ERRATA.

P.25 table 2.2, line 8, for 'oo' read 'oo'

P.35 line 11 should read $ E = U_c \left( \frac{R}{r} \right) - 2U_c \left( \frac{R}{r} \right)^2 + \frac{1}{2}K\left(1-l_\circ \right)^2 + \frac{1}{2}K_s \left(e-e_\circ \right)^2$

P.34 table 3.10, line 10, column 1, read ' $\Delta H^o f \text{cis NOCH(CH}_2\text{CH}_2\text{)}_2\text{CHCH}$'

P.128 table 6.3, line 7, column 2 for '60.065' read '61.065'

P.144 line 23, for ' $\frac{N_4}{n} \beta$' read ' $\frac{N_4}{p} \beta$'

P.147 line 20, for 'Chidtovski' read 'Shidlovski'

P.147 line 22, for ' $S_8$' read ' $S_2O_8$'

P.149 table 6.3, line 4, column 1, read ' $\Delta H^o f K_{(1)} - \Delta H^o f K_{(2)}$'

P.152, line 2, for 'peroxide' read 'peroxydisulphate'

P.153 line 2, table 6.8

P.216 line 2, Reference Rossini and Deming, 1939 is


P.217 ' $\mathbf{g} - \mathbf{g}$' etc. should read ' $\mathbf{g} \cdot \mathbf{g}$', the vector dot product.
The Synthesis and Thermochemistry of some Organoboron compounds and Adiabatic Calorimetry

A thesis submitted by Glyn Richard Wellum
in candidature for the degree of Doctor of Philosophy of the University of London.

November, 1969. Royal Holloway College,
Englefield Green,
Surrey.
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Finally the author would like to take the opportunity of thanking Catherine Smith without whose efforts this thesis might never have been typed.
Abstract

Some acylxy and aclyloxyboranes have been prepared with a view to
determining the relative thermodynamic stabilities of triacylxyboranes and
acyls(diclyloxyboranes) with respect to the disproportionation
\[ 2(\text{acylxy})_n H \leftrightarrow (\text{acylxy})_2 \text{BOH(acylxy)}_2 + (\text{acylxy})_2 O. \]
In contrast to literature reports a triacylxyborane structure was never obtained, but the existence of a higher polymer (when \( n = 0 \)) was noted. This behaviour has been rationalised in terms of the molecular structures involved.

The standard heats of formation \( \Delta H^\circ_f \) of
\[ O(CH_2)_x CO-n-C_6H_5, \quad x = 2, 3, 4 \text{ and } (C_6H_5O)_2 CO-n-C_6H_5, \]
and \( O(CH_2)_y OOC-n-C_6H_5, \quad y = 2, 3, 4 \text{ and } OCH(OCH_2CH_2)_2 COO-n-C_6H_5 \)
and \( (C_6H_5O)_2 CO-n-C_6H_5 \) have been determined by means of solution phase reaction calorimetry together with \( \Delta \text{Evaporation} \) data, to be respectively -699.6 \( \pm \) 2.5, -715.3 \( \pm \) 2.9, -722.1 \( \pm \) 2.9 and -825.9 \( \pm \) 2.6 and -927.5 \( \pm \) 2.5, -940.0 \( \pm \) 2.5, -561.0 \( \pm \) 2.9, -565.8 \( \pm \) 2.4 and -602.1 \( \pm \) 2.9 \( \text{kJ mole}^{-1} \). The concept of ring strain has been
discussed and the ring strains of the \( 8-n \)-butyl and \( 8 \)-phenyl heterocycles,
with respect to their acyclic dicthoxyn-butylborane and dicthoxynphenylborane
analogues, determined to be:
\[ O(CH_2)_x OCH-n-C_6H_5, \quad x = 2, 3, 4 \text{ and } 4, 40.9 \pm 5.4, 45.6 \pm 4.2 \text{ and } 39.2 \pm 3.8 \text{kJ mole}^{-1} \]
respectively and for \( O(CH_2)_y OOC-n-C_6H_5, \quad y = 2, 3 \text{ and } 4 \) and
\[ OCH(OCH_2CH_2)_2 COO-n-C_6H_5, \quad -0.9 \pm 5.4, -3.7 \pm 4.2 \text{ and } -3.5 \pm 4.2 \]
and 19.3 \( \pm \) 6.7 \( \text{kJ mole}^{-1} \) respectively. It has been shown that dicthoxynphenyl-
boran is not a good strainless reference molecule and that the ring strains of the \( 8 \)-phenyl heterocycles given here should be increased by ca. 41 \( \text{kJ mole}^{-1} \).

