) = 1 B 2 O 3(C ) +18 C 1 O 2(G ) +21 H 2 O 1(L )          -3291,400  2,800 63/9
                                                                                               RESIDUAL -0,185
16   2 B 1 ( C 3 H 7 ) 3(L2) +30 O 2(GS) = 2 H 3 B 1 O 3(C ) +18 C 1 O 2(G ) +18 H 2 O 1(L )      -3305,000  2,800 72/2
                                                                                               RESIDUAL  0,413
17   1 B 1 ( C 3 H 7 ) 3(L2) = 1 B 1 ( C 3 H 7 ) 3(G2)                                              10,000  0,500 46/2
18   2 B 1 C10 H21(L ) +32 O 2(GS) = 2 H 3 B 1 O 3(C ) +20 C 1 O 2(G ) +18 H 2 O 1(L )            -3499,200  1,200 72/2
19   2 B 1 ( C 4 H 9 ) 3(L1) +39 O 2(GS) = 1 B 2 O 3(AM) +24 C 1 O 2(G ) +27 H 2 O 1(L )         -4236,400  2,000 64/4
                                                                                               RESIDUAL -2,685
20   2 B 1 ( C 4 H 9 ) 3(L1) +39 O 2(GS) = 2 H 3 B 1 O 3(C ) +24 C 1 O 2(G ) +24 H 2 O 1(L )     -4254,600  4,80061/12
                                                                                               RESIDUAL -2,729
     2 B 1 ( C 4 H 9 ) 3(L1) +39 O 2(GS) = 2 H 3 B 1 O 3(C ) +24 C 1 O 2(G ) +24 H 2 O 1(L )     -4251,200  1,000 66/5
                                                                                               RESIDUAL  0,671
21   1 B 1 ( C 4 H 9 ) 3(L1) + 1 H 1BR 1(G ) = 1 ( C 4 H 9 ) 2 B 1BR 1(L ) + 1 C 4 H10(G )          -22,560  0,500 53/2
                                                                                               RESIDUAL  0,073
22   1 B 1 ( C 4 H 9 ) 3(L1) + 1 H 1 I 1(G ) = 1 ( C 4 H 9 ) 2 B 1 I 1(L ) + 1 C 4 H10(G )          -20,160  1,500 53/2
                                                                                               RESIDUAL -0,600
23   1 B 1 ( C 4 H 9 ) 3(L1) = 1 B 1 ( C 4 H 9 ) 3(G1)                                              14,800  0,500 63/8
24   2 B 1 ( C 4 H 9 ) 3(L2) +39 O 2(GS) = 1 B 2 O 3(AM) +24 C 1 O 2(G ) +27 H 2 O 1(L )         -4218,200  2,00064/15
                                                                                               RESIDUAL  4,011
25   2 B 1 ( C 4 H 9 ) 3(L2) +39 O 2(GS) = 1 B 2 O 3(C ) +24 C 1 O 2(G ) +27 H 2 O 1(L )         -4222,600  1,300 63/9
                                                                                               RESIDUAL  4,770
26   1 B 2 H 6(G ) + 6 C 4 H 8(G ) = 2 B 1 ( C 4 H 9 ) 3(L2)                                      -146,200  1,500 63/8
                                                                                               RESIDUAL 15,955
27   2 B 1 ( C 4 H 9 ) 3(L2) +39 O 2(GS) = 2 H 3 B 1 O 3(C ) +24 C 1 O 2(G ) +24 H 2 O 1(L )     -4236,000  1,300 72/2
                                                                                               RESIDUAL  5,565
28   1 B 1 ( C 4 H 9 ) 3(L2) = 1 B 1 ( C 4 H 9 ) 3(G2)                                              13,800  2,00064/15
29   2 B 1 ( C 4 H 9 ) 3(L3) +39 O 2(GS) = 1 B 2 O 3(AM) +24 C 1 O 2(G ) +27 H 2 O 1(L )         -4244,800  2,00064/15
30   1 B 1 ( C 4 H 9 ) 3(L3) = 1 B 1 ( C 4 H 9 ) 3(G3)                                              14,300  1,00064/15
31   2 B 1 ( C 1 H 2 C 4 H 9 ) 3(L ) +48 O 2(GS) = 1 B 2 O 3(AM) +30 C 1 O 2(G ) +33 H 2 O 1(L )-5159,000  2,00064/15

                                                                                               RESIDUAL -0,190
32   2 B 1 ( C 1 H 2 C 4 H 9 ) 3(L ) +48 O 2(GS) = 1 B 2 O 3(C ) +30 C 1 O 2(G ) +33 H 2 O 1(L )-5163,400  1,600 63/9
          ------------------------------------------------------------------------------------------------------------
                                                                                               RESIDUAL -0,231
33   2 B 1 ( C 1 H 2 C 4 H 9 ) 3(L ) +48 O 2(GS) = 2 H 3 B 1 O 3(C ) +30 C 1 O 2(G ) +30 H 2 O 1-5177,000  1,600 72/2
      (L )
                                                                                               RESIDUAL  0,364
34   1 B 1 ( C 1 H 2 C 4 H 9 ) 3(L ) = 1 B 1 ( C 1 H 2 C 4 H 9 ) 3(G )                              17,200  0,600 63/9
35   1 B 1 ( C 6 H 5 ) 3(C ) + 3 H 2 O 2(L ) = 3 C 6 H 5 O 1 H 1(C ) + 1 H 3 B 1 O 3(C )          -256,800  1,600 67/5
36   1 B 1 ( C 6 H 5 ) 3(C ) = 1 B 1 ( C 6 H 5 ) 3(G )                                              19,500  0,500 67/5
37   1 ( C 6 H11 ) 3 B 1(C ) + 3 H 2 O 2(L ) = 3 C 6 H11 O 1 H 1(L ) + 1 H 3 B 1 O 3(C )          -261,900  2,300 67/5
38   1 ( C 6 H11 ) 3 B 1(C ) = 1 ( C 6 H11 ) 3 B 1(G )                                              19,500  1,000 67/5
39   1 B 2 H 6(G ) + 6 C 6 H12(L ) = 2 ( C 6 H13 ) 3 B 1(L )                                      -136,600  0,80061/13
                                                                                               RESIDUAL  1,575
40   2 ( C 6 H13 ) 3 B 1(L ) +57 O 2(GS) = 2 H 3 B 1 O 3(C ) +36 C 1 O 2(G ) +36 H 2 O 1(L )     -6134,600  0,700 72/2
                                                                                               RESIDUAL  1,157
41   1 ( C 6 H13 ) 3 B 1(L ) = 1 ( C 6 H13 ) 3 B 1(G )                                              21,200  0,700 63/8
42   1 B 2 H 6(G ) + 6 C 7 H14(L ) = 2 ( C 7 H15 ) 3 B 1(L )                                      -135,400  0,40061/13
43   1 ( C 7 H15 ) 3 B 1(L ) = 1 ( C 7 H15 ) 3 B 1(G )                                              24,400  0,700 63/8
44   1 B 2 H 6(G ) + 6 C 8 H16(L1) = 2 ( C 8 H17 ) 3 B 1(L1)                                      -135,700  0,50061/13
45   1 ( C 8 H17 ) 3 B 1(L1) = 1 ( C 8 H17 ) 3 B 1(G1)                                              27,600  0,700 63/8
46   1 B 2 H 6(G ) + 6 C 8 H16(L2) = 2 ( C 8 H17 ) 3 B 1(L2)                                      -116,300  0,60061/13
47   1 ( C 8 H17 ) 3 B 1(L2) = 1 ( C 8 H17 ) 3 B 1(G2)                                              26,600  2,000 63/8
48   2 B10 C 2 H12(C1) +25 O 2(GS) +18 H 2 O 1(L ) =20 H 3 B 1 O 3(C ) + 4 C 1 O 2(G )            -4296,400  2,600 72/2
49   2 B10 C 2 H12(C2) +25 O 2(GS) +18 H 2 O 1(L ) =20 H 3 B 1 O 3(C ) + 4 C 1 O 2(G )            -4262,600  3,200 72/2
50   2 B10 C 2 H12(C3) +25 O 2(GS) +18 H 2 O 1(L ) =20 H 3 B 1 O 3(C ) + 4 C 1 O 2(G )            -4229,000  3,200 72/2
51   2 B 1 H 3 C 1 O 1(G ) = 1 B 2 H 6(G ) + 2 C 1 O 1(G )                                           8,610  0,050 52/4
52   1 B 1 H 1 ( O 1 C 1 H 3 ) 2(L ) + 3 H 2 O 1(L ) = 1 H 2(GS) + 1 H 3 B 1 O 3(AO) + 2 C 1 H 3   -24,240  0,24060/15
      O 1 H 1(A )
53   1 B 1 H 1 ( O 1 C 1 H 3 ) 2(L ) = 1 B 1 H 1 ( O 1 C 1 H 3 ) 2(G )                               6,160  1,00060/15
54   1 B 1 ( O 1 C 1 H 3 ) 3(L ) + 3 H 2 O 1(L ) = 3 C 1 H 3 O 1 H 1(L ) + 1 H 3 B 1 O 3(C )         -4,615  0,050 52/3
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55   1 B 1 ( O 1 C 1 H 3 ) 3(L ) = 1 B 1 ( O 1 C 1 H 3 ) 3(G )                                                8,300  0,500 52/3
56  10 C 1(CS) +11 H 2(GS) + 2 B 1(CS) + 1 O 2(GS) = 2 C 5 H11 O 1 B 1(L )                                -166,600  1,400 70/1
                                                                                                        RESIDUAL  0,124
57   2 C 5 H11 O 1 B 1(L ) +16 O 2(GS) = 2 H 3 B 1 O 3(C ) +10 C 1 O 2(G ) + 8 H 2 O 1(L )             -1825,400  0,800 72/2
                                                                                                        RESIDUAL  0,042
58   1 C 6 H 5 B 1 ( O 1 H 1 ) 2(C ) + 1 H 2 O 2(L ) = 1 C 6 H 5 O 1 H 1(C ) + 1 H 3 B 1 O 3(C )   -84,000  0,400 66/6
                                                                                                        RESIDUAL  0,040
     1 C 6 H 5 B 1 ( O 1 H 1 ) 2(C ) + 1 H 2 O 2(L ) = 1 C 6 H 5 O 1 H 1(C ) + 1 H 3 B 1 O 3(C )   -84,050  0,200 66/6

                                                                                                        RESIDUAL -0,010
59   1 C 6 H 5 B 1 ( O 1 H 1 ) 2(C ) = 1 C 6 H 5 B 1 ( O 1 H 1 ) 2(A )                                        3,200  0,100 66/6
60   1 C 6 H 5 B 1CL 2(L ) + 2 H 2 O 1(L ) = 1 C 6 H 5 B 1 ( O 1 H 1 ) 2(A ) + 2 H 1CL 1(1500 H2   -40,300  0,300 67/5
      O)
61   1 B 2 H 6(G ) + 4 ( C 1 H 3 ) 2 C 1 O 1(L ) = 2 ( C 3 H 7 O 1 ) 2 B 1 H 1(L )                     -137,400  0,70062/14
                                                                                                        RESIDUAL -0,361
62   1 B 2 H 6(G ) + 4 C 3 H 7 O 1 H 1(L2) = 4 H 2(GS) + 2 ( C 3 H 7 O 1 ) 2 B 1 H 1(L )                -69,900  0,40062/14
                                                                                                        RESIDUAL  0,139
63   1 B 1 ( O 1 C 2 H 5 ) 3(L ) + 3 H 2 O 1(L ) = 3 C 2 H 5 O 1 H 1(L ) + 1 H 3 B 1 O 3(C )               -5,380  0,060 52/3
64   1 B 1 ( O 1 C 2 H 5 ) 3(L ) = 1 B 1 ( O 1 C 2 H 5 ) 3(G )                                               10,500  0,500 52/3
65   1 ( C 4 H 9 ) 2 B 1BR 1(L ) + 1 H 2 O 1(L ) = 1 ( C 4 H 9 ) 2 B 1 O 1 H 1(L ) + 1 H 1BR 1(7   -21,960  0,750 53/2
      000 H2O)

                                                                                                        RESIDUAL  0,174
66   1 ( C 4 H 9 ) 2 B 1 I 1(L ) + 1 H 2 O 1(L ) = 1 ( C 4 H 9 ) 2 B 1 O 1 H 1(L ) + 1 H 1 I 1(7    -24,960  0,750 53/2
      000 H2O)

                                                                                                        RESIDUAL -0,174
67   1 ( C 4 H 9 ) 2 B 1 O 1 H 1(L ) = 1 ( C 4 H 9 ) 2 B 1 O 1 H 1(G )                                      15,000  2,000 53/2
68  18 C 1(CS) +21 H 2(GS) + 1 O 2(GS) + 2 B 1(CS) = 2 C 9 H21 O 1 B 1(L )                                -263,600  1,800 70/1
                                                                                                        RESIDUAL  0,099
69   2 C 9 H21 O 1 B 1(L ) +29 O 2(GS) = 2 H 3 B 1 O 3(C ) +18 C 1 O 2(G ) +18 H 2 O 1(L )             -3181,800  0,600 72/2
                                                                                                        RESIDUAL  0,025
70   1 B 1 ( O 1 C 3 H 7 ) 3(L ) + 3 H 2 O 1(L ) = 3 C 3 H 7 O 1 H 1(L1) + 1 H 3 B 1 O 3(C )               -4,600  0,060 52/3
71   1 B 1 ( O 1 C 3 H 7 ) 3(L ) = 1 B 1 ( O 1 C 3 H 7 ) 3(G )                                               11,600  1,000 52/3
72   1 ( C 6 H 5 ) 2 B 1CL 1(L ) + 1 H 2 O 1(L ) = 1 C12 H11 O 1 B 1(L ) + 1 H 1CL 1(2000 H2O)      -17,200  0,200 67/5
                                                                                                        RESIDUAL  0,043
     1 ( C 6 H 5 ) 2 B 1CL 1(L ) + 1 H 2 O 1(L ) = 1 C12 H11 O 1 B 1(L ) + 1 H 1CL 1(2000 H2O)      -17,250  0,080 67/8
                                                                                                        RESIDUAL -0,007
73  24 C 1(CS) +27 H 2(GS) + 1 O 2(GS) + 2 B 1(CS) = 2 C12 H27 O 1 B 1(L )                                -310,000  2,000 70/1
                                                                                                        RESIDUAL  2,976
74   2 C12 H27 O 1 B 1(L ) +36 O 2(GS) = 2 H 3 B 1 O 3(C ) +24 C 1 O 2(G ) +24 H 2 O 1(L )             -4106,200  1,000 72/2
                                                                                                        RESIDUAL  0,744
75  24 C 1(CS) +27 H 2(GS) + 2 O 2(GS) + 2 B 1(CS) = 2 C12 H27 O 2 B 1(L )                                -448,000  4,800 70/1
                                                                                                        RESIDUAL  0,496
76   2 C12 H27 O 2 B 1(L ) +37 O 2(GS) = 2 H 3 B 1 O 3(C ) +24 C 1 O 2(G ) +24 H 2 O 1(L )             -3963,800  2,400 72/2
                                                                                                        RESIDUAL  1,624
77   1 B 1 ( O 1 C 4 H 9 ) 3(L ) + 3 H 2 O 1(L ) = 3 C 4 H 9 O 1 H 1(L ) + 1 H 3 B 1 O 3(C )               -4,660  0,060 52/3
                                                                                                        RESIDUAL  0,088
78   2 B 1 ( O 1 C 4 H 9 ) 3(L ) +36 O 2(GS) = 2 H 3 B 1 O 3(C ) +24 C 1 O 2(G ) +24 H 2 O 1(L )-3850,400  1,200 72/2

                                                                                                        RESIDUAL -3,970
79   1 B 1 ( O 1 C 4 H 9 ) 3(L ) = 1 B 1 ( O 1 C 4 H 9 ) 3(G )                                               12,500  1,000 52/3
80   1 ( C 1 H 3 O 1 ) 4 B 2(L ) + 1 H 2 O 2(AO) + 4 H 2 O 1(L ) = 2 H 3 B 1 O 3(25000H2O) + 4 C -149,500  0,600 72/1
      1 H 3 O 1 H 1(25000H2O)
81   1 ( C 1 H 3 O 1 ) 4 B 2(L ) = 1 ( C 1 H 3 O 1 ) 4 B 2(G )                                               10,680  0,040 72/1
82  32 C 1(CS) +36 H 2(GS) + 1 O 2(GS) + 4 B 1(CS) = 2 C16 H36 O 1 B 2(L )                                -425,600  2,600 70/1
                                                                                                        RESIDUAL  0,[illegible]98
83   1 C16 H36 O 1 B 2(L ) +26 O 2(GS) = 2 H 3 B 1 O 3(C ) +16 C 1 O 2(G ) +15 H 2 O 1(L )             -2839,700  1,100 72/2
                                                                                                        RESIDUAL  0,078
84   1 ( C12 H10 ) 2 B 2 O 1(C ) + 4 H 2 O 2(L ) + 1 H 2 O 1(L ) = 4 C 6 H 5 O 1 H 1(C ) + 2 H 3 -349,000  1,900 66/6
      B 1 O 3(C )
                                                                                                        RESIDUAL  0,043
     1 ( C12 H10 ) 2 B 2 O 1(C ) + 4 H 2 O 2(L ) + 1 H 2 O 1(L ) = 4 C 6 H 5 O 1 H 1(C ) + 2 H 3 -349,050  0,750 66/6
      B 1 O 3(C )
                                                                                                        RESIDUAL -0,007
85   1 ( C 6 H 5 B 1 O 1 ) 3(C ) + 3 H 2 O 2(L ) + 3 H 2 O 1(L ) = 3 C 6 H 5 O 1 H 1(C ) + 3 H 3 -262,000  2,000 66/6
      B 1 O 3(C )
                                                                                                        RESIDUAL  0,038
     1 ( C 6 H 5 B 1 O 1 ) 3(C ) + 3 H 2 O 2(L ) + 3 H 2 O 1(L ) = 3 C 6 H 5 O 1 H 1(C ) + 3 H 3 -262,050  1,100 66/6
      B 1 O 3(C )
                                                                                                        RESIDUAL -0,012
                                                                                                          31,500  2,000 66/6
86   1 ( C 6 H 5 B 1 O 1 ) 3(C ) = 1 ( C 6 H 5 B 1 O 1 ) 3(G )
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87   1 ( C 1 H 3 ) 2 O 1(G2) + 2 B 2 H 6(G ) = 1 ( C 1 H 3 ) 2 O 1 ( B 2 H 6 ) 2(G )                    -5,300  0,100 55/5
88   2 B10 C 2 H11 C 1 O 1 O 1 H 1(C1) +25 O 2(GS) +18 H 2 O 1(L ) =20 H 3 B 1 O 3(C ) + 6 C 1 O-4306,800  3,600 72/2
      2(G )
89   2 B10 C 2 H11 C 1 O 1 O 1 H 1(C2) +25 O 2(GS) +18 H 2 O 1(L ) =20 H 3 B 1 O 3(C ) + 6 C 1 O-4250,800  3,600 72/2
      2(G )
90   2 B10 C 2 H11 C 1 O 1 O 1 H 1(C3) +25 O 2(GS) +18 H 2 O 1(L ) =20 H 3 B 1 O 3(C ) + 6 C 1 O-4266,400  5,800 72/2
      2(G )
91   1 C 1 H 3 B 1 F 2(G ) = 1 C 1 H 3(G ) + 1 B 1 F 2(G )                                              95,000 10,00062/15
92   1 C 1 H 2 C 1 H 1 B 1 F 2(G ) = 1 C 1 H 2 C 1 H 1(G ) + 1 B 1 F 2(G )                             111,000  3,00062/15
93   1 C 2 H 5 B 1 F 2(G ) = 1 C 2 H 5(G ) + 1 B 1 F 2(G )                                             101,000  3,00062/15
94   1 C 3 H 7 B 1 F 2(G ) = 1 C 3 H 7(G ) + 1 B 1 F 2(G )                                              96,000  3,00062/15
95   1 ( C 1 H 3 ) 2 O 1 B 1 F 3(L ) = 1 ( C 1 H 3 ) 2 O 1 B 1 F 3(G )                                   6,800  0,200 42/1
96   1 ( C 1 H 3 ) 2 O 1 B 1 F 3(G ) = 1 ( C 1 H 3 ) 2 O 1(G2) + 1 B 1 F 3(G )                          13,300  0,200 42/1
97   1 ( C 2 H 5 ) 2 O 1 B 1 F 3(L ) = 1 ( C 2 H 5 ) 2 O 1 B 1 F 3(G )                                  10,700  0,20060/16
98   1 ( C 2 H 5 ) 2 O 1 B 1 F 3(G ) = 1 ( C 2 H 5 ) 2 O 1(G2) + 1 B 1 F 3(G )                          11,800  0,20060/16
99   1 C 6 H 5 B 1CL 2(L ) = 1 C 6 H 5 B 1CL 2(G )                                                      11,300  0,400 70/2
100  1 ( C 4 H 9 ) 2 B 1CL 1(L ) + 1 H 2 O 1(L ) = 1 ( C 4 H 9 ) 2 B 1 O 1 H 1(L ) + 1 H 1CL 1(5  -18,540  0,100 55/2
      000 H2O)
101  1 ( C 4 H 9 ) 2 B 1CL 1(L ) = 1 ( C 4 H 9 ) 2 B 1CL 1(G )                                         12,000  0,300 53/2
102  1 ( C 6 H 5 ) 2 B 1CL 1(L ) + 2 H 2 O 2(L ) + 1NA 1 O 1 H 1(C ) = 2 C 6 H 5 O 1 H 1(C ) + 1 -215,400  0,600 67/5
      H 3 B 1 O 3(C ) + 1NA 1CL 1(C )
103  1 ( C 6 H 5 ) 2 B 1CL 1(L ) = 1 ( C 6 H 5 ) 2 B 1CL 1(G )                                          9,900  0,500 67/5
104  1 C 2 H 4 O 2CL 1 B 1(L ) + 3 H 2 O 1(L ) = 1 H 3 B 1 O 3(C ) + 1 H 1CL 1(G ) + 1 H 1 O 1 C   -6,900  0,60064/16
      1 H 2 C 1 H 2 O 1 H 1(L )
105  1 ( C 1 H 3 O 1 ) 2 B 1CL 1(L ) + 3 H 2 O 1(L ) = 1 H 3 B 1 O 3(C ) + 2 C 1 H 3 O 1 H 1(L )   -6,400  0,20061/15
      + 1 H 1CL 1(G )
106  1 ( C 1 H 3 O 1 ) 2 B 1CL 1(L ) = 1 ( C 1 H 3 O 1 ) 2 B 1CL 1(G )                                  8,200  0,50061/15
107  1 C 2 H 5 O 1 B 1CL 2(L ) + 3 H 2 O 1(L ) = 1 H 3 B 1 O 3(3500 H2O) + 2 H 1CL 1(4000 H2O) +  -42,500  0,800 54/4
      1 C 2 H 5 O 1 H 1(3500 H2O)
108  1 C 2 H 5 O 1 B 1CL 2(L ) = 1 C 2 H 5 O 1 B 1CL 2(G )                                              8,400  0,200 54/4
109  1 B 1CL 3(L ) + 1 C 1 H 3 C 1 O 1CL 1(L ) = 1 C 1 H 3 C 1 O 1CL 1 B 1CL 3(L )                     -0,680  0,050 58/5
110  1 C 3 H 6 O 2CL 1 B 1(L ) + 3 H 2 O 1(L ) = 1 H 3 B 1 O 3(C ) + 1 H 1CL 1(G ) + 1 C 3 H 8 O   -7,200  0,300 64/5
      2(L )
111  1 ( C 2 H 5 O 1 ) 2 B 1CL 1(L ) + 3 H 2 O 1(L ) = 1 H 3 B 1 O 3(2500 H2O) + 1 H 1CL 1(3000    -23,500  0,700 54/4
      H2O) + 2 C 2 H 5 O 1 H 1(2500 H2O)
112  1 ( C 2 H 5 O 1 ) 2 B 1CL 1(L ) = 1 ( C 2 H 5 O 1 ) 2 B 1CL 1(G )                                  9,300  0,200 54/4
113  1 C 6 H 5 B 1BR 2(L ) + 2 H 2 O 1(L ) = 1 C 6 H 5 B 1 ( O 1 H 1 ) 2(A ) + 2 H 1BR 1(2000 H2  -46,900  0,300 67/5
      O)
114  1 C 6 H 5 B 1BR 2(L ) = 1 C 6 H 5 B 1BR 2(G )                                                     10,500  0,500 67/5
115  1 ( C 4 H 9 ) 2 B 1BR 1(L ) = 1 ( C 4 H 9 ) 2 B 1BR 1(G )                                         12,500  0,300 53/2
116  1 ( C 6 H 5 ) 2 B 1BR 1(L ) + 1 H 2 O 1(L ) = 1 C12 H11 O 1 B 1(L ) + 1 H 1BR 1(1500 H2O)      -22,000  0,400 67/5
117  1 ( C 6 H 5 ) 2 B 1BR 1(L ) = 1 ( C 6 H 5 ) 2 B 1BR 1(G )                                         14,400  0,500 67/5
118  1 ( C 4 H 9 ) 2 B 1 I 1(L ) = 1 ( C 4 H 9 ) 2 B 1 I 1(G )                                         13,000  0,600 53/2
119  1 ( C 1 H 3 ) 2 S 1 B 1 H 3(L ) = 1 ( C 1 H 3 ) 2 S 1 B 1 H 3(G )                                  10,100  0,200 59/6
120  2 ( C 1 H 3 ) 2 S 1 B 1 H 3(G ) = 1 B 2 H 6(G ) + 2 ( C 1 H 3 ) 2 S 1(G2)                          12,000  0,200 59/6
121  1 ( C 1 H 3 S 1 ) 3 B 1(L ) + 3 H 2 O 1(L ) = 3 C 1 H 3 S 1 H 1(G ) + 1 H 3 B 1 O 3(AO)        -17,600  0,300 67/7
122  1 ( C 1 H 3 S 1 ) 3 B 1(L ) = 1 ( C 1 H 3 S 1 ) 3 B 1(G )                                         12,900  0,200 67/7
123  2 ( C 2 H 5 ) 2 S 1 B 1 H 3(G ) = 2 ( C 2 H 5 ) 2 S 1(G2) + 1 B 2 H 6(G )                          12,800  0,200 59/6
124  1 ( C 2 H 5 S 1 ) 3 B 1(L ) + 3 H 2 O 1(L ) = 3 C 2 H 5 S 1 H 1(L ) + 1 H 3 B 1 O 3(AO)        -22,400  0,400 66/7
125  1 ( C 2 H 5 S 1 ) 3 B 1(L ) = 1 ( C 2 H 5 S 1 ) 3 B 1(G )                                         14,700  0,500 66/7
126  1 C 8 H 9 S 2 B 1(L ) + 2 H 2 O 1(L ) = 1 H 1 S 1 C 1 H 2 C 1 H 2 S 1 H 1(L ) + 1 C 6 H 5 B  -12,900  0,500 66/7
      1 ( O 1 H 1 ) 2(A )
127  1 C 9 H11 S 2 B 1(L ) + 2 H 2 O 1(L ) = 1 H 1 S 1 ( C 1 H 2 ) 3 S 1 H 1(L1) + 1 C 6 H 5 B 1  -14,300  0,600 66/7
      ( O 1 H 1 ) 2(A )
128  1 ( C 3 H 7 S 1 ) 3 B 1(L ) + 3 H 2 O 1(L ) = 3 C 3 H 7 S 1 H 1(L ) + 1 H 3 B 1 O 3(AO)        -22,300  0,600 67/7
129  1 ( C 3 H 7 S 1 ) 3 B 1(L ) = 1 ( C 3 H 7 S 1 ) 3 B 1(G )                                         20,800  0,500 67/7
130  1 ( C 4 H 9 S 1 ) 3 B 1(L ) + 3 H 2 O 1(L ) = 3 C 4 H 9 S 1 H 1(L ) + 1 H 3 B 1 O 3(AO)        -23,700  0,300 67/7
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131  1 ( C 4 H 9 S 1 ) 3 B 1(L ) = 1 ( C 4 H 9 S 1 ) 3 B 1(G )                                      22,900  0,500 67/7

132  1 ( C 5 H11 S 1 ) 3 B 1(L ) + 3 H 2 O 1(L ) = 3 C 5 H11 S 1 H 1(L ) + 1 H 3 B 1 O 3(AO)        -24,200  0,200 67/7

133  1 ( C 5 H11 S 1 ) 3 B 1(L ) = 1 ( C 5 H11 S 1 ) 3 B 1(G )                                      25,000  0,500 67/7

134  1 ( C 6 H 5 S 1 ) 3 B 1(C ) + 3 H 2 O 1(L ) = 3 C 6 H 5 S 1 H 1(L ) + 1 H 3 B 1 O 3(AO)        -21,600  0,300 67/7

135  1 ( C 6 H 5 S 1 ) 3 B 1(C ) = 1 ( C 6 H 5 S 1 ) 3 B 1(G )                                      30,000  1,600 67/7

136  1 C 2 H 4 S 2CL 1 B 1(L ) + 3 H 2 O 1(L ) = 1 H 1 S 1 C 1 H 2 C 1 H 2 S 1 H 1(L ) + 1 H 3 B   -36,300  0,400 66/7
      1 O 3(AO) + 1 H 1CL 1(A )

137  1 C 3 H 6 S 2CL 1 B 1(L1) + 3 H 2 O 1(L ) = 1 H 1 S 1 ( C 1 H 2 ) 3 S 1 H 1(L1) + 1 H 3 B 1   -37,300  0,400 66/7
      O 3(AO) + 1 H 1CL 1(A )

138  1 C 3 H 6 S 2CL 1 B 1(L2) + 3 H 2 O 1(L ) = 1 C 3 H 8 S 2(L2) + 1 H 3 B 1 O 3(AO) + 1 H 1CL   -36,000  0,400 66/7
      1(A )

139  2 C 1 H 3 N 1 H 2(G ) + 1 B 2 H 6(G ) = 2 B 1 H 3 N 1 H 2 C 1 H 3(C )                          -62,200  0,400 56/5

140  1 ( C 1 H 3 ) 3 N 1 B 1 H 3(C1) = 1 ( C 1 H 3 ) 3 N 1 B 1 H 3(G1)                              13,600  0,200 66/1

141  1 ( C 1 H 3 ) 3 B 1 N 1 H 3(C2) = 1 ( C 1 H 3 ) 3 B 1 N 1 H 3(G2)                              13,600  0,200 44/1

142  1 ( C 1 H 3 ) 3 B 1 N 1 H 3(G2) = 1 N 1 H 3(G ) + 1 B 1 ( C 1 H 3 ) 3(G )                      13,400  0,200 44/1

143  1 B 1 ( C 1 H 3 ) 3 N 1 H 2 C 1 H 3(C ) = 1 B 1 ( C 1 H 3 ) 3 N 1 H 2 C 1 H 3(G )              11,700  0,200 44/1

144  1 B 1 ( C 1 H 3 ) 3 N 1 H 2 C 1 H 3(G ) = 1 B 1 ( C 1 H 3 ) 3(G ) + 1 C 1 H 3 N 1 H 2(G )      17,400  0,200 44/1

145  4 ( C 1 H 3 ) 4 N 1 B 1 H 4(C ) +35 O 2(GS) =16 C 1 O 2(G ) + 2 N 2(GS) +30 H 2 O 1(L ) + 4-4156,000  8,00060/15
      H 1 B 1 O 2(C3)

146  1 ( C 1 H 3 ) 4 N 1 B 1 H 4(C ) = 1 ( C 1 H 3 ) 4 N 1 B 1 H 4(A )                               5,500  0,10060/15

147  1 ( C 1 H 3 ) 3 N 1 B 1 ( C 1 H 3 ) 3(C1) = 1 ( C 1 H 3 ) 3 N 1 B 1 ( C 1 H 3 ) 3(G1)          14,000  0,200 44/1

148  1 ( C 1 H 3 ) 3 N 1 B 1 ( C 1 H 3 ) 3(G1) = 1 B 1 ( C 1 H 3 ) 3(G ) + 1 ( C 1 H 3 ) 3 N 1(G   17,100  0,200 44/1
      )

149  4 ( C 2 H 5 ) 3 N 1 B 1 H 3(L2) +45 O 2(GS) +16 H 1 F 1(3,0H2O) =24 C 1 O 2(G ) + 2 N 2(GS)-5226,400  1,120 67/6
      + 4 H 1 B 1 F 4(A ) +42 H 2 O 1(L )

150  1 ( C 2 H 5 ) 3 N 1 B 1 H 3(L2) = 1 ( C 2 H 5 ) 3 N 1 B 1 H 3(G2)                              14,500  0,200 67/6

151  1 ( C 1 H 3 ) 6 N 3 B 1(L ) + 3 H 2 O 1(L ) + 3 H 1CL 1(50 H2O) = 1 H 3 B 1 O 3(AO) + 3 ( C   -68,800  0,300 53/3
      1 H 3 ) 2 N 1 H 2CL 1(50 H2O)

152  1 ( C 1 H 3 ) 6 N 3 B 1(L ) = 1 ( C 1 H 3 ) 6 N 3 B 1(G )                                      11,200  0,200 53/3

153  1 C 7 H20 N 1 B 1(C ) = 1 C 7 H20 N 1 B 1(G )                                                  16,300  0,200 47/1

154  1 C 7 H20 N 1 B 1(G ) = 1 ( C 2 H 5 ) 2 N 1 H 1(G ) + 1 B 1 ( C 1 H 3 ) 3(G )                  16,100  0,200 47/1

155 16 C 1(CS) +20 H 2(GS) + 1 N 2(GS) + 2 B 1(CS)                                                -190,400  1,800 70/1
                                                                                                 RESIDUAL*-190,400

156  4 ( C 4 H 9 ) 2 B 1 N 1 H 2(L1) +55 O 2(GS) = 4 H 3 B 1 O 3(C ) +32 C 1 O 2(G ) +34 H 2 O 1-6025,200  2,600 72/2
     (L ) + 2 N 2(GS)

157  4 ( C 4 H 9 ) 2 B 1 N 1 H 2(L2) +55 O 2(GS) = 4 H 3 B 1 O 3(C ) +32 C 1 O 2(G ) +34 H 2 O 1-6018,400  2,600 72/2
     (L ) + 2 N 2(GS)

158 24 C 1(CS) +28 H 2(GS) + 1 N 2(GS) + 2 B 1(CS) = 2 ( C 4 H 9 ) 2 B 1 N 1 H 1 C 4 H 9(L )       -216,000  2,600 70/1
                                                                                                 RESIDUAL  0,988

159  4 ( C 4 H 9 ) 2 B 1 N 1 H 1 C 4 H 9(L ) +79 O 2(GS) = 4 H 3 B 1 O 3(C ) +48 C 1 O 2(G ) +50-8542,000  2,400 72/2
      H 2 O 1(L ) + 2 N 2(GS)
                                                                                                 RESIDUAL  0,494

160  2 C 4 H 9 B 1 ( N 1 H 1 C 4 H 9 ) 2(L ) +40 O 2(GS) = 2 H 3 B 1 O 3(C ) +24 C 1 O 2(G ) +26-4316,200  6,200 72/2
      H 2 O 1(L ) + 2 N 2(GS)