An automatic adiabatic solution reaction calorimeter suitable for slow
reactions has been developed and a value for the heat of solution THAM in
0.1M HCl at 298K of -29.7 \( \pm \) 0.021 \( \text{kJ mole}^{-1} \) for a series of ten runs obtained
(c.f. -27.7 \( \pm \) 0.003 \( \text{kJ mole}^{-1} \), lit). It has been used for reactions of up
to two hours duration. Possible standard slow reactions have been investigated

R. H. C.
and the use of the reaction between potassium peroxysulphate and aqueous potassium iodide (K₂S₂O₈(aq) + 2KI(aq) → K₂SO₄(aq) + 2I⁻(aq)) is recommended as a slow test reaction for solution reaction calorimeters.
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Chapter One

Acyloxyboranes and Diboroboron Heterocyclics

Organoboron chemistry has been the subject of several texts and reviews, boro-carbon and boro-oxygen chemistry in particular being covered by Gerrard (1961), Steinberg (1964), Steinberg and Schlenk (1966) and Hestert (1967). Heterocyclic organoboron chemistry was reviewed by Hailie (1962).

1. Acyloxyboranes

Nomenclature

The first type of compound to be considered in this thesis may be regarded as the mixed acid anhydride of boric acid and a carboxylic acid and as such contains the group

\[
\begin{array}{c}
\text{O} \\
\text{B-OCR}
\end{array}
\]

Such compounds are named 'acyloxyboranes' as derivatives of the simplest hypothetical borane \( \text{BH}_2 \). If, in such a system, the boro atom is bonded to three oxygen atoms

\[
\begin{array}{c}
\text{O} \\
\text{B-OCR} \\
\text{O}
\end{array}
\]

then the compounds may be named as derivatives of boric acid, i.e. acyl borates. In the literature such compounds are frequently referred to as boro carboxylates, e.g. boro acetate.

The first reported observation of this type of compound was by Schützenberger (1861) who reacted boric oxide with acetic anhydride to obtain a solid mass. This work was repeated by Schiff (1867) who isolated a white glasier substance from the reaction mixture, but a structure was not proposed until 1903 when Pictet and Geismann, after carrying out the same
reaction, precipitated a white crystalline product from acetic acid solution by the addition of dry ether. Analysis and cryoscopic molecular weight determinations indicated that triacetoxyborane, mpt 121°C had been formed.

An identical product was obtained from the reaction of boric acid with acetic anhydride, and the following equations were proposed:

$$\text{B}_2\text{O}_3 + 3(\text{CH}_3\text{CO})_2\text{O} \rightarrow 2(\text{CH}_3\text{COO})_2\text{B}$$

$$\text{B(OH)}_3 + 3(\text{CH}_3\text{CO})_2\text{O} \rightarrow (\text{CH}_3\text{COO})_2\text{B} + \text{CH}_3\text{COOH}$$

A change of recrystallizing solvent appeared to give a different compound because Dimroth (1926), following the procedure of Pictet and Geleznoff but recrystallizing the product from a chloroform/benzene mixture, obtained a material mpt 192-193°C which analysed accurately for a 2:1 ratio of acetate:boron. From these results Dimroth proposed the structure $$(\text{CH}_3\text{CO}_2)_2\text{B} $$

which he termed boric pyrocetate $$\text{B} $$

Cook et al. (1950), by following Pictet and Geleznoff's procedure, recrystallizing from acetic acid, obtained a material mpt 120°C and this was the same as the product obtained, by the same method, by Ahmad and Khandkar (1954) who suggested that in certain circumstances the triacetoxyborane might disproportionate into oxabis(diacetoxyborane) and acetic acid,

$$2(\text{CH}_3\text{COO})_2\text{B} \rightarrow (\text{CH}_3\text{COO})_2\text{B} + (\text{CH}_3\text{CO})_2\text{B}$$

although this behaviour was never observed, even in a sample of the triacetoxyborane kept in a vacuum desiccator for more than two months.