161  4 B 1 ( N 1 H 1 C 4 H 9 ) 3(L1) +81 O 2(GS) = 4 H 3 B 1 O 3(C ) +54 H 2 O 1(L ) +48 C 1 O 2-8683,600  3,200 72/2
     (G ) + 6 N 2(GS)

162  4 B 1 ( N 1 H 1 C 4 H 9 ) 3(L2) +81 O 2(GS) = 4 H 3 B 1 O 3(C ) +54 H 2 O 1(L ) +48 C 1 O 2-8806,800  3,200 72/2
     (G ) + 6 N 2(GS)

163  1 ( C 1 H 3 ) 2 N 1 B 2 H 5(L ) + 6 H 2 O 1(L ) = 1 ( C 1 H 3 ) 2 N 1 H 1(G ) + 2 H 3 B 1 O   -89,620  0,65061/14
      3(C ) + 5 H 2(GS)

164  1 ( C 1 H 3 ) 2 N 1 B 2 H 5(L ) = 1 ( C 1 H 3 ) 2 N 1 B 2 H 5(G )                               6,890  0,05061/14

165  1 B 1 ( O 1 C 1 H 3 ) 3 N 1 H 3(C ) = 1 B 1 ( O 1 C 1 H 3 ) 3(G ) + 1 N 1 H 3(G )              28,400  0,200 59/7

166  4 B 1 C 9 N 1 O 1 H22(L ) +59 O 2(GS) = 4 H 3 B 1 O 3(C ) +36 C 1 O 2(G ) +38 H 2 O 1(L ) +-6443,600  1,600 72/2
      2 N 2(GS)

167  1 ( C 1 H 3 ) 3 N 1 B 1 F 3(G ) = 1 ( C 1 H 3 ) 3 N 1(G ) + 1 B 1 F 3(G )                      26,800  0,200 56/5

168  1 ( C 1 H 3 ) 2 N 1 B 1CL 2(L ) + 3 H 2 O 1(L ) = 1 H 3 B 1 O 3(4000 H2O) + 1 ( C 1 H 3 ) 2   -55,100  0,800 54/5
      N 1 H 2CL 1(4000 H2O) + 1 H 1CL 1(4000 H2O)

169  1 ( C 1 H 3 ) 2 N 1 B 1CL 2(L ) = 1 ( C 1 H 3 ) 2 N 1 B 1CL 2(G )                               8,900  0,300 54/5

170  1 ( C 1 H 3 ) 4 N 2 B 1CL 1(L ) + 3 H 2 O 1(L ) + 1 H 1CL 1(50 H2O) = 1 H 3 B 1 O 3(AO) + 2   -59,100  0,800 54/5
      ( C 1 H 3 ) 2 N 1 H 2CL 1(50 H2O)

171  1 ( C 1 H 3 ) 4 N 2 B 1CL 1(L ) = 1 ( C 1 H 3 ) 4 N 2 B 1CL 1(G )                              10,000  0,500 54/5
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172   1 ( C 1 H 3 ) 3 P 1 B 1 ( C 1 H 3 ) 3(C ) = 1 ( C 1 H 3 ) 3 P 1 B 1 ( C 1 H 3 ) 3(G )            13,500  0,200 49/4
173   1 ( C 1 H 3 ) 3 P 1 B 1 ( C 1 H 3 ) 3(G ) = 1 ( C 1 H 3 ) 3 P 1(G ) + 1 B 1 ( C 1 H 3 ) 3(G    15,900  0,100 49/4
        )
174   1 B 1 F 3 P 1 ( C 1 H 3 ) 3(C ) = 1 B 1 F 3 P 1 ( C 1 H 3 ) 3(G )                               14,800  0,200 52/4
175   1 B 1 F 3 P 1 ( C 1 H 3 ) 3(G ) = 1 ( C 1 H 3 ) 3 P 1(G ) + 1 B 1 F 3(G )                       18,200  0,100 52/4
176   1 ( C 1 H 3 ) 3AS 1 B 1 ( C 1 H 3 ) 3(C ) = 1 ( C 1 H 3 ) 3AS 1(G ) + 1 B 1 ( C 1 H 3 ) 3(G    22,700  0,200 51/2
        )
177   1 B 1 F 3AS 1 ( C 1 H 3 ) 3(C ) = 1 ( C 1 H 3 ) 3AS 1(G ) + 1 B 1 F 3(G )                       22,800  0,200 51/2
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COMPOUND	FORMULA WEIGHT	ΔH_f° kcal mol^{-1}	ERROR	ΔH_f° kJ mol^{-1}	REACTIONS FOR ΔH_f°
B 1(CS)	10.810	0.000	0.000	0.000	0
B 1(L)	10.810	5.260	1.000	22.008	1
B 1 +(G)	10.810	326.100	1.429	1364.402	2
B 2(G)	21.620	192.700	5.000	806.257	3
B 1 O 1(G)	26.809	-44.800	5.000	-187.443	4
B 1 O 2(G)	42.809	-74.338	2.519	-311.031	5
B 1 O 2 -(A)	42.809	-184.600	0.100	-772.366	6
B 2 O 1(G)	37.619	23.000	5.000	96.232	7
B 2 O 2(G)	53.619	-105.780	2.411	-442.585	8 9 10
B 2 O 3(L)	69.618	-297.416	0.617	-1244.390	8 11 12 42 52 55
B 2 O 3(G)	69.618	-196.573	4.002	-822.463	9 12
B 1 H 1(G)	11.818	104.653	1.429	437.868	13
B 1 H 2(G)	12.826	46.180	2.500	193.217	14
B 1 H 3(G)	13.834	24.280	2.500	101.588	15
B 1 H 4 -(A)	14.842	11.510	0.100	48.158	16
B 4 H10(G)	53.320	16.888	1.250	70.659	17
B 5 H 9(L)	63.122	11.164	1.250	46.709	18
B 5 H 9(G)	63.122	18.424	1.250	77.085	19
B 5 H11(L)	65.138	17.500	1.000	73.220	20
B 5 H11(G)	65.138	26.060	1.667	109.035	21
B 6 H10(L)	74.940	13.450	0.100	56.275	22
B 6 H10(G)	74.940	24.232	2.500	101.387	23
B10 H14(C)	122.212	-7.279	1.562	-30.457	24 25 27
B10 H14(L)	122.212	-2.049	1.562	-8.572	25 28
B10 H14(G)	122.212	10.770	1.562	45.063	26 27 28
H 1 B 1 O 2(C1)	43.817	-189.866	0.109	-794.400	29 37 38
H 1 B 1 O 2(C2)	43.817	-189.800	0.333	-794.123	30
H 1 B 1 O 2(C3)	43.817	-188.000	0.333	-786.592	31
H 1 B 1 O 2(G)	43.817	-140.074	2.519	-586.069	32
B 1 (O 1 H 1) 2(G)	44.825	-114.000	10.000	-476.976	33
H 2 B 1 O 1 H 1(G)	29.833	-69.169	0.333	-289.404	34
H 1 B 1 (O 1 H 1) 2(G)	45.833	-153.119	0.276	-640.649	35
H 3 B 1 O 3(G)	61.832	-237.258	0.625	-992.687	36
B 2 (O 1 H 1) 4(C)	89.650	-334.655	5.000	-1400.197	39
B 2 (O 1 H 1) 4(G)	89.650	-307.000	5.000	-1284.488	40
B 3 O 3 H 3(C)	83.452	-301.860	1.171	-1262.982	41
(B 1 O 1 H 1) 3(G)	83.452	-291.160	0.610	-1218.213	42 43 44 64
(H 1 B 1 O 2) 3(G)	131.450	-555.267	1.907	-2323.237	45
B 1 F 1(G)	29.808	-28.741	2.425	-120.254	46 47 48
B 1 F 2(G)	48.807	-130.000	5.000	-543.920	49
B 1 F 4 -(A)	86.804	-376.400	1.000	-1574.858	50
B 2 F 4(G)	97.616	-344.200	1.000	-1440.133	51
B 1 O 1 F 1(G)	45.808	-143.544	0.947	-600.587	52 53
B 1 O 1 F 2(G)	64.806	-250.000	5.000	-1046.000	54

(B 1 O 1 F 1) 3(G)	137.423	-565.102	0.632	-2364.387	53 56 63	55 62
B 1 H 1 F 2(G)	49.815	-176.381	0.333	-737.979	57	
B 1 (O 1 H 1) 2 F 1(G)	63.823	-249.373	0.515	-1043.375	58	
B 1 O 1 H 1 F 2(G)	65.814	-260.687	0.305	-1090.716	59	
B 1 F 3 O 1 H 1 -(A)	84.813	-365.000	1.000	-1527.160	60	
B 3 O 3 F 1 H 2(G)	101.443	-382.993	0.950	-1602.441	61 64	63
B 3 O 3 F 2 H 1(G)	119.433	-476.483	1.244	-1993.603	62 64	63
B 3 F 4 O 3 O 1 H 1--(A)	173.429	-753.500	5.000	-3152.644	65	
B 1CL 1(G)	46.263	32.489	1.429	135.934	66	
B 1CL 1 +(G)	46.263	269.139	0.526	1126.078	67	
B 1CL 2(G)	81.716	-150.179	2.244	-628.349	68	
B 1CL 2 +(G)	81.716	158.228	0.526	662.026	69	
B 1CL 3 +(G)	117.169	171.017	0.526	715.535	70	
B 2CL 2 +(G)	92.526	86.571	2.241	362.213	71	
B 2CL 3 +(G)	127.979	-16.340	2.182	-68.367	72	
B 2CL 4(L)	163.432	-260.966	2.000	-1091.882	73	
B 2CL 4(G)	163.432	-253.051	2.124	-1058.765	74	
B 2CL 4 +(G)	163.432	-15.051	2.182	-62.973	75	
B 1 O 1CL 1(G)	62.262	-75.000	1.679	-313.799	76	
(B 1 O 1CL 1) 3(G)	186.787	-388.589	1.175	-1625.857	77	
(B 1 O 1CL 1) 4(G)	249.050	-502.000	10.000	-2100.368	78	
B 1CL 2 H 1(G)	82.724	-59.671	0.204	-249.662	79	80
B 3 O 3 H 2CL 1(G)	117.897	-314.000	5.000	-1313.776	81	
B 3 O 3 H 1CL 2(G)	152.342	-339.000	5.000	-1418.376	82	
B 1CL 1 F 1(G)	65.261	-140.089	3.709	-586.134	83	
B 1CL 1 F 2(G)	84.260	-212.672	0.196	-889.821	84	
B 1CL 2 F 1(G)	100.714	-154.123	0.208	-644.849	85	
B 1BR 1(G)	90.714	53.735	2.500	224.827	86	
B 1BR 2(G)	170.618	15.000	10.000	62.760	87	
B 1BR 3(L)	250.522	-57.141	1.000	-239.078	88	
B 1BR 3(G)	250.522	-48.941	1.414	-204.769	89	
B 1 O 1BR 1(G)	106.713	-110.565	7.071	-462.604	90	
B 1BR 2 H 1(G)	171.626	-25.000	5.000	-104.600	91	
B 1BR 1 F 1(G)	109.712	-57.500	6.124	-240.580	92	
B 1BR 1 F 2(G)	128.711	-197.315	1.732	-825.566	93	
B 1 F 1BR 2(G)	189.616	-123.128	1.915	-515.168	94	
B 1BR 1CL 1(G)	126.167	-67.589	5.702	-282.794	95	
B 1CL 2BR 1(G)	161.620	-80.636	1.732	-337.380	96	
B 1CL 1BR 2(G)	206.071	-64.788	1.915	-271.074	97	
B 1 I 1(G)	137.715	73.000	5.000	305.432	98	
B 1 I 2(G)	264.619	58.000	10.000	242.672	99	
B 1 I 3(C)	391.523	-9.937	1.000	-41.576	100	
B 1 I 3(G)	391.523	5.563	1.744	23.276	101	
B 1 S 1(G)	42.870	79.080	10.000	330.871	102	
B 1 S 2(G)	74.930	29.000	1.000	121.336	103	
B 2 S 2(G)	85.740	36.000	1.000	150.624	104	
B 2 S 3(C)	117.800	-57.500	1.000	-240.580	105	
B 2 S 3(G)	117.800	16.000	1.000	66.944	106	
S 1 F 4 B 1 F 3(C)	175.859	-484.000	1.000	-2025.056	107	

B 1 N 1(G)	24.817	154.072	1.300	644.637	108
(N 1 H 3) 2 B 2 H 6(C)	61.729	-46.000	1.000	-192.464	109
B 3 N 3 H 6(L)	80.498	-129.300	1.000	-540.991	110
B 3 N 3 H 6(G)	80.498	-122.310	1.000	-511.745	111
B10 H18 N 2(C)	154.257	-70.503	3.333	-294.984	112
N 1 H 4 B 1 O 2(A)	60.847	-216.270	1.000	-904.874	113
N 1 H 4 B 1 O 2(220H2O)	60.847	-216.000	1.000	-903.744	114
N 1 H 4 B 1 O 3(A)	76.847	-195.400	1.000	-817.554	115
(N 1 H 4 B 1 O 3) 2 H 2 O 1(C)	171.709	-238.300	1.000	-997.047	116
N 1 H 3 B 1 F 3(C)	84.836	-323.600	1.000	-1353.942	117
B 3 N 3 H 3CL 3(C)	183.833	-254.963	0.769	-1066.765	118
B 3 N 3 H 3CL 3(G)	183.833	-237.863	1.262	-995.219	119
B 1 P 1(C)	41.784	-19.000	1.000	-79.496	120
B13 P 2(C)	202.478	-40.000	1.000	-167.360	121
(P 1 H 3) 2 B 2 H 6(C)	95.664	-27.000	1.000	-112.968	122
P 1 F 3 B 1 H 3(G)	101.803	-204.100	1.000	-853.954	123
P 1 O 1CL 3 B 1CL 3(C)	270.501	-256.300	1.000	-1072.359	124
P 1 H 3 B 1CL 3(C)	151.167	-120.900	1.000	-505.846	125
B 1 C 2(G)	34.832	169.750	2.500	710.234	126
PB 1 O 1 B 2 O 3(C)	292.818	-379.536	5.000	-1587.979	127
PB 1 O 1 (B 2 O 3) 2(C)	362.436	-683.632	2.000	-2860.316	128
PB 1 O 1 (B 2 O 3) 3(C)	432.054	-1004.828	2.000	-4204.200	129
(PB 1 O 1) 2 (B 2 O 3) 5(C)	794.490	-1696.660	2.500	-7098.825	130
AL 1 B 2(C)	48.601	-17.651	3.333	-73.853	131
AL 1 B12(C)	156.702	-63.446	0.995	-265.456	132 133
AL 1 B 1 O 2(G)	69.790	-129.400	3.333	-541.410	134
AL 1 (B 1 H 4) 3(L)	71.508	-76.000	3.333	-317.984	135
AL 1 (B 1 H 4) 3(G)	71.508	-68.400	3.480	-286.186	136
CR 1 B 2(C)	73.616	-31.000	5.000	-129.704	137
MO 1 B 1(C)	106.750	-21.000	5.000	-87.864	138
MO 2 B 1(C)	202.690	-29.000	5.000	-121.336	139
V 1 B 2(C)	72.561	-24.000	5.000	-100.416	140
NB 1 B 2(C)	114.526	-36.000	5.000	-150.624	141
TA 1 B 2(C)	202.568	-51.700	1.000	-216.313	142
TI 1 B 1(C)	58.710	-38.300	10.000	-160.247	143
TI 1 B 2(C)	69.520	-77.080	0.909	-322.501	144
TI 1 B 2(L)	69.520	-45.000	5.000	-188.280	145
ZR 1 B 2(C)	112.840	-78.702	1.118	-329.287	146 147
ZR 1 B 2(L)	112.840	-54.190	0.100	-226.731	148
HF 1 B 2(C)	200.110	-78.600	2.000	-328.862	149
BE 1 B 1 O 2(G)	51.821	-115.200	10.000	-481.997	150
BE 1 B 2 O 4(G)	94.630	-323.000	10.000	-1351.432	151
BE 3 B 2 O 6(C)	144.653	-741.960	2.000	-3104.361	152
MG 1 B 2(C)	45.925	-21.950	2.600	-91.839	153
MG 1 B 4(C)	67.545	-25.100	1.429	-105.018	154
LI 1 B 1 O 2(C)	49.750	-244.884	0.102	-1024.593	155 158
LI 1 B 1 O 2(L)	49.750	-240.414	0.143	-1005.890	156
LI 1 B 1 O 2(G)	49.750	-161.974	0.143	-677.698	157
LI 1 B 1 H 4(C)	21.783	-45.775	0.154	-191.523	163
LI 2 B 4 O 7(C)	169.118	-803.600	1.000	-3362.262	159
LI 2 B 4 O 7(L)	169.118	-792.900	1.667	-3317.494	160

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LI 2 B 6 O10(C )                 238.736  -1107.449  2.105  -4633.566 161
LI 2 B 8 O13(C )                 308.354  -1405.415  2.471  -5880.257 162
NA 1 B 1 O 2(C )                  65.799   -233.998  0.128   -979.048 164
NA 1 B 1 O 2(L )                  65.799   -229.338  0.163   -959.550 166
NA 1 B 1 O 2(G )                  65.799   -160.998  3.336   -673.616 165
NA 2 B 4 O 7(C )                 201.215   -779.433  1.589  -3261.146 167
NA 2 B 4 O 7(L )                 201.215   -774.633  1.589  -3241.063 168
NA 2 B 6 O10(C )                 270.834  -1089.169  1.855  -4557.082 169
NA 1 B 1 H 4(C )                  37.832    -44.964  0.154   -188.129 170
 K 2 B 4 O 7(C )                 233.440   -796.900  1.000  -3334.230 171
 K 2 B 4 O 7(L )                 233.440   -786.100  1.000  -3289.042 172
 K 2 B 6 O10(C )                 303.058  -1101.449  2.105  -4608.462 173
 K 2 B 8 O13(C )                 372.676  -1413.065  2.664  -5912.264 174
 K 2 B 8 O13(L )                 372.676  -1395.715  2.471  -5839.672 175
 K 1 B 1 H 4(C )                  53.944    -54.115  0.455   -226.417 176
 K 1 B 1 F 4(C )                 125.906   -413.785  0.323  -1731.277 177
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COMPOUNDS FROM OTHER SECTIONS ↓

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 O 2(GS)                          31.999      0.000  0.000      0.000
 H 1(G )                           1.008     52.103  0.000    217.999
 H 2(GS)                           2.016      0.000  0.000      0.000
 H 2 O 1(L )                      18.015    -68.315  0.000   -285.830
 F 2(GS)                          37.997      0.000  0.000      0.000
 H 1 F 1(G )                      20.006    -65.320  0.072   -273.297
 H 1 F 1(3.0H2O)                  20.006    -76.735  0.070   -321.059
 H 1 F 1(25 H2O)                  20.006    -77.015  0.070   -322.230
CL 1(G )                          35.453     28.989  0.001    121.290
CL 2(GS)                          70.906      0.000  0.000      0.000
 H 1CL 1(G )                      36.461    -22.063  0.003    -92.312
 H 1CL 1(200H2O)                  36.461    -39.721  0.001   -166.193
BR 1(G )                          79.904     26.735  0.001    111.859
BR 2(LS)                         159.808      0.000  0.000      0.000
 H 1BR 1(2000 H2O)                80.912    -28.971  0.001   -121.215
 I 2(CS)                         253.809      0.000  0.000      0.000
 H 1 I 1(2000 H2O)               127.913    -13.537  0.004    -56.639
 S 1(G )                          32.060     66.200  0.000    276.981
 S 1(CS)                          32.060      0.000  0.000      0.000
 H 1 N 1 O 3(1000 H2O)            63.013    -49.442  0.112   -206.864
 N 2(GS)                          28.013      0.000  0.000      0.000
 K 1 H 4CL 1(300H2O)              53.492    -71.678  0.002   -299.901
 H 1 N 1 O 3(100H2O)              63.013    -49.398  0.112   -206.679
 P 1(CS)                          30.974      0.000  0.000      0.000
 C 1(CS)                          12.011      0.000  0.000      0.000
PB 1 O 1(C2)                     223.199    -52.340  0.000   -218.991
 B 1(CS)                          10.810      0.000  0.000      0.000
 B 1(G )                          10.810    130.500  1.000    546.012
 B 2 O 3(C )                      69.618   -303.996  0.235  -1271.919
 B 2 H 6(G )                      27.668      9.360  0.264     39.162
 B 1(AM)                          10.810      1.172  0.214      4.904
 H 3 B 1 O 3(C )                  61.832   -261.568  0.117  -1094.401
 H 3 B 1 O 3(500H2O)              61.832   -256.182  0.117  -1071.865
 H 3 B 1 O 3(1000 H2O)            61.832   -256.179  0.117  -1071.833
 B 2 O 3(AM)                      69.618   -299.637  0.236  -1253.681
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 B 1 F 3(G )                              67.805  -271.502   0.127  -1135.964
 B 1CL 3(G )                             117.169   -96.483   0.170   -403.685
 H 3 B 1 O 3(5000 H2O)                    61.832  -256.173   0.117  -1071.828
 H 3 B 1 O 3(7000 H2O)                    61.832  -256.171   0.117  -1071.819
 B 1 N 1(C )                              24.817   -60.028   0.222   -251.157
 H 1 B 1 F 4(A )                          87.812  -376.354   0.162  -1574.665
 H 3 B 1 O 3(300H2O)                      61.832  -256.188   0.117  -1071.891
 B 4 C 1(C )                              55.251   -17.000   1.000    -71.128
 H 3 B 1 O 3(100H2O)                      61.832  -256.207   0.117  -1071.970
 H 3 B 1 O 3(AO)                          61.832  -256.160   0.117  -1071.773
AL 1(CS)                                  26.981     0.000   0.000      0.000
AG 1 N 1 O 3(1000 H2O)                   169.873   -24.328   0.000   -101.788
AG 1(CS)                                 107.868     0.000   0.000      0.000
CR 1(CS)                                  51.996     0.000   0.000      0.000
MO 1(CS)                                  95.940     0.000   0.000      0.000
 V 1(CS)                                  50.941     0.000   0.000      0.000
NB 1(CS)                                  92.906     0.000   0.000      0.000
TA 1(CS)                                 180.948     0.000   0.000      0.000
TI 1(CS)                                  47.900     0.000   0.000      0.000
ZR 1 C 1(C )                             103.231   -48.500   0.000   -202.924
ZR 1 O 2(C )                             123.219  -263.040   0.000  -1100.559
ZR 1(CS)                                  91.220     0.000   0.000      0.000
HF 1(CS)                                 178.490     0.000   0.000      0.000
BE 1(CS)                                   9.012     0.000   0.000      0.000
MG 1 O 1(C )                              40.304  -143.810   0.000   -601.701
MG 1(G )                                  24.305    35.300   0.000    147.695
CA 1(G )                                  40.080    42.600   0.000    178.238
CA 1 F 2(G )                              78.077  -186.800   0.000   -781.571
CA 1 F 1(G )                              59.078   -65.000   0.000   -271.960
LI 2 O 1(C )                              29.881  -142.400   0.000   -595.802
LI 1 N 1 O 3(100H2O)                      68.946  -115.721   0.000   -484.177
LI 1(CS)                                   6.941     0.000   0.000      0.000
LI 1CL 1(60 H2O)                          42.394  -106.221   0.000   -444.429
NA 2 O 1(C )                              61.979   -99.400   0.000   -415.890
NA 1CL 1(60 H2O)                          58.443   -97.340   0.000   -407.271
 K 1(CS)                                  39.102     0.000   0.000      0.000
 K 2 O 1(C )                              94.203   -86.400   0.000   -361.498
 K 1CL 1(C )                              74.555  -104.175   0.000   -435.868
 K 1 N 1 O 3(C )                         101.107  -117.760   0.000   -492.708
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                                                                    ΔH°     ERROR
REACTIONS                                                           kcal mol⁻¹     REF.

 1   1 B 1(CS) = 1 B 1(L )                                           5,260   1.000 71/2
 2   1 B 1(G ) = 1 B 1 +(G )                                       195,600   1.000 NBS
 3   1 B 2(G ) = 1 B 1(G ) + 1 B 1(CS)                             -62,200   5.000 62/1
 4   2 B 1 O 1(G ) = 2 B 1(G ) + 1 O 2(GS)                         350,600  10.000 71/2
 5   2 B 2 O 3(L ) + 1 O 2(GS) = 4 B 1 O 2(G )                     297,480  10.000 61/2
 6   1 B 1(CS) + 1 O 2(GS) = 1 B 1 O 2 -(A )                      -184,600   0.100 NBS
 7   4 B 1(CS) + 1 O 2(GS) = 2 B 2 O 1(G )                          46,000  50.000 71/2
 8   2 B 1(CS) + 2 B 2 O 3(L ) = 3 B 2 O 2(G )                     282,000  15.000 56/1
                                                                 RESIDUAL   4.509
     2 B 1(CS) + 2 B 2 O 3(L ) = 3 B 2 O 2(G )                     267,930  15.000 58/2
                                                                 RESIDUAL  -9.591

 9   2 B 1(CS) + 2 B 2 O 3(G ) = 3 B 2 O 2(G )                      74,400  15.000 56/1
                                                                 RESIDUAL  -1.406

10   2MG 1 O 1(C ) + 2 B 1(CS) = 2MG 1(G ) + 1 B 2 O 2(G )         255,400   5.000 57/1
                                                                 RESIDUAL   2.960

11   1 B 2 O 3(C ) = 1 B 2 O 3(L )                                   2,880   1.000 71/2
                                                                 RESIDUAL  -3.700

12   1 B 2 O 3(L ) = 1 B 2 O 3(G )                                 100,140   5.000 71/2
                                                                 RESIDUAL  -0.703

13   1 B 1 H 1(G ) = 1 B 1(G ) + 1 H 1(G )                          77,950   1.000 61/3
14   1 B 2 H 6(G ) = 2 B 1 H 2(G ) + 1 H 2(GS)                      83,000   5.000 64/6
15   1 B 2 H 6(G ) = 2 B 1 H 3(G )                                  39,200   5.000 64/6
16.  1 B 1(CS) + 2 H 2(GS) = 1 B 1 H 4 -(A )                        11,510   0.100 NBS
17   1 B 4 H10(G ) = 4 B 1(AM) + 5 H 2(GS)                         -12,200   1.000 61/5
18   1 B 5 H 9(L ) = 1 B 5 H 9(G )                                   7,260   0.030 56/2
19   2 B 5 H 9(G ) =10 B 1(AM) + 9 H 2(GS)                         -25,980   0.800 58/1
                                                                 RESIDUAL  -0.852
     2 B 5 H 9(G ) =10 B 1(AM) + 9 H 2(GS)                         -19,800   2.000 61/5
                                                                 RESIDUAL   5.328

20  10 B 1(CS) +11 H 2(GS) = 2 B 5 H11(L )                          35,000   2.000 NBS
21   2 B 5 H11(G ) =10 B 1(AM) +11 H 2(GS)                         -40,400   2,000 61/5
22   6 B 1(CS) + 5 H 2(GS) = 1 B 6 H10(L )                          13,450   0.100 NBS
23   1 B 6 H10(G ) = 6 B 1(AM) + 5 H 2(GS)                         -17,200   2,000 61/5
24   1 B10 H14(C ) =10 B 1(AM) + 7 H 2(GS)                          19,800   1.400 60/4
                                                                 RESIDUAL   0.801
     1 B10 H14(C ) =10 B 1(AM) + 7 H 2(GS)                          18,000   1.000 62/5
                                                                 RESIDUAL  -0.999

25   1 B10 H14(C ) = 1 B10 H14(L )                                   5,250   0.010 55/1
                                                                 RESIDUAL   0.020

26   1 B10 H14(G ) =10 B 1(AM) + 7 H 2(GS)                           1,200   0.500 61/5
                                                                 RESIDUAL   0,250

27   1 B10 H14(C ) = 1 B10 H14(G )                                  18,200   0.930 55/1
                                                                 RESIDUAL   0,150
     1 B10 H14(C ) = 1 B10 H14(G )                                  16,650   0.930 55/1
                                                                 RESIDUAL  -1,420
     1 B10 H14(C ) = 1 B10 H14(G )                                  18,270   0.010 63/2
                                                                 RESIDUAL   0,220
     1 B10 H14(C ) = 1 B10 H14(G )                                  17,810   0.010 63/2
                                                                 RESIDUAL  -0,240

28   1 B10 H14(L ; = 1 B10 H14(G )                                  15,060   0.060 55/1
                                                                 RESIDUAL   0,241
     1 B10 H14(L ) = 1 B10 H14(G )                                  13,280   0.060 55/1
                                                                 RESIDUAL   0,461

29   2 B 1(CS) + 1 H 2(GS) + 2 O 2(GS) = 2 H 1 B 1 O 2(C1)        -382,200   0,700 71/1
                                                                 RESIDUAL  -2,468

30   2 B 1(CS) + 1 H 2(GS) + 2 O 2(GS) = 2 H 1 B 1 O 2(C2)        -379,600   0.680 71/1
31   2 B 1(CS) + 1 H 2(GS) + 2 O 2(GS) = 2 H 1 B 1 O 2(C3)        -376,000   0.680 71/1
32   1 B 2 O 3(L ) + 1 H 2 O 1(L ) = 2 H 1 B 1 O 2(G )              90,320  10.000 60/5
                                                                 RESIDUAL   4.737
     1 B 2 O 3(L ) + 1 H 2 O 1(L ) = 2 H 1 B 1 O 2(G )              88,240  10.000 60/6
                                                                 RESIDUAL   2.657
     1 B 2 O 3(L ) + 1 H 2 O 1(L ) = 2 H 1 B 1 O 2(G )              88,140  10.000 62/6
                                                                 RESIDUAL   2.557
     1 B 2 O 3(L ) + 1 H 2 O 1(L ) = 2 H 1 B 1 O 2(G )              81,800  10.000 62/6
                                                                 RESIDUAL  -3.763
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     1 B 2 O 3(L ) + 1 H 2 O 1(L ) = 2 H 1 B 1 O 2(G )                                      78,600 10.000 62/6
                                                                                          RESIDUAL -6.983
     1 B 2 O 3(L ) + 1 H 2 O 1(L ) = 2 H 1 B 1 O 2(G )                                      86.400 10.000 62/5
                                                                                          RESIDUAL  0.817

33   1 B 1(CS) + 1 H 2(GS) + 1 O 2(GS) = 1 B 1 ( O 1 H 1 ) 2(G )                           -114,000 15.000 71/2

34   1 B 2 H 6(G ) + 1 H 3 B 1 O 3(C ) = 3 H 2 B 1 O 1 H 1(G )                               44,700  1.000 64/7

35   1 B 2 H 6(G ) + 4 H 3 B 1 O 3(C ) = 6 H 1 B 1 ( O 1 H 1 ) 2(G )                        118,200  1.500 64/7

36   1 H 3 B 1 O 3(C ) = 1 H 3 B 1 O 3(G )                                                   24,310  0.600 37/1

37   1 H 1 B 1 O 2(C1) + 1 H 2 O 1(L ) = 1 H 3 B 1 O 3(C )                                   -1,280  0.500 60/7
                                                                                          RESIDUAL  2.107

38   1 H 1 B 1 O 2(C1) + 1 H 2 O 1(L ) = 1 H 3 B 1 O 3(500H2O)                                1.760  0.010 61/6
                                                                                          RESIDUAL -0.239

39   1 B 2 ( O 1 H 1 ) 4(C ) + 2AG 1 N 1 O 3(1000 H2O) + 2 H 2 O 1(L ) = 2AG 1(CS) + 2 H 3 B 1 O  -91,300  5.000 65/2
       3(1000 H2O) + 2 H 1 N 1 O 3(1000 H2O)

40   2 B 1(CS) + 2 H 2(GS) + 2 O 2(GS) = 1 B 2 ( O 1 H 1 ) 4(G )                           -307,000  5.000 71/2

41   1 B 3 O 3 H 3(C ) = 1 ( B 1 O 1 H 1 ) 3(G )                                             10,700  1.000 71/2

42   3 H 2(GS) + 2 B 1(AM) + 2 B 2 O 3(L ) = 2 ( B 1 O 1 H 1 ) 3(G )                        -11,800  2.000 63/3
                                                                                          RESIDUAL-21.969

43   2 ( B 1 O 1 H 1 ) 3(G ) = 1 B 2 H 6(G ) + 2 B 2 O 3(C )                                -22,220  2.000 64/8
                                                                                          RESIDUAL -5.908

44   2 ( B 1 O 1 H 1 ) 3(G ) = 1 B 2 H 6(G ) + 2 B 2 O 3(AM)                                -24,420  2.000 64/6
                                                                                          RESIDUAL-16.826

45   3 B 2 O 3(L ) + 3 H 2 O 1(L ) = 2 ( H 1 B 1 O 2 ) 3(G )                                -13,340  4.000 64/9

46   2 B 1(CS) + 1 B 1 F 3(G ) = 3 B 1 F 1(G )                                              185,840 15.00064/10
                                                                                          RESIDUAL -1.438

47   1 B 1 F 3(G ) + 1CA 1(G ) = 1 B 1 F 1(G ) + 1CA 1 F 2(G )                               12,200  5.000 65/3
                                                                                          RESIDUAL -1.161

48.  1 B 1 F 3(G ) + 2CA 1(G ) = 1 B 1 F 1(G ) + 2CA 1 F 1(G )                               29,800  5.000 65/3
                                                                                          RESIDUAL  2.239

49   1 B 1(CS) + 1 F 2(GS) = 1 B 1 F 2(G )                                                 -130,000  6.000 62/7

.50  1 B 1(CS) + 2 F 2(GS) = 1 B 1 F 4 -(A )                                               -376,400  1.000 NBS

51   2 B 1(CS) + 2 F 2(GS) = 1 B 2 F 4(G )                                                 -344,200  1.000 NBS

52   1 B 2 O 3(L ) + 1 B 1 F 3(G ) = 3 B 1 O 1 F 1(G )                                      149,000  5.000 62/8
                                                                                          RESIDUAL 10,713

53   1 ( B 1 O 1 F 1 ) 3(G ) = 3 B 1 O 1 F 1(G )                                            129,800  3.000 63/4
                                                                                          RESIDUAL -4.761

54   2 B 1(CS) + 1 O 2(GS) + 2 F 2(GS) = 2 B 1 O 1 F 2(G )                                 -500,000 50,000 71/2

55   1 B 1 F 3(G ) + 1 B 2 O 3(L ) = 1 ( B 1 O 1 F 1 ) 3(G )                                  4,330  0.50062/10
                                                                                          RESIDUAL  0.604
     1 B 1 F 3(G ) + 1 B 2 O 3(L ) = 1 ( B 1 O 1 F 1 ) 3(G )                                  4.060  1.000 63/4
                                                                                          RESIDUAL  0.334
     1 B 1 F 3(G ) + 1 B 2 O 3(L ) = 1 ( B 1 O 1 F 1 ) 3(G )                                  3,410  1.000 61/7
                                                                                          RESIDUAL -0.316
     1 B 1 F 3(G ) + 1 B 2 O 3(L ) = 1 ( B 1 O 1 F 1 ) 3(G )                                  4.030  1.000 61/6
                                                                                          RESIDUAL  0.304
     1 B 1 F 3(G ) + 1 B 2 O 3(L ) = 1 ( B 1 O 1 F 1 ) 3(G )                                  5,250  1.000 62/9
                                                                                          RESIDUAL  1.524