In no instance was the formation of the triacetoxyborane observed by Gerrard and Wheelans (1954) who reacted boric acid with acetic anhydride in varying proportions, a 2:1 ratio of acetate:boron being noted for the product in every case, the reaction occurring as

$$28(\text{OH})_3 + 5(\text{CH}_3\text{CO})_2\text{O} \rightarrow (\text{CH}_3\text{COO})_2\text{B} + 6\text{CH}_3\text{COOH}$$

The reactions between boric acid and acetyl chloride and boron trichloride and acetic acid also gave the same product, but the methods of purification used
in any of these preparations were not disclosed.

From the reaction between boric acid and acetic anhydride, Hayter et al. (1957) reported a product which, when recrystallized from a benzene/chloroform mixture, melted at 147-148°C. An identical compound was also obtained by the addition of dry ether to an acetic acid solution of the same product. The use of Karl Fischer reagent was also reported to show that the oxybis(diacectoxyborane) structure was correct, it reacting with the B-O-B group present as

\[(\text{CH}_2\text{CO}_2)_2\text{BO}(\text{OOCCH}_3)_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + 2(\text{CH}_2\text{CO}_2)_2\text{BO} + \text{the triacetoxyborane, not containing a B-O-B group, being unable to undergo this type of reaction.}

Molecular weight determinations (ebullioscopically in dry chloroform) gave values which agreed with the oxybis(diacectoxyborane) structure, but an attempt to further acetylate the product by heating with acetic anhydride resulted in a substance with a melting range of 120-140°C and whose analysis indicated a reduced acetate content.

A thorough investigation of possible synthetic routes for triacetoxyborane was carried out by Carpenter et al. (1954). In no instance was triacetoxyborane synthesized. The melting behaviour of the acetoxyboranes produced was found to be inconsistent and varied, depending upon the rate of heating, type of heating apparatus and the type of capillary tube employed, the usual behaviour in a demountable guarded tube with a metal heating block - was shrinkage at 100-110°C changing to an amorphous mass at 120-130°C and finally yielding a clear liquid at 140-150°C which resalted over a range 140-150°C. Acetoxyborane was found to be very soluble in chloroform, acetone and ethyl acetate, fairly soluble in glacial acetic acid and dioxane, less soluble in benzene, nitrobenzene and polyglycol ethers and insoluble in diethyl ether and carbon tetrachloride. The chemical composition of the product was not constant, the ratio of boronacetae varying from 1.1 to 1.25 and ebulioscopic and cryoscopic molecular weight determinations ranging from 133 to 380.
On the basis of this evidence Carpenter concluded that the oxybis-
(diacetoxyborane) structure was the most representative but the occurrence
of higher molecular weight species seemed probable, such as

\[
\text{(CH}_3\text{CO}_2\text{O)}_2\text{B} = \text{O} \longrightarrow \frac{\text{B(OCOCH}_3)}{\text{OCOCH}_3} \]

or cyclic structures such as \( \text{CH}_2\text{CO}_2\text{B} = \text{B} = \text{B} = \text{B} = \text{OCOCH}_3 \)

and also possibly incompletely acetylated molecules \((\text{HO})_n\text{B(OCOCH}_3)_{n-3} n = 0, 1, 2\)

The inability to synthesise triacetoxyborane was taken to be an
indication of great instability or non-existence of this molecule.

Gerrard et al. (1958) investigated certain acyloxyboranes in which the
boron atom is linked directly to either an aromatic or an aliphatic carbon
and in the following paper (Duncanson et al., 1958) the structural
implications of their infra red spectra were discussed.

Tri(trifluoroacetoxy)borane, \( (\text{CF}_3\text{COO})_3\text{B} \); diacetoxy phenyl boronate,
\( (\text{CH}_3\text{COO})_2\text{B} = \text{H}_2 \); trifluoroacetoxy di-\( \alpha \)-butylborinates, \( (\text{CF}_3\text{COO})\text{B} = \text{B} = \text{H}_2 \) and
acetoxy di-\( \alpha \)-butylborinates \( (\text{CH}_3\text{COO})\text{B} = \text{B} = \text{H}_2 \) were prepared from the respective
boron chloride and carboxylic acid, but similar procedures using phenylboron
dichloride and trifluoroacetic acid and diphenylboron chloride and acetic acid
 gave dephenylation reactions

\[
\text{CH}_3\text{COO} = \text{OC} \longrightarrow (\text{CF}_3\text{COO})_3\text{B} + \text{C}_6\text{H}_6 + 2\text{HCl}
\]

\[
(\text{CH}_3\text{COO})_2\text{B} + 2\text{HCl} \longrightarrow (\text{CF}_3\text{COO})_2\text{B} + \text{C}_6\text{H}_6 + \text{HCl}
\]