56   1 B 1 F 3(G ) + 1 B 2 O 3(C ) = 1 ( B 1 O 1 F 1 ) 3(G )                                  2,560  1.000 62/9
                                                                                          RESIDUAL -7.746

57   1 B 2 H 6(G ) + 4 B 1 F 3(G ) = 6 B 1 H 1 F 2(G )                                       18,360  2.000 65/5

58   1 B 1 F 3(G ) + 2 H 3 B 1 O 3(G ) = 3 B 1 ( O 1 H 1 ) 2 F 1(G )                         -2,100  0.90062/10

59   2 B 1 F 3(G ) + 1 H 3 B 1 O 3(G ) = 3 B 1 O 1 H 1 F 2(G )                               -1,800  0.60062/10

60   2 B 1(CS) + 3 F 2(GS) + 1 O 2(GS) + 1 H 2(GS) = 2 B 1 F 3 O 1 H 1 -(A )               -730,000  2.000 NBS

61   6 B 1(CS) + 3 O 2(GS) + 2 H 2(GS) + 1 F 2(GS) = 2 B 3 O 3 F 1 H 2(G )                 -766,000 20.000 NBS
                                                                                          RESIDUAL -0.015

62   1 H 2(GS) + 1 ( B 1 O 1 F 1 ) 3(G ) = 1 H 1 F 1(G ) + 1 B 3 O 3 F 2 H 1(G )             18,800  2.00062/11
                                                                                          RESIDUAL -4.590

63   2 B 3 O 3 F 2 H 1(G ) = 1 B 3 O 3 F 1 H 2(G ) + 1 ( B 1 O 1 F 1 ) 3(G )                  1,720  2.00062/11
                                                                                          RESIDUAL -3.060

64   2 B 3 O 3 F 1 H 2(G ) = 1 ( B 1 O 1 H 1 ) 3(G ) + 1 B 3 O 3 F 2 H 1(G )                 -2,040  1.00062/11
                                                                                          RESIDUAL -0.383

65   6 B 1(CS) + 4 F 2(GS) + 4 O 2(GS) + 1 H 2(GS) = 2 B 3 F 4 O 3 O 1 H 1--(A )          -1507,000 10.000 NBS

66   1 B 1CL 1(G ) = 1 B 1(G ) + 1CL 1(G )                                                  127,000  1.000 60/9

67   1 B 1CL 3(G ) = 1 B 1CL 1 +(G ) + 2CL 1(G )                                            425,600  0.500 69/4

68   1 B 2CL 4(G ) = 1 B 1CL 2 +(G ) + 1 B 1CL 2(G )                                        261,100  0.500 69/4
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69    1 B 1CL 3(G ) = 1 B 1CL 2 +(G ) + 1CL 1(G )                                        283.700  0.500 69/4
70    1 B 1CL 3(G ) = 1 B 1CL 3 +(G )                                                    267.500  0.500 69/4
71    1 B 2CL 4(G ) = 1 B 2CL 2 +(G ) + 2CL 1(G )                                        397.600  0.700 69/4
72    1 B 2CL 4(G ) = 1 B 2CL 3 +(G ) + 1CL 1(G )                                        265.700  0.500 69/4
73    1 B 2CL 4(L ) + 1CL 2(GS) = 2 B 1CL 3(G )                                           68.000  2.000 59/5
74    1 B 2CL 4(L ) = 1 B 2CL 4(G )                                                        7.800  1.000 NBS
                                                                                    RESIDUAL -0.115
      1 B 2CL 4(L ) = 1 B 2CL 4(G )                                                        8.030  1.000 54/1
                                                                                    RESIDUAL  0.115
75    1 B 2CL 4(G ) = 1 B 2CL 4 +(G )                                                    238.000  0.500 69/4
76    1 B 2 O 3(L ) + 1 B 1CL 3(G ) = 3 B 1 O 1CL 1(G )                                  168.900  5.00064/11
77    1 B 2 O 3(L ) + 1 B 1CL 3(G ) = 1 ( B 1 O 1CL 1 ) 3(G )                              5.310  1.000 65/5
78    4 B 1(CS) + 2 O 2(GS) + 2CL 2(GS) = 1 ( B 1 O 1CL 1 ) 4(G )                       -502.000 10.000 NBS
79    1 B 1CL 3(G ) + 1 H 2(GS) = 1 B 1CL 2 H 1(G ) + 1 H 1CL 1(G )                       15.050  1.000 65/6
                                                                                    RESIDUAL  0.301
80    6 B 1CL 2 H 1(G ) = 1 B 2 H 6(G ) + 4 B 1CL 3(G )                                  -16.470  1.00064/12
                                                                                    RESIDUAL  0.078
81    6 B 1(CS) + 3 O 2(GS) + 2 H 2(GS) + 1CL 2(GS) = 2 B 3 O 3 H 2CL 1(G )             -626.000 10.000 NBS
82    6 B 1(CS) + 3 O 2(GS) + 1 H 2(GS) + 2CL 2(GS) = 2 B 3 O 3 H 1CL 2(G )             -678.000 10.000 NBS
83    1 B 1CL 2(G ) + 1 B 1 F 2(G ) = 2 B 1CL 1 F 1(G )                                    0.000  5.000 71/2
84    2 B 1 F 3(G ) + 1 B 1CL 3(G ) = 3 B 1CL 1 F 2(G )                                    1.470  0.50062/10
85    2 B 1CL 3(G ) + 1 B 1 F 3(G ) = 3 B 1CL 2 F 1(G )                                    2.100  0.50062/10
86    1 B 1BR 1(G ) = 1 B 1(G ) + 1BR 1(G )                                              105.500  2.000 60/9
87    1 B 1(CS) + 1BR 2(LS) = 1 B 1BR 2(G )                                               15.000 15.000 71/2
88.   1 B 1BR 3(L ) + 3 H 2 O 1(L ) = 1 H 3 B 1 O 3(5000 H2O) + 3 H 1BR 1(2000 H2O)      -81.000  1.000 55/2
89    1 B 1BR 3(L ) = 1 B 1BR 3(G )                                                        8.200  1.000 55/2
90    1 B 1 O 1BR 1(G ) = 1 B 1 O 1(G ) + 1BR 1(G )                                       92.500  5.000 71/2
91    2 B 1(CS) + 2BR 2(LS) + 1 H 2(GS) = 2 B 1BR 2 H 1(G )                              -50.000 10.000 71/2
92    1 B 1BR 2(G ) + 1 B 1 F 2(G ) = 2 B 1BR 1 F 1(G )                                    0.000  5.000 71/2
93    2 B 1 F 3(G ) + 1 B 1BR 3(G ) = 3 B 1BR 1 F 2(G )                                    0.000  5.000 71/2
94    2 B 1BR 3(G ) + 1 B 1 F 3(G ) = 3 B 1 F 1BR 2(G )                                    0.000  5.000 71/2
95    1 B 1CL 2(G ) + 1 B 1BR 2(G ) = 2 B 1BR 1CL 1(G )                                    0.000  5.000 71/2
96    1 B 1BR 3(G ) + 2 B 1CL 3(G ) = 3 B 1CL 2BR 1(G )                                    0.000  5.000 71/2
97    2 B 1BR 3(G ) + 1 B 1CL 3(G ) = 3 B 1CL 1BR 2(G )                                    0.000  5.000 71/2
98    2 B 1(CS) + 1 I 2(CS) = 2 B 1 I 1(G )                                              146.000 20.000 71/2
99    1 B 1(CS) + 1 I 2(CS) = 1 B 1 I 2(G )                                               58.000 15.000 71/2
100   1 B 1 I 3(C ) + 3 H 2 O 1(L ) = 1 H 3 B 1 O 3(7000 H2O) + 3 H 1 I 1(2000 H2O)      -81.900  1.000 65/2
101   1 B 1 I 3(C ) = 1 B 1 I 3(G )                                                       15.500  1.50062/12
102   1 B 1 S 1(G ) = 1 B 1(G ) + 1 S 1(G )                                              117.620 18.000 71/2
103   1 B 1(CS) + 2 S 1(CS) = 1 B 1 S 2(G )                                               29.000  1.000 NBS
104   2 B 1(CS) + 2 S 1(CS) = 1 B 2 S 2(G )                                               36.000  1.000 NBS
105   2 B 1(CS) + 3 S 1(CS) = 1 B 2 S 3(C )                                              -57.500  1.000 NBS
106   2 B 1(CS) + 3 S 1(CS) = 1 B 2 S 3(G )                                               16.000  1.000 NBS
107   2 S 1(CS) + 7 F 2(GS) + 2 B 1(CS) = 2 S 1 F 4 B 1 F 3(C )                         -968.000  2.000 NBS
108   1 B 1 N 1(C ) = 1 B 1 N 1(G )                                                      214.100  1.000 NBS
109   1 N 2(GS) + 2 B 1(CS) + 6 H 2(GS) = 1 ( N 1 H 3 ) 2 B 2 H 6(C )                    -46.000  1.000 NBS
110   6 B 1(CS) + 3 N 2(GS) + 6 H 2(GS) = 2 B 3 N 3 H 6(L )                             -258.600  2.000 NBS
111   6 B 1(CS) + 3 N 2(GS) + 6 H 2(GS) = 2 B 3 N 3 H 6(G )                             -244.620  2.000 NBS
112   1 B10 H18 N 2(C ) +12 O 2(GS) +40 H 1 F 1(3.0H2O) = 1 N 2(GS) +10 H 1 B 1 F 4(A ) +24 H 2 O-2243.200  1.500 66/1
        1(L )
113   2 B 1(CS) + 1 N 2(GS) + 4 H 2(GS) + 2 O 2(GS) = 2 N 1 H 4 B 1 O 2(A )              -432.540  2.000 NBS
114   2 B 1(CS) + 1 N 2(GS) + 4 H 2(GS) + 2 O 2(GS) = 2 N 1 H 4 B 1 O 2(220H2O)          -432.000  2.000 NBS
115   2 B 1(CS) + 1 N 2(GS) + 4 H 2(GS) + 3 O 2(GS) = 2 N 1 H 4 B 1 O 3(A )              -390.800  2.000 NBS
116   4 B 1(CS) + 2 N 2(GS) +10 H 2(GS) + 7 O 2(GS) = 2 ( N 1 H 4 B 1 O 3 ) 2 H 2 O 1(C ) -476.600  2.000 NBS
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117   1 N 2(GS) + 2 B 1(CS) + 3 F 2(GS) + 3 H 2(GS) = 2 N 1 H 3 B 1 F 3(C )                              -647,200  2,000 NBS
118   1 B 3 N 3 H 3CL 3(C ) + 9 H 2 O 1(L ) = 3 H 3 B 1 O 3(300H2O) + 3 N 1 H 4CL 1(300H2O)              -113,800  0,700 52/2
119   1 B 3 N 3 H 3CL 3(C ) = 1 B 3 N 3 H 3CL 3(G )                                                        17,100  1,000 52/2
120   1 B 1(CS) + 1 P 1(CS) = 1 B 1 P 1(C )                                                               -19,000  1,000 NBS
121  13 B 1(CS) + 2 P 1(CS) = 1 B13 P 2(C )                                                               -40,000  1,000 NBS
122   2 P 1(CS) + 2 B 1(CS) + 6 H 2(GS) = 1 ( P 1 H 3 ) 2 B 2 H 6(C )                                     -27,000  1,000 NBS
123   2 P 1(CS) + 3 F 2(GS) + 2 B 1(CS) + 3 H 2(GS) = 2 P 1 F 3 B 1 H 3(G )                              -408,200  2,000 NBS
124   2 P 1(CS) + 1 O 2(GS) + 6CL 2(GS) + 2 B 1(CS) = 2 P 1 O 1CL 3 B 1CL 3(C )                          -512,600  2,000 NBS
125   2 P 1(CS) + 3 H 2(GS) + 2 B 1(CS) + 3CL 2(GS) = 2 P 1 H 3 B 1CL 3(C )                              -241,800  2,000 NBS
126   1 B 4 C 1(C ) + 7 C 1(CS) = 4 B 1 C 2(G )                                                           696,000 10,000 64/1
127   1PB 1 O 1(C2) + 1 B 2 O 3(C ) = 1PB 1 O 1 B 2 O 3(C )                                               -23,200  4,000 71/2
128   1PB 1 O 1(C2) + 2 B 2 O 3(C ) = 1PB 1 O 1 ( B 2 O 3 ) 2(C )                                        -25,300  2,000 71/2
129   1PB 1 O 1(C2) + 3 B 2 O 3(C ) = 1PB 1 O 1 ( B 2 O 3 ) 3(C )                                        -40,500  2,000 54/3
130   2PB 1 O 1(C2) + 5 B 2 O 3(C ) = 1 (PB 1 O 1 ) 2 ( B 2 O 3 ) 5(C )                                  -72,000  2,000 54/3
131   1AL 1(CS) + 2 B 1(CS) = 1AL 1 B 2(C )                                                               -16.000  3.000 67/3
                                                                                                          RESIDUAL  1.651
      1AL 1(CS) + 2 B 1(CS) = 1AL 1 B 2(C )                                                               -36,000 10,000 NBS
                                                                                                          RESIDUAL-18.349

132   1AL 1(CS) +12 B 1(CS) = 1AL 1 B12(C )                                                               -48.000 10.000 67/3
                                                                                                          RESIDUAL 15.446

133   1AL 1(CS) +12 B 1(CS) = 1AL 1 B12(C )                                                               -63.600  1.000 NBS
                                                                                                          RESIDUAL -0.154

134   1AL 1(CS) + 1 B 1(CS) + 1 O 2(GS) = 1AL 1 B 1 O 2(G )                                              -129.400  4.000 71/2
135   1AL 1(CS) + 3 B 1(CS) + 6 H 2(GS) = 1AL 1 ( B 1 H 4 ) 3(L )                                         -76.000  4.000 69/2
136.  1AL 1 ( B 1 H 4 ) 3(L ) = 1AL 1 ( B 1 H 4 ) 3(G )                                                     7.600  1.000 40/1
137   1CR 1(CS) + 2 B 1(CS) = 1CR 1 B 2(C )                                                               -31.000  5.000 55/4
138   1MO 1(CS) + 1 B 1(CS) = 1MO 1 B 1(C )                                                               -21.000  5.000 69/1
139   2MO 1(CS) + 1 B 1(CS) = 1MO 2 B 1(C )                                                               -29.000  5.000 69/1
140   1 V 1(CS) + 2 B 1(CS) = 1 V 1 B 2(C )                                                               -24.000  5.000 56/4
141   1NB 1(CS) + 2 B 1(CS) = 1NB 1 B 2(C )                                                               -36.000  5.000 55/4
142   1TA 1(CS) + 2 B 1(CS) = 1TA 1 B 2(C )                                                               -51.700  1.00062/13
143   1TI 1(CS) + 1 B 1(CS) = 1TI 1 B 1(C )                                                               -38.300  9.000 71/2
144   1TI 1(CS) + 2 B 1(CS) = 1TI 1 B 2(C )                                                               -66.800  4.000 71/2
                                                                                                          RESIDUAL 10.280
      1TI 1(CS) + 2 B 1(CS) = 1TI 1 B 2(C )                                                               -77.600  0.900 66/4
                                                                                                          RESIDUAL -0.520

145   1TI 1(CS) + 2 B 1(CS) = 1TI 1 B 2(L )                                                               -45.000  5.000 71/2
146   1ZR 1 B 2(C ) + 1 C 1(CS) = 1ZR 1 C 1(C ) + 2 B 1(G )                                               289.700  1.00064/13
                                                                                                          RESIDUAL -1.502

147   2ZR 1 B 2(C ) + 5 O 2(GS) = 2ZR 1 O 2(C ) + 2 B 2 O 3(AM)                                          -967.200  2.80064/14
                                                                                                          RESIDUAL  0.751

148   1ZR 1(CS) + 2 B 1(CS) = 1ZR 1 B 2(L )                                                               -54.190  0.100 71/2
149   1HF 1(CS) + 2 B 1(CS) = 1HF 1 B 2(C )                                                               -78.600  2.100 67/4
150   1BE 1(CS) + 1 B 1(CS) + 1 O 2(GS) = 1BE 1 B 1 O 2(G )                                              -115.200  8.000 71/2
151   1BE 1(CS) + 2 B 1(CS) + 2 O 2(GS) = 1BE 1 B 2 O 4(G )                                              -323.000 10.000 71/2
152   3BE 1(CS) + 2 B 1(CS) + 3 O 2(GS) = 1BE 3 B 2 O 6(C )                                              -741.960  2.000 71/2
153   2MG 1 B 2(C ) = 1MG 1(G ) + 1MG 1 B 4(C )                                                            54,100  5.000 58/4
154   1MG 1 B 4(C ) = 1MG 1(G ) + 4 B 1(CS)                                                                60,400  1.500 58/4
155   1LI 2 O 1(C ) + 1 B 2 O 3(C ) = 2LI 1 B 1 O 2(C )                                                   -45,200  0.100 54/3
                                                                                                          RESIDUAL -1.829

156   1LI 1 B 1 O 2(C ) = 1LI 1 B 1 O 2(L )                                                                 4,470  0.100 71/2
157   1LI 1 B 1 O 2(C ) = 1LI 1 B 1 O 2(G )                                                                82,910  0.100 63/6
158   1LI 1 B 1 O 2(C ) + 1 H 1 N 1 O 3(100H2O) + 1 H 2 O 1(L ) = 1LI 1 N 1 O 3(100H2O) + 1 H 3 B  -10,930  0.05060/13
       1 O 3(100H2O)
                                                                                                          RESIDUAL -1.598

159   4LI 1(CS) + 8 B 1(CS) + 7 O 2(GS) = 2LI 2 B 4 O 7(C )                                             -1607,200  2,000 71/2

160   4LI 1(CS) + 8 B 1(CS) + 7 O 2(GS) = 2LI 2 B 4 O 7(L )                                             -1585,800  5.000 71/2

161   1LI 2 O 1(C ) + 3 B 2 O 3(L ) = 1LI 2 B 6 O10(C )                                                   -72,800  1,000 54/3
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162   1LI 2 O 1(C ) + 4 B 2 O 3(L ) = 1LI 2 B 8 O13(C )                                                   -73,350  0,100 54/3

163   1LI 1 B 1 H 4(C ) + 1 H 1CL 1(200H2O) + 3 H 2 O 1(L ) = 1LI 1CL 1(60 H2O) + 1 H 3 B 1 O 3(A   -71,940  0,100 49/2
       O) + 4 H 2(GS)

164   1NA 2 O 1(C ) + 1 B 2 O 3(C ) = 2NA 1 B 1 O 2(C )                                                  -54,600  0,100 71/2

165   1NA 1 B 1 O 2(C ) = 1NA 1 B 1 O 2(G )                                                                73,000  3,000 65/7

166   1NA 1 B 1 O 2(C ) = 1NA 1 B 1 O 2(L )                                                                 4,660  0,100 71/2

167   1NA 2 O 1(C ) + 2 B 2 O 3(L ) = 1NA 2 B 4 O 7(C )                                                  -85,200  1,000 54/3

168   1NA 2 O 1(C ) + 2 B 2 O 3(L ) = 1NA 2 B 4 O 7(L )                                                  -80,400  1,000 54/3

169   1NA 2 O 1(C ) + 3 B 2 O 3(L ) = 1NA 2 B 6 O10(C )                                                  -97,520  0,100 54/3

170   1NA 1 B 1 H 4(C ) + 1 H 1CL 1(200H2O) + 3 H 2 O 1(L ) = 1NA 1CL 1(60 H2O) + 1 H 3 B 1 O 3(A   -65,870  0,100 49/2
       O) + 4 H 2(GS)

171   4 K 1(CS) + 8 B 1(CS) + 7 O 2(GS) = 2 K 2 B 4 O 7(C )                                            -1593,800  2,000 71/2

172   4 K 1(CS) + 8 B 1(CS) + 7 O 2(GS) = 2 K 2 B 4 O 7(L )                                            -1572,200  2,000 71/2

173   1 K 2 O 1(C ) + 3 B 2 O 3(L ) = 1 K 2 B 6 O10(C )                                                 -122,800  1,000 54/3

174   1 K 2 O 1(C ) + 4 B 2 O 3(L ) = 1 K 2 B 8 O13(C )                                                 -137,000  1,000 54/3

175   1 K 2 O 1(C ) + 4 B 2 O 3(L ) = 1 K 2 B 8 O13(L )                                                 -119,650  0,100 54/3

176   1 K 1 B 1 H 4(C ) + 1 H 1CL 1(G ) + 3 H 2 O 1(L ) = 1 K 1CL 1(C ) + 1 H 3 B 1 O 3(C ) + 4 H   -84,620  0,44001/11
        2(GS)

177   1 H 3 B 1 O 3(C ) + 4 H 1 F 1(25 H2O) + 1 K 1 N 1 O 3(C ) = 1 K 1 B 1 F 4(C ) + 1 H 1 N 1 O    19,260  0,000
        3(100H2O) + 3 H 2 O 1(L )
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APPENDIX III

Standard Enthalpy of Formation of Tertiary-butyl hydroperoxide

It is extremely difficult to obtain standard enthalpies of formation of either peroxides or hydroperoxides from combustion calorimetry or other thermochemical measurements. The reasons for this are at least twofold. Firstly there is the difficulty of obtaining pure compounds and secondly problems imposed due to their thermal instability. Both of these are minimal for the fairly stable tertiary-butyl peroxide and maximal in the case small alkyl hydroperoxides which decompose heterogeneously on metal and glass surfaces.

There are two independent values for ΔH_f^o[t-BuOOH,l] both determined by combustion calorimetry; -266.9 ± 1.3 kJ mol^{-1} in 1949[155] and -293.7 ± 5.0 kJ mol^{-1} in 1964.[69] In a review[156] of the kinetics of pyrolysis and O–O bond dissociation energies of some alkyl hydroperoxides, an estimated value of ΔH_f^o[t-BuOOH, g] using a group additivity scheme revealed a difference of 26.4 kJ mol^{-1} when compared with the 1949 value (Table A III.1). Combining this estimate with ΔH_{vap}^o (47.74 ± 0.17 kJ mol^{-1})[69] gives ΔH_f^o[t-BuOOH, l] $= -292.7 \pm 4$ kJ mol^{-1}, which is in good agreement with the 1964 figure.

The solution calorimetric method used in this work is based on reactions (2.3) – (2.5) described in Chapter II. This exploits the observation that in the presence of excess ferrous ion, (2.4) predominates (2.5) following the initial quantitative reaction (2.3). The calorimetric fluid used was 0.9 mol dm^{-3} ammonium ferrous sulphate in 1 mol dm^{-3} H_2SO_4 freshly prepared and checked for Fe^{3+} ion content.

The relevant equations are:

$$t\text{-BuOOH(l)} + Fe^{2+} \longrightarrow t\text{-BuO}^{\bullet} + Fe^{3+} + OH^{-} \quad \ldots \quad (2.3)$$

$$t\text{-BuO}^{\bullet} + Fe^{2+} + H^{+} \longrightarrow t\text{-BuOH} + Fe^{3+} \quad \ldots \quad (2.4)$$

$$t\text{-BuO}^{\bullet} \longrightarrow (CH_3)_2CO + CH_3^{\bullet} \quad \ldots \quad (2.5)$$

The methyl radicals produced in (2.5) react to form ethane, $2CH_3^{\bullet} \longrightarrow C_2H_6,g.$[44, 157]

The relative proportions of reactions (2.4) and (2.5) can therefore be determined from a ferric iron analysis of the final reaction mixture since (2.3) is quantitative. A standard spectrophotometric method was used[158] and the usual precautions to prevent aerial oxidation were observed. The derived thermochemical equation relating reactions (2.3) - (2.5) is given below:

$$\Delta H_f^o[t\text{-BuOOH},l] = (1-x).\Delta H_f^o[t\text{-BuOH},aq] + (2-x).\Delta H_f^o[Fe^{3+},aq] + \Delta H_f^o[OH^-,aq]$$
$$+ x.\Delta H_f^o[(CH_3)_2CO,aq] + x/2.\Delta H_f^o[C_2H_6,g] - (2-x).\Delta H_f^o[Fe^{2+},aq] - \Delta H_f^o[H^+,aq] - \Delta H. \quad (III.1)$$

where x (moles) is the fraction of t-BuO$^{\bullet}$ radicals reacting via route (2.5). Post-calorimetry analysis (Table 3.3, Chapter III) gave x = 0.16 (average of three independent results). This value in combination with ΔH (Table 3.2, Chapter III) gave $\Delta H_f^o[t\text{-BuOOH},l] = -293.3 \pm 4.1$ kJ mol^{-1}, which is compared with other values in Table AIII.2.

Table AIII.1

Comparison of some observed values of ΔH_f^o for ROOR(g) and ROOH(g) with those estimated by a group additivity method.[156]

Compound	$-\Delta H_f^o$/kJ mol^{-1}		Δ
	Observed	Estimated($\pm$ 4kJ mol^{-1})	
t-Bu_2O_2	354.4 $\pm$ 4	357.7	3.3
Me_2O_2	133.9 $\pm$ 4	130.2	3.0
Et_2O_2	200.0	200.0	0.0
n-Pr_2O_2	...	241.8	-
i-Pr_2O_2	...	276.6	-
MeOOH	...	134.3	-
EtOOH	188.2 $\pm$ 48	168.2	20.0
n-PrOOH	...	189.1	-
i-PrOOH	...	206.3	-
t-BuOOH	218.8	245.2	26.4
n-$C_6H_{13}OOH$	245.2 $\pm$ 5	251.0	5.8
n-$C_7H_{15}OOH$	276.1 $\pm$ 5	271.9	4.2
n-C_6H_{13}-2-OOH	259.4 $\pm$ 5	268.2	8.8
n-C_7H_{15}-2-OOH	292.0 $\pm$ 5	289.1	2.9

Table AIII.2

Collected standard enthalpies of formation of

t-BuOOH(l)

$-\Delta H_f^o$/kJ mol^{-1}	Source
266.9 ± 1.3	combustion, 1949[155]
293.7 ± 5.0	combustion, 1964[79]
292.7 ± 4.0	estimate*
293.3 ± 4.1	solution calorimetry

* using ΔH^o_{vap} = 47.7 kJ mol^{-1}, ref. 69.

This independent determination of the standard enthalpy of formation of t-BuOOH(l) allows a high accuracy to be achieved in the derived value of $\Delta H_f^o[(t\text{-BuOO})_3B,l]$; the interdependence of the standard enthalpies of formation of the two peroxides can be gauged from equation (3.1) (Chapter III)

$$(t\text{-BuOO})_3B(l) + (N + 3)H_2O(l) \longrightarrow [3.t\text{-BuOOH} + B(OH)_3]N.H_2O,aq. \quad \ldots \quad (3.1)$$

APPENDIX IV

Estimation of Lattice Energies

The lattice energy of an ionic compound, U_o at OK, may be defined as the internal energy change that takes place when one mole of the compound (at one atmosphere pressure) is converted into its gaseous ions at infinite separation. At OK these ions are stationary.

$$MX_n(c) \longrightarrow M^{n+}(g) + nX^-(g) \quad \Delta H = U_o \quad \ldots \quad (IV.1)$$

This energy arises predominatly from the coulombic attraction and interatomic repulsion terms. At temperatures above OK a further small quantity, $(n+1)RT$, must be added to take account of the volume work in expanding $(n+1)$ moles of gas (assumed ideal).

The lattice energy at 298 K, U_{298}, can be related to other thermodynamic quantities by the Born-Haber cycle; this is shown below:

$$\begin{tikzcd}
MX_n(c) \arrow[r, "U_{298}[MX_n] + (n+1)RT"] & M^{n+}(g) \; + & n\,X^-(g) \\
 & M(g) \arrow[u, "\sum_1^n I_n + \frac{5}{2}\,nRT"] & nX(g) \arrow[u, "-nE_a - \frac{5}{2}\,nRT"'] \\
 & M(s.s) \arrow[u, "\Delta H_f^o[M,g]"] \arrow[uul, "\Delta H_f^o[MX_n, c]"] & nX(s.s) \arrow[u, "n\Delta H_f^o[X,g]"']
\end{tikzcd}$$

$\Delta H_f^o[MX_n, c]$, $\Delta H_f^o[M,g]$ and $\Delta H_f^o[X,g]$ are the enthalpies of formation of crystalline MX_n, gaseous M and gaseous X. $\sum_i^n I_n$ is the sum of the first n ionisation potentials of M and E_a is the electron affinity of the radical X; these values are converted to enthalpies and corrected to 298 K by the addition of $\frac{5}{2}$ nRT terms. This follows from:

$$M(g) \longrightarrow M^{+}(g) + e^{-}(g) \quad I = U_o$$

$$M(g) \longrightarrow M^{+}(g) + e^{-}(g) \qquad U_{298}$$

$$U_{298} - U_o = \int \Delta C_v dT$$

$$= \int (\tfrac{3}{2}R + \tfrac{3}{2}R - \tfrac{3}{2}R)\, dT = \tfrac{3}{2}RT$$

$$\therefore\ U_{298} = I + \tfrac{3}{2}RT$$

Now $H_{298} = U_{298} + \Delta\nu(RT)$

$$= U_{298} + RT$$

$$= I + \tfrac{3}{2}RT + RT = I + \tfrac{5}{2}RT$$

$$\therefore\ H_{298} = I + \tfrac{5}{2}RT.$$

No interaction need be considered between the ions $M^{n+}(g)$ and $X^{-}(g)$ as they are in the hypothetical ideal gas state. From the Born-Haber cycle the following equation is derived,

$$U_{298}[MX_n] = \Delta H_f^o[M,g] + n\Delta H_f^o[X,g] + \sum_{1}^{n} I_n - nE_a - \Delta H_f^o[MX_n, c] - (n+1)RT \quad \ldots \quad (IV.2)$$

Consider $M(s.s.) \rightarrow M^{n+}(g) + ne^{-}(g)$ $\Delta H_f^o[M^{n+},g]$

and $nX(s.s.) + ne^{-}(g) \rightarrow nX^{-}(g)$ $n\Delta H_f^o[X,g]$, then equation (2) becomes,

$$U_{298}[MX_n] = \Delta H_f^o[M^{+},g] + n\Delta H_f^o[X,g] - \Delta H_f^o[MX_{n,}c] - (n+1)RT \qquad \ldots \quad (IV.3)$$

The lattice energy at 298 K is related to the lattice energy at OK by,

$$U_{298} = U_o + \int_{o}^{298} (C_p^o[M^{+}] + nC_p^o[X] - C_p^o[MX_n])\, dT - (n+1)RT \qquad \ldots \quad (IV.4)$$

assuming the specific heats $C_p^o[M^{+}]$ and $C_p^o[X^{-}]$ are $\frac{5}{2}R$ for an ideal monoatomic gas, then equation (4) becomes,

$$U_{298} = U_o + \frac{3}{2}(n+1)RT - \int_o^{298} C_p^o[MX_n]dT \qquad \ldots \qquad (IV.5)$$

This integration can be performed if the specific heat - temperature function of the compound MX_n is known from 0-298 K.

The use of the Born-Haber cycle in calculating lattice energies is necessarily restricted to those compounds for which the appropriate ionisation potentials and electron affinity data are available. For ionic compounds with exactly known structural parameters, lattice energies can be obtained from extended 'term by term' calculations. These calculations involve the summing of attractive and repulsive interactions and have been discussed in detail.[138]

A semi-empirical expression has been developed for the determination of lattice energies in cases where structural data are lacking.[139] It was demonstrated that if the Madelung constants (the coefficient of the sum of the coulombic interaction terms characteristic of a crystal structure) for a number of structures were divided by V, the number of ions in one molecule, the values obtained were almost constant, (Table A IV.1).

Table A IV.1

The ratio M/V for a number of structures

Structure	Madelung Const.M	M/V	Average coordination No.
Caesium chloride	1.763	0.88	8.0
Sodium chloride	1.748	0.87	6.0
Fluorite	2.519	0.84	5.33
Wurtzite	1.641	0.82	4.0
Rutile	2.408	0.80	4.0
Amattase	2.400	0.80	4.0
Cuprite	2.221	0.74	2.67

The equilibrium internuclear distance, r_o, in an ionic compound generally increases slightly with coordination number, thereby making the variations in M/Vr_o even less than M/V. This alternative treatment considers all salts to crystallise in a sodium chloride type lattice.

The Born-Meyer expression for calculating the lattice energy of a cyrstal is given by:

$$U_o = \frac{NMz_1, z_2e^2}{r_o}\left[1 - \frac{\rho}{r_o}\right] \quad \ldots \quad (IV.6)$$

where N is the Avogadro constant, M = Madelung constant, z_1 and z_2 are the cationic and anionic charges, e = electronic charge, r_o = equilibrium internuclear charge and ρ is a constant. For the six-coordination sodium chloride lattice, M/Vr_o is $0.874/r_o$ and ρ is almost constant at 0.345. It was further assumed that the cation and anion 'touch' so that

r_o may be replaced by r_c and r_a, the cationic and anionic radii for six-coordination.

Thus the modified Born-Meyer equation becomes:

$$U_o = \frac{287.2\ \mathbf{V}_{\mathbf{Z+Z-}}}{(r_c + r_a)} \left[1 - \frac{0.345}{(r_c+r_a)} \right] \quad \ldots \qquad (IV.7)$$

an equation, initially derived by, and now associated with the name of Kapustinskii. It is generally found that lattice energies given by the semi-empirical equation (7) are lower than those by extended calculations or Born-Haber cycles. Attempts to extend this equation by wholly empirical deductions give closer results but do not, of course, have a firm theoretical justification.

A difficulty when using the Kapustinskii equation is to assign a value to the ionic radius if a complex cation or anion is present. A method has been proposed which overcomes this difficulty.[140]

Consider the reaction:

$$MX(c) \longrightarrow M^+(g) + X^-(g)$$

the enthalpy of reaction is given by $U_o + 2RT$. It therefore follows that:

$$U_o + 2RT = \Delta H_f^o[M^+,g] + \Delta H_f^o[X^-,g] - \Delta H_f^o(MX,c] \ \ldots \quad \ldots \qquad (IV.8)$$

Now, if two salts, M_1X and M_2X, have a common anion, then:

$$U_1 + 2RT = \Delta H_f^o[M_1{}^+,g] + \Delta H_f^o[X^-,g] - \Delta H_f^o[M_1X,c] \quad \ldots \qquad (IV.9)$$

$$U_2 + 2RT = \Delta H_f^o[M_2{}^+,g] + \Delta H_f^o[X^-,g] - \Delta H_f^o[M_2X,c] \quad \ldots \qquad (IV.10)$$

Equation (9) - (10) yields:

$$U_1 - U_2 = \Delta H_f^o[M_1{}^+, g] - \Delta H_f^o[M_2{}^+, g] - \Delta H_f^o[M_1X, c] + \Delta H_f^o(M_2X, c] \quad \ldots \quad (IV.11)$$

From the Kapustinskii equation:

$$U_1 - U_2 = \text{const.}\left[\frac{1}{(r_{M_1^+} + r_{X^-})}\left(1 - \frac{0.345}{(r_{M_1^+} + r_{X^-})}\right) - \frac{1}{(r_{M_2^+} + r_{X^-})}\left(\frac{0.345}{(r_{M_2^+} + r_{X^-}}\right)\right] \quad \ldots \quad (IV.12)$$

Therefore, if the enthalpies of formation of the gaseous ions and crystalline salts and the ionic radii of $M_1{}^+$ and $M_2{}^+$ are known, equations (11) and (12) may be equated and the quantity r_{X^-} calculated. A radius calculated in this way is known as a 'thermochemical radius'. Calculated values inserted into equation (7) yield lattice energies of salts containing that anion provided, of course, that the ionic radius of the cation is known. Also, substitution of the lattice energy into equations (9) or (10) will give the standard enthalpy of formation of the complex anion, $\Delta H_f^o[X^-, g]$.