Di(trifluoroacetoxy)phenylboronate, \( (\text{CF}_3\text{COO})_2\text{B} = \text{H}_2 \) and trifluoroacetoxy
diphenylborinates, \( (\text{CF}_3\text{COO})\text{B} = \text{B} = \text{H}_2 \) were obtained from the reactions of the
boron chlorides with sodium trifluoroacetate. Oxybis(trifluoroacetoxy
n-butylborane) was formed from the reaction of di-n-butylboronous anhydride with trifluoroacetic acid by elimination of n-butane

$$(\text{Bu}_2\text{B})_2\text{O} + 2\text{CF}_3\text{COOH} \rightarrow [(\text{CH}_3\text{COO})\text{B(OBu)}]^2\text{O} + 2\text{n-C}_4\text{H}_10$$

and oxybis(di-trifluoroacetoxyborane) was produced during the vacuum sublimation of tri(trifluoroacetoxyborane) with the elimination of the volatile

$$2(\text{CF}_3\text{COO})_3\text{B} \rightarrow (\text{CF}_3\text{COO})_2\text{B(OOCF}_3)_2 + (\text{CF}_3\text{CO})_2\text{O}$$

trifluoroacetic anhydride. The reactions between n-butoxyboron dichloride and di-n-butoxyboron chloride and acetic acid both gave oxybis(diacetoxyborane), presumably due to the spontaneous breakdown of the n-butoxy acetoxyborane intermediates

$$3\text{Cl}_2\text{B(OBu)} + 6\text{CH}_3\text{COOH} \rightarrow 3[(\text{CH}_3\text{COO})_2\text{B(OBu)}]^2\text{O}$$

$$+ 3\text{B(OBu)}_3 + (\text{CH}_3\text{CO})_2\text{O}$$

$$6\text{ClB(OBu)}_2 + 6\text{CH}_3\text{COOH} \rightarrow 6[(\text{CH}_3\text{COO})_2\text{B(OBu)}]^2\text{O}$$

$$+ 6\text{B(OBu)}_3 + (\text{CH}_3\text{CO})_2\text{O}$$

Three types of disproportionation in acyloxyboranes were noted

$$(\text{RCOO})_3\text{B} \rightarrow [(\text{RCOO})_2\text{B}]^2\text{O} + (\text{RCOO})_2\text{O}$$

$$3(\text{RCOO})_2\text{BR}_1 \rightarrow (\text{RCOO})_2\text{B} + 3(\text{RCOO})_2\text{O}$$

$$2(\text{RCOO})_2\text{BR}_2 \rightarrow (\text{RCOO})_2\text{B} + (\text{RCOO})_2\text{O}$$

Disproportionation was found to be more likely when $R = \text{CH}_3$ rather than $R = \text{CF}_3$, this order being rationalized as follows. For mixed halogenated carboxylic acid anhydrides, e.g. acetic chloroacetic anhydride (Emery and Gold, 1950a,b) and acetic trifluoroacetic anhydride (Bourne et al., 1954) the following dissociation occurs.
where R is the halogenated alkyl group. Similar dissociations were therefore proposed for the mixed boric acid, carboxylic acid anhydrides:

\[
\begin{align*}
\text{CH}_2 & \overset{\cdot \cdot \cdot}{\Rightarrow} \text{O} - \text{O} - \text{B} & \overset{\cdot \cdot \cdot}{\Rightarrow} \text{CH}_3\text{CO}^+ + \text{O}_2^-
\text{CF}_2 & \overset{\cdot \cdot \cdot}{\Rightarrow} \text{O} - \text{O} - \text{B} & \overset{\cdot \cdot \cdot}{\Rightarrow} \text{CF}_3\text{CO}^+ + \text{O}_2^-
\end{align*}
\]

thereby allowing the diacyloxyborane structure to be formed more readily in the case of the non-fluorinated acyloxyboranes than the fluorinated molecules.

The infra red spectra (Huncanson et al., 1955) of the compounds mentioned in Gerrard's (1955) paper were investigated and abnormally low carbonyl stretching frequencies were noted in most cases. This was attributed to co-ordination to the boron atom by the carbonyl oxygen, this co-ordination tending to reduce the carbonyl stretching frequencies from an unco-ordinated value of about 1740 cm