Although it is necessary to make several assumptions in obtaining the modified equation (7), it provides a widely used and simple technique for estimating lattice energies in the absence of detailed structural information.

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The Thermochemistry of *o*- and *p*-Tolyldichloroboranes and the Boron-to-Carbon Bond Strength

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The standard enthalpies of formation of *o*- and *p*-tolyldichloroboranes have been determined from a thermochemical study of their oxidative hydrolyses in an isoperibol reaction calorimeter. Combination of these results with enthalpies of vaporization give the standard enthalpies of formation of these compounds in the gas phase (−253·8 ± 2·7 and −294·1 ± 3·8 kJ mol^{-1} respectively) from which the boron–carbon bond energy is derived. Structural implications of these results are discussed.

PREVIOUS thermochemical studies[1,2] of $PhBX_2$ (I), Ph_2BX (II), Ph_3B (III), and (cyclo-$C_6H_{11})_3B$ (IV) where X = Cl and Br showed the order of boron–carbon bond strength (E) in these molecules to be $E(I) > E(II) > E(III) \gg E(IV)$. The marked enhancement of the boron–aromatic-carbon bond energy compared with the boron–aliphatic-carbon bond energy was discussed in terms of $p\pi$–$p\pi$ bonding. The successive decrease in E on replacement of halogen by phenyl in the series $Ph_{3-n}BX_n$ (n = 0, 1, and 2) was rationalized by suggesting increasing steric interaction causing the phenyl groups to be twisted out of plane with concomitant reduction in resonance stabilization. By inference, *ortho*-substitution in $PhBCl_2$ should cause a decrease in E and *para*-substitution should have no steric effect. Accordingly, calorimetric measurements on *o*- and *p*-$Me{\cdot}C_6H_4{\cdot}BCl_2$ were made.

EXPERIMENTAL

Materials.—The aryldichloroboranes were synthesized by established procedures[3-5] according to the reaction scheme

$$Me{\cdot}C_6H_4{\cdot}Br \xrightarrow{Mg/THF} Me{\cdot}C_6H_4{\cdot}MgBr \xrightarrow[reflux]{HgCl_2/THF}$$

$$Me{\cdot}C_6H_4{\cdot}HgCl \xrightarrow[reflux]{BCl_3/C_6H_6} Me{\cdot}C_6H_4{\cdot}BCl_2 \quad (A)$$

(A) (THF = tetrahydrofuran). The b.p.s were 362 K/12 mmHg † for *o*-$Me{\cdot}C_6H_4{\cdot}BCl_2$ (lit.,[5] 361—365 K/12 mmHg) and 363 K/10 mmHg for *p*-$Me{\cdot}C_6H_4{\cdot}BCl_2$ (lit.,[5] 365 K/10 mmHg). Analyses for chloride on hydrolysis and for boron were by conventional titrimetric procedures (Found for *ortho*-isomer: B, 6·25; Cl$^-$, 41·1. Found for *para*-isomer: B, 6·26; Cl$^-$, 40·6. Calc. for $C_7H_7BCl_2$: B, 6·25; Cl, 41·02%). This synthesis occasionally results in the contamination[6] of the *ortho*-isomer by *meta*-isomer from isomerization. Hence the isomeric purities of the samples were checked by ^1H n.m.r. spectroscopy. Comparison of the intensity of the signal from the *meta*-isomer methyl protons (δ = 2·15 p.p.m.) with the intensities of the signals from the ^{13}C satellites from the *ortho*-isomer methyl protons (δ = 2·44 p.p.m., J_{C-H} = 127 Hz) showed the concentration of *meta*-isomer in the *ortho*-isomer sample to be less than 0·5 mass % (δ values relative to tetramethylsilane). No isomeric contamination could be detected in the sample of the *para*-isomer. The isomeric purity of the *ortho*-isomer was checked after calorimetry and no significant increase in impurity was found.

Calorimeters.—The glass calorimeter was operated in the isoperibol mode at 298·15 ± 0·01 K or 303·15 ± 0·01 K, and is fully described elsewhere.[7,8] The performance was checked periodically by measuring the enthalpy of neutralization of tris(hydroxymethyl)aminomethane (THAM) in excess of 0·1 mol dm^{-3} HCl. The mean of ten determinations was $\Delta H(298{\cdot}15\ K,\ 1200 < N < 1364) = -29{\cdot}79 \pm 0{\cdot}08$ kJ mol^{-1}. Hill *et al.*[9] report $\Delta H(298{\cdot}15\ K,\ 1182 < N < 1569) = -29{\cdot}744 \pm 0{\cdot}006$ kJ mol^{-1} for the same reaction. N is the mole ratio of water to THAM. Samples for calorimetry were handled in dry nitrogen and contained[8] in glass ampoules with two fracture bulbs.

Differential Scanning Calorimetry.—The enthalpy of fusion of *p*-tolyldichloroborane was determined by use of the Perkin-Elmer D.S.C. 1B instrument. 'Volatile Sample' pans (part no. 219–0062) were filled in an atmosphere of dry nitrogen and then sealed. The instrument was calibrated with pure indium metal (99·999 mol %, Halewood Chemicals Ltd.). The heat of fusion of *p*-tolyldichloroborane was calculated from the average area of three replicate scans of the same sample, this process being repeated for two further samples. No attack of the aluminium sample pan and lid was evident from the observed constancy of the scan area for several repeated meltings and freezings of the same sample. Exothermic peaks were not observed on any of the scans; this was taken as additional evidence of no chemical reaction taking place.

Enthalpies of Vaporization.—These were determined from vapour pressures obtained over a range of temperature (360—440 K) by use of semimicro ebulliometer based on the design[10] of Hoover *et al.* and tested as described.[1] These enthalpies were converted from the mean of the experimental temperature interval to 298·15 K by use of Watson's equation.[11]

Errors.—Uncertainties are quoted throughout as $\pm 2\bar{s}$

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† Throughout this paper, mmHg = (101·325/760) kPa.

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($\bar{s}$ being the standard deviation of the mean) except in the case of the d.s.c. result (see Table 3).

RESULTS

The calorimeter contained 200 cm^3 of an aqueous solution, 0·1 mol dm^{-3} with respect to H_2O_2 and 1·00 mol dm^{-3} with respect to NaOH (this mixture designated aqueous excess of base, a.e.b.). Quantities of arylhalogenoborane were chosen so that both peroxide and base were in excess. The *para*-isomer was studied at 303·15 K where the sample is liquid and the correction of the results to 298·15 K was ignored as were the enthalpies of mixing of the products. The enthalpies of solution of H_2O_2, NaCl, and NaOH in (a.e.b.) were assumed equal to the corresponding values in water. The thermal effect of the catalysis of the decomposition of H_2O_2 by base was found to be negligible. Therefore

TABLE 1

Enthalpies of reaction for equation (1) at 298·15 K: *n* is the mole ratio of water to arylhalogenoborane

n	$-\Delta H_1$/kJ mol^{-1} for *ortho*-isomer	*n*	$-\Delta H_1{}^a$/kJ mol^{-1} for *para*-isomer
28 812	720·9	25 431	686·2
23 760	723·4	20 269	677·8
35 540	724·2	32 499	679·9
23 269	720·0	24 028	687·0
42 414	715·5	28 115	685·3
28 182	715·0	26 159	686·2
25 671	722·2	28 878	678·2
30 727	716·7	20 508	675·7
30 341	716·3	30 054	674·9
29 230	718·4		
32 387	720·9	Mean ($\pm 2\bar{s}$)	681·2 ± 3·3
Mean ($\pm 2\bar{s}$)	719·4 ± 1·9		

^{a} At 303·15 K.

for reaction (1) where Ar = *o*- or *p*-Me·C_6H_4· we have relation (B). Enthalpies of neutralization of the phenols

$$ArBCl_2(liq) + [H_2O_2 + 2NaOH](a.e.b.) = [ArOH + H_3BO_3 + 2NaCl](a.e.b.) \quad (1)$$

$$\Delta H_f^0[ArBCl_2,liq] = \Delta H_f^0[ArOH,a.e.b.] + \Delta H_f^0[H_3BO_3,a.e.b.] + 2\Delta H_f^0[NaCl,a.e.b.] - 2\Delta H_f^0[NaOH,a.e.b.] - \Delta H_f^0[H_2O_2,a.e.b.] - \Delta H_1 \quad (B)$$

(ArOH) were determined in the same calorimeter. The corresponding figure for boric acid is available.[12]

TABLE 3

Enthalpies of formation and transition for *o*- and *p*-tolyldichloroboranes at 298·15 K in kJ mol^{-1}

	$\Delta H_f{}^0$(c)	ΔH(c $\longrightarrow$ liq)	$\Delta H_f{}^0$(liq)	ΔH(liq $\longrightarrow$ g)	$\Delta H_f{}^0$(g)
o-Me·C_6H_4·BCl_2	—	—	−300·7 ± 2·5	46·9 ± 0·9	−253·8 ± 2·7
p-Me·C_6H_4·BCl_2 ^{a}	−339·2 ± 3·6	4·39 ± 0·13 ^{b}	−334·8 ± 3·6	40·7 ± 1·3	−294·1 ± 3·8

^{a} M.p. 300·1 K. ^{b} The uncertainty interval is the range of three determinations and includes a calibration error.

Experimental results are in Tables 1 and 2. With the above approximations the term (ΔH_f^0[NaCl,a.e.b.] − ΔH_f^0[NaOH,a.e.b.]) reduces to (ΔH_f^0[Cl$^-$,aq] − ΔH_f^0[OH$^-$,aq]) and this and the value for H_2O_2(aq) were taken from ref. 13. Using heats of formation for the cresols from ref. 11, $\Delta H_f^0[H_3BO_3,c] = -1094·5 \pm 1·2$ kJ mol^{-1} (mean of two [14,15] reliable determinations) and the enthalpies of fusion and vaporization, we obtain the derived enthalpies of formation collected in Table 3.

TABLE 2

Enthalpies of neutralization for ArOH(cryst.) + a.e.b. = [ArOH,a.e.b.] at 298·15 K: *n* is the mole ratio of water to phenol

n	$-\Delta H$/kJ mol^{-1} for *ortho*-isomer	*n*	$-\Delta H$/kJ mol^{-1} for *para*-isomer
979	15·5	738	17·3
860	15·5	656	17·4
884	15·9	737	16·7
925	16·3	776	16·9
855	16·3	Mean ($\pm 2\bar{s}$)	17·1 ± 0·3
Mean ($\pm 2\bar{s}$)	15·9 ± 0·4		

DISCUSSION

The boron–carbon bond energy in the arylhalogenoboranes is defined by equations (2) and (3). Hence the

$$MeC_6H_4{\cdot}BCl_2(g) = Me{\cdot}C_6H_4{\cdot}(g) + B(g) + 2Cl(g) \; \Delta H_2 \quad (2)$$

$$\Delta H_2 = 2E(B\text{–}Cl) + E(B\text{–}C) \quad (3)$$

difference in the bond energies for the isomers is given by equations (4)—(7). Equating the term in parentheses

$$E(B\text{–}C)_p - E(B\text{–}C)_o = \Delta H_2(para\text{-isomer}) - \Delta H_2(ortho\text{-isomer}) \quad (4)$$

$$= \Delta H_f^0[o\text{-}Me{\cdot}C_6H_4{\cdot}BCl_2,g] - \Delta H_f^0[p\text{-}Me{\cdot}C_6H_4{\cdot}BCl_2,g] + (\Delta H_f^0[p\text{-}Me{\cdot}C_6H_4{\cdot},g] - \Delta H_f^0[o\text{-}Me{\cdot}C_6H_4{\cdot},g]) \quad (5)$$

$$\approx \Delta H_f^0[o\text{-}Me{\cdot}C_6H_4{\cdot}BCl_2,g] - \Delta H_f^0[p\text{-}Me{\cdot}C_6H_4{\cdot}BCl_2,g] \quad (6)$$

$$= 40·3 \pm 4·7 \text{ kJ mol}^{-1} \quad (7)$$

in equation (5) to zero is equivalent to equating the carbon to *ortho*-hydrogen bond dissociation energy to the carbon to *para*-hydrogen bond dissociation energy in toluene. There is no direct evidence [16,17] to support this assumption but it is likely that the steric effect of a methyl group on an *ortho*-hydrogen is small and that the difference in

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the electronic effect of the methyl group on the *ortho*- and *para*-hydrogens is similarly small. The assumption is probably valid to within ± 4 kJ mol^{-1}. In order to derive explicit values for the boron–carbon bond energies rather than their difference it is necessary to estimate $\Delta H_f^0[\text{Me}\cdot\text{C}_6\text{H}_4\cdot,\text{g}]$. If we assume that $D(\text{C}_6\text{H}_5\text{–H}) \approx D(\text{Me}\cdot\text{C}_6\text{H}_4\text{–H})$ this function is readily obtained from equation (8). In support of this second assumption,

$$\Delta H_f^0[\text{Me}\cdot\text{C}_6\text{H}_4,\text{g}] = D(\text{C}_6\text{H}_5\text{–H})^{18} - \Delta H_f^0[\text{H},\text{g}]^{12} + \Delta H_f^0[\text{MePh},\text{g}]^{13} = 192 \pm 8 \text{ kJ mol}^{-1} \quad (8)$$

gas-phase kinetic studies[19] indicate $D(\text{CF}_3\cdot\text{C}_6\text{H}_4\text{–H}) = 456 \pm 10$ kJ mol, a figure close to the accepted value[18] for $D(\text{C}_6\text{H}_5\text{–H}) = 460 \pm 8$ kJ mol^{-1}. It is probable that –CF_3 will have a more marked influence on the ring C–H bond energies than –CH_3 so the assumption is probably valid to within the difference between $D(\text{CF}_3\cdot\text{C}_6\text{H}_4\text{–H})$ and $D(\text{C}_6\text{H}_5\text{–H})$, *i.e.*, ± 4 kJ. Values for the carbon–boron bond energies in the title compounds are compared in Table 4 with corresponding recalculated results for $\text{Ph}_{3-n}\text{BX}_n$ ($n = 0$, 1, and 2, X = Cl and Br). The latter results differ from those originally reported[20] because of (*a*) the use of $\Delta H_f^0[\text{C}_6\text{H}_5\cdot,\text{g}] = 325 \pm 18$[18] kJ mol^{-1} instead of 301 ± 18[1,20] kJ mol^{-1} and (*b*) the conversion[21] of the original[1] enthalpies of vaporization to 298·15 K by use of Watson's equation.[13]

TABLE 4

Values for the boron–carbon bond energy[b] [defined by equations (2) and (3)] in arylhalogenoboranes and triphenylborane at 298·15 K

Compound	E(B–C)[a]/kJ mol^{-1}
o-Me·C$_6$H$_4$BCl$_2$	463 ± 10
p-Me·C$_6$H$_4$·BCl$_2$	504 ± 10
PhBCl$_2$	508 ± 10
PhBBr$_2$	489 ± 10
Ph$_2$BCl	485 ± 10
Ph$_2$BBr	475 ± 10
Ph$_3$B	462 ± 10

[a] The major part of the error in these values is from ΔH_f^0[B,g] and ΔH_f^0[aryl radical, g.] The difference between appropriate values will lead to error cancellation. [b] Ancillary heats of formation at 298·15 K required for the calculation of these results were taken from ref. (21) unless indicated otherwise and are as follows: B(g), $555{\cdot}6 \pm 16{\cdot}7$; Cl(g), $121{\cdot}0 \pm 0{\cdot}1$; Br(g), $111{\cdot}9 \pm 0{\cdot}3$; Ph(g), 325 ± 8;[18] PhBCl$_2$(g), $-265{\cdot}9 \pm 1{\cdot}7$; PhBBr$_2$(g), $-115{\cdot}5 \pm 1{\cdot}7$; Ph$_2$BCl(g), $-84{\cdot}1 \pm 3{\cdot}8$; Ph$_2$BBr(g), $2{\cdot}5 \pm 3{\cdot}8$; Ph$_3$B(g), $143{\cdot}1 \pm 4{\cdot}2$ kJ mol^{-1}; also required are E(B–Cl) = 440·1 and E(B–Br) = 365·7 kJ mol^{-1} BX$_3$.

The difference between the boron–carbon bond energy in p-Me·C$_6$H$_4$·BCl$_2$ and PhBCl$_2$ is 4 kJ mol^{-1} which is within experimental error and so is not significant. If we accept the validity of the assumptions discussed above and the transferability[1] of the B–Cl bond energy from BCl$_3$ to ArBCl$_2$, this implies that the electronic effect of a *para*-methyl substituent on the B–C bond energy in the aryldichloroboranes is small. In contrast, the B–C bond energy in p-Me·C$_6$H$_4$·BCl$_2$ is greater than in the *ortho*-isomer by *ca.* 40 kJ mol^{-1}. This is significant and reflects the steric effect of an *ortho*-methyl substituent. It is known that the atoms in PhBCl$_2$(g) are coplanar[22] and a vibrational spectroscopic study[23] of the diphenylhalogenoboranes supports the suggestion[1] that the phenyl groups are twisted out of the skeletal plane in these molecules. Similarly, it is probable that in o-Me·C$_6$H$_4$·BCl$_2$(g) the –BCl$_2$ group is twisted out of the ring plane to minimize steric interaction resulting in loss of $p\pi$–$p\pi$ character to the B–C bond. A significant $p\pi$ contribution persists in this bond, however, as the boron to aliphatic carbon bond strength[1] (*ca.* 370 kJ mol^{-1}) is much smaller.

A mass spectrometric study[24] of photoionization yields from B$_2$Cl$_4$ and BCl$_3$ gives $\Delta H_f^0[\text{BCl}_2\cdot,\text{g}]298 = -61 \pm 5$ kJ mol^{-1}. Using this result we can calculate bond dissociation energies in the aryldichloroboranes which do not include the implicit assumption of bond-energy transferability as do the bond energy calculations described above. The same trends are observed in the bond dissociation energy results although the absolute magnitudes differ.

TABLE 5

Bond dissociation energies in the aryldihalogenoboranes at 298·15 K

Compound	o-Me·C$_6$H$_4$·BCl$_2$	p-Me·C$_6$H$_4$·BCl$_2$	PhBCl$_2$
D(Aryl–BCl$_2$)/kJ mol^{-1}	485 ± 10	525 ± 10	530 ± 10

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Synthesis and Thermodynamic Functions of Rubidium and Caesium Tetrachloroborates

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Synthesis and Thermodynamic Functions of Rubidium and Caesium Tetrachloroborates

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Pure rubidium and caesium tetrachloroborates have been prepared by a modification of an established method. Their standard heats of formation at 298·15 K are −220·7 ± 0·4 and −225·0 ± 0·3 kcal mol^{-1} respectively as obtained from a thermochemical study of their hydrolyses. Dissociation pressures of caesium tetrachloroborate have been determined over the range 55—80 °C, from which the equilibrium constant for the dissociation at 25 °C has been estimated as 8×10^{-5}.

In contrast to the ready preparation of tetrafluoroborates, corresponding tetrachloroborates have proved difficult to isolate and were not characterised until 1957[1] when pyridinium tetrachloroborate was prepared. Subsequently Muetterties[2] reported autoclave syntheses at 500 °C of $M^I[BCl_4]$ (M = Cs, Rb, and K) from M^ICl and BCl_3 (under these conditions $Na[BCl_4]$ was not formed). This synthetic route was modified later[3] by inclusion of a nitrobenzene solvent when smooth reaction proceeded at *ca.* 100 °C. Approximate measurements by Muetterties revealed that the alkali-metal tetrachloroborates are thermodynamically less stable than the corresponding tetrafluoroborates in terms of both lower enthalpies of dissociation and higher dissociation pressures.

This paper describes a modification of Muetterties' synthetic procedure for rubidium and caesium tetrachloroborates and the aqueous-solution thermochemistry of these compounds; dissociation pressures and derived thermodynamic functions are reported for $Cs[BCl_4]$.

EXPERIMENTAL

Materials.—Rubidium and caesium chlorides (B.D.H.) were dried at 110 °C. Chloroform (ethanol removed by water extraction), nitrobenzene, and carbon tetrachloride were dried over type 4A molecular sieves (B.D.H.).

Syntheses.—Caesium chloride [6·0 g or rubidium chloride (4·0 g)] was added to nitrobenzene (50 cm^3) in a Pyrex glass ampoule (a spherical bulb with an 8 cm neck and volume of *ca.* 80 cm^3) in a nitrogen-filled dry-box. The ampoule contents were cooled to *ca.* −80 °C and boron trichloride (20 cm^3) was added after which the ampoule was sealed. The autoclave (series 4652, internal volume 500 cm^3, Parr Instrument Co., Moline, Illinois) was charged with the ampoule and isopentane (100 cm^3) to act as a pressure equaliser (rough calculation indicates the pressure differential across the ampoule wall at 90 °C was 0·9 atm and the total autoclave internal pressure was 7 atm).‡ The autoclave was maintained at 90 °C for 4 h when the ampoule was removed and opened at −80 °C. The following operations were carried out in a nitrogen-filled dry-box. The ampoule contents were washed into a conical flask with nitrobenzene (50 cm^3), allowed to settle, and the supernatant liquid decanted into chloroform (500 cm^3) when the tetrachloroborate precipitated. The impure product was collected on a glass sinter (No. 3) and vacuum-dried, followed by redissolution in nitrobenzene–boron trichloride (100 cm^3; 15 cm^3) and reprecipitation with chloroform. The white precipitate was filtered off, washed with chloroform, and dried at room temperature for 2 h at 0·001 Torr.

Analysis.—Raman spectra (Coderg PHO, 6 471 Å exciting line) were compared with literature spectra[4] of other tetrachloroborates and the presence of $[BCl_4]^-$ and the absence of BCl_3 confirmed. Alkali-metal contents were determined gravimetrically[5] using a sodium tetraphenylborate precipitant and total chloride contents were obtained from a Volhard titration[6] on the hydrolysate. The liberated hydrochloric and boric acids in the hydrolysate were determined *via* potentiometric titration {Found: B, 4·55; Cl$^-$, 59·5; Cl$^-$ (equivalent to liberated HCl), 44·6; Rb, 36·0. Calc. for $Rb[BCl_4]$: B, 4·55; Cl, 59·55; Rb, 35·9. Found: B, 3·80; Cl$^-$, 49·5; Cl$^-$ (equivalent to liberated HCl), 37·2; Cs, 46·6. Calc. for $Cs[BCl_4]$: B, 3·80; Cl, 49·65; Cs, 46·55%}. Densities at 25 °C were measured under carbon tetrachloride as 2·40 and 2·68 g cm^{-3} for $Rb[BCl_4]$ and $Cs[BCl_4]$ respectively.

Solution Calorimeter.—This was of all-glass construction, operated in the isoperibol mode at 25 °C and has been previously described[7] except for the following modifications. The calorimeter (of round-bottomed design) contained liquid (200 cm^3) and additional stirrer blades [fabricated in poly(tetrafluoroethylene) (ptfe)] were fixed to the stirrer shaft *ca.* 1 cm below the surface of the liquid. The calibration heater was replaced by a nominal 100 Ω ptfe-encapsulated resistor (Tronac Inc., Provo, Utah) of low thermal capacity, and the platinum-resistance thermometer for ancillary temperature monitoring has been abandoned. The out-of-balance bridge signal was displayed directly on a 1 mV pen recorder so that the sensitivity was *ca.* 1 Ω cm^{-1} pen displacement with a thermistor of *ca.* 150 Ω K^{-1}. The reaction resistance change was obtained by back extrapolation to a point corresponding to 63% of the total change and the calibration resistance change obtained similarly to a point corresponding to 50% of the total change. The ampoules had two fracture bulbs[8] and reaction was initiated by breaking the bulbs with the stirrer blades. The theoretical precision of this system has been discussed briefly in

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‡ 1 cal = 4·184 J, 1 atm = 101·325 kPa, 1 Torr = (101·325/760) kPa, and 1 Å = 10^{-10} m.

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refs. 9 and 10 and the experimental precision and accuracy were checked by measuring the enthalpy of neutralisation of tris[(hydroxymethyl)amino]methane (thm) in excess of 0·1 mol dm^{-3} aqueous hydrochloric acid. The mean of 10 runs was ΔH(298·15 K, 1 200 < N < 1 364) = −(7·12 ± 0·02) kcal mol^{-1}. Hill *et al.*[11] obtained ΔH (298·15 K, 1 170 < N < 1 574) = −(7·109 ± 0·003) kcal mol^{-1}, where N is the mol ratio of water to thm. The uncertainties in the solution calorimetric results are quoted as $\pm 2\sigma$, σ being the standard deviation of the mean.

Dissociation Pressures.—These were measured with a strain-gauge pressure transducer (Bell and Howell, type 4-366) fused to a glass U tube. The sensitivity of this transducer is low ($\approx$0·08 mV Torr^{-1}) so the output was amplified using a chopper-stabilised amplifier (Ancom, type 15C-3) and displayed on a 3½-digit digital voltmeter. This combination gave a sensitivity of $\approx$12 mV Torr^{-1}, giving a theoretical resolution of $\approx \pm$0·08 Torr, but thermal zero and sensitivity shift combine to give an operating resolution of $\approx \pm$0·3 Torr. The gauge was tested using water and the gradient of a graph of log$_e$(output voltage) against T^{-1} gave ΔH (vaporization, 316 K) = 10·4 kcal mol^{-1} (lit.[12] 10·52 kcal mol^{-1} at 298·15 K). The results from this experiment were also used to calibrate the gauge. Temperature measurement was accurate to ±0·05 K.

RESULTS

The tetrachloroborates hydrolysed rapidly and quantitatively[2] according to equation (1). The observed

$$\mathrm{M[BCl_4](c)} + (n+3)\mathrm{H_2O(l)} = (\mathrm{MCl} + \mathrm{H_3BO_3} + 3\mathrm{HCl}),n\mathrm{H_2O(soln.)} \quad (1)$$

enthalpies of reaction are collected in Table 1. Standard enthalpies of formation were calculated from equation (2), which assumes the enthalpies of mixing of the products are zero, and the following ancillary data: $\Delta H_f^{\ominus}$(RbCl, 10 000 H$_2$O) = −99·923 ± 0·037;[13,14] $\Delta H_f^{\ominus}$(CsCl, 10 000 H$_2$O) = −101·606 ± 0·037;[13,14] $\Delta H_f^{\ominus}$(HCl, 3 300 H$_2$O) = 39·875 ± 0·021;[12,15] $\Delta H_f^{\ominus}$(H$_3$BO$_3$, 10 000 H$_2$O) = −256·34 ± 0·31;[13,16,17] and $\Delta H_f^{\ominus}$(H$_2$O, l) = −68·315 ± 0·010[15] kcal

$$\Delta H_f^{\ominus}(\mathrm{M[BCl_4],c}) = \Delta(H_f^{\ominus}\mathrm{MCl,\ 10\,000\ H_2O}) + \Delta H_f^{\ominus}(\mathrm{H_3BO_3,\ 10\,000\ H_2O}) + 3\Delta H_f^{\ominus}(\mathrm{HCl,\ 3\,330\ H_2O}) - 3\Delta H_f^{\ominus}(\mathrm{H_2O,l}) - \Delta H(\mathrm{M = Rb\ or\ Cs}) \quad (2)$$

mol^{-1} (ignoring the thermal effect of the different extent of dilution of the products introduces a maximum error of 0·025 kcal mol^{-1}). Hence $\Delta H_f^{\ominus}$(Rb[BCl$_4$],c, 298·15 K) = −220·7 ± 0·4 kcal mol^{-1} and $\Delta H_f^{\ominus}$(Cs[BCl$_4$],c, 298·15 K) = −225·0 ± 0·3 kcal mol^{-1}. The dissociation-pressure measurements for Cs[BCl$_4$] are given in Table 2. A least-squares fit of the results in Table 2 gives equation (3).

TABLE 1

Heats of hydrolysis of rubidium and caesium tetrachloroborates

n *	$-\Delta H$(M = Rb)/ kcal mol^{-1}	n *	$-\Delta H$(M = Cs)/ kcal mol^{-1}
14 411	50·15	10 725	47·56
14 374	50·82	10 394	47·55
12 237	50·43	9 815	47·57
11 167	50·53	9 721	47·31
10 203	50·24	9 004	47·72
9 842	49·89	7 754	47·53
9 747	50·00	7 068	47·79
9 078	50·19	Mean (±2σ)	47·5 ± 0·1
9 004	49·99		
7 559	49·92		
Mean (±2σ)	50·2 ± 0·2		

* These mol ratios from equation (1) include a buoyancy correction for sample mass.

TABLE 2

Dissociation pressures for Cs[BCl$_4$]

θ_c/°C	55	60	65	70	75	80
p/Torr	2·0	4·0	6·7	10·5	16·7	27·2

$$\log_e p = -[(11\,790 \pm 360)/T] + (36{\cdot}7 \pm 10 \pm 1) \quad (3)$$

DISCUSSION

Assuming the dissociation of Cs[BCl$_4$] is given by equation (4), we may write $K_p = p_{\mathrm{BCl_3}}$ Torr and $K_{p/p^{\ominus}}$ =

$$\mathrm{Cs[BCl_4](c)} \rightleftharpoons \mathrm{CsCl(c)} + \mathrm{BCl_3(g)} \quad (4)$$

0·001316 $p_{\mathrm{BCl_3}}$ taking the activities of the crystalline phases as unity. Hence equation (5) applies over the

$$\ln K_{p/p^{\ominus}} = -[(11\,790 \pm 360)/T] + (30{\cdot}1 \pm 1{\cdot}1) \quad (5)$$

range 55—80 °C. From equation (5) we obtain $\Delta H_4^{\ominus}$ at the mid-point of the temperature range, *i.e.* $\Delta H_4^{\ominus}$ (341 K) = 23·4 ± 0·7 kcal mol^{-1}. Using $\Delta H_f^{\ominus}$(BCl$_3$, g) = −96·15 ± 0·30 kcal mol^{-1},[18] $\Delta H_f^{\ominus}$(CsCl,c) = −103·5 ± 0·3 kcal mol^{-1},[14] and the calorimetric results described above, $\Delta H_4^{\ominus}$ may be obtained directly, *i.e.* $\Delta H_4^{\ominus}$(298·15 K) = 25·3 ± 0·5 kcal mol^{-1}. Using heat capacities of similar substances, $\Delta C_p^{\ominus}(4) \approx -3$ cal K^{-1} mol^{-1}, gives a correction of $\approx$0·12 kcal mol^{-1} for the temperature difference in two measurements of $\Delta H_4^{\ominus}$. Thus the agreement is only fair, although more confidence should be attached to the calorimetric result. Extrapolating equation (5) to 298·15 K we obtain the following estimates at 298·15 K: $K_{p/p^{\ominus}} \approx 8 \times 10^{-5}$; $\Delta G_4^{\ominus} \approx 6$ kcal mol^{-1}; and $\Delta S_4^{\ominus} \approx 60$ cal K^{-1} mol^{-1}.

Heats of formation of two salts with a common anion

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may be used,[19] in combination with readily available ancillary data, to determine a ' thermochemical radius ' for that anion. This permits estimation of the lattice energies of salts containing that anion *via* Kapustinskii's equation.[19,20] This method of estimation is only useful when crystallographic dimensions are not available and hence a more refined calculation [19] of lattice energy is not possible. The equation for ' thermochemical radius ' is a quartic whose coefficients include the differences between the heats of formation of the salts and the cation gases. Unfortunately the heats of sublimation [21,22] of Rb and Cs, and hence the heats of formation of the ion gases, are not known to high accuracy. Hence the derived thermochemical radius for $[BCl_4]^-$ ($4{\cdot}48 \pm 1{\cdot}45$ Å) has a large uncertainty. The ancillary data for this calculation were: $r(Rb^+) = 1{\cdot}48$;[23] $r(Cs^+) = 1{\cdot}69$ Å;[23] $\Delta H_f^\ominus(Rb^+,g) = 116{\cdot}78 \pm 1{\cdot}00$;[21,24] and $\Delta H_f^\ominus(Cs^+,g) = 109{\cdot}58 \pm 1{\cdot}00$ kcal mol^{-1}.[22,24] From covalent bond lengths and van der Waals radii, the radii of circumscribing spheres for $[BCl_4]^-$ and $[BF_4]^-$ may be estimated as 3·5 and 2·9 Å respectively. The ' thermochemical radius ' of $[BF_4]^-$ is 2·4 Å (calculated using recent heats of formation [25] for the Group 1 tetrafluoroborates) and this figure in comparison with the radii derived above leads us to prefer the lower limit of 3·0 Å for the ' thermochemical radius ' of $[BCl_4]^-$.

Using this value in the Kapustinskii equation we obtain the lattice-energy estimates $\Delta H_L(Rb[BCl_4]) = 119$ and $\Delta H_L(Cs[BCl_4]) = 114$ kcal mol^{-1}, from which $\Delta H_f^\ominus([BCl_4]^-,g) \approx -220$ kcal mol^{-1} {*cf.* $\Delta H_f^\ominus([BF_4]^-,g) \approx -432$ kcal mol^{-1}, calculated using 2·4 Å for the thermochemical radius of $[BF_4]^-$ in Kapustinskii's equation and recent heat of formation [25] data for $Li[BF_4]$, $Na[BF_4]$, and $K[BF_4]$}. The sensitivity of these lattice enthalpies to choice of anion radius is *ca.* 20 kcal mol^{-1} Å^{-1}. The enthalpy change in the gas-phase formation of $[BCl_4]^-$ [equation (6)] is −65 kcal mol^{-1} compared with −79 [19] for $[BH_4]^-$ and −96 for $[BF_4]^-$.

$$BCl_3(g) + Cl^-(g) \longrightarrow [BCl_4]^-(g) \qquad (6)$$

Thus the thermodynamic instability of the tetrachloroborates compared with tetrafluoroborates may not be readily deduced from the relative magnitudes of the lattice energies {$\Delta H_L(Rb[BF_4]) \approx 135$, $\Delta H_L(Cs[BF_4]) \approx 129$ kcal mol^{-1} *via* Kapustinskii's equation}, although the difference in the gas-phase heats of formation of the complex ions is significant. The relative stability is clearly demonstrated in the dissociation pressures and enthalpies given in Table 3.

TABLE 3

Enthalpy changes and dissociation pressures for the reaction $M^I[BX_4](c) \longrightarrow M^IX(c) + BX_3(g, p_{BX_3})$ (M = Rb or Cs; X = F or Cl)

Compound	$\Delta H^\ominus$ (25 °C)/ kcal mol^{-1}	p_{BX_3} (60 °C)/ Torr
$Rb[BCl_4]$	21·7	≈20 *
$Rb[BF_4]$	>44 †	5×10^{-11} ‡
$Cs[BCl_4]$	25·3	4·0
$Cs[BF_4]$	>44 †	5×10^{-11} ‡

* Unpublished results. † Based on $\Delta H^\ominus(Li[BF_4]) < \Delta H^\ominus(Na[BF_4]) < \Delta H^\ominus(K[BF_4]) = 44$ kcal mol^{-1}.[25] ‡ Extrapolated (J. H. de Boer and J. A. M. van Liempt, *Rec. Trav. chim.*, 1927, **46**, 317).

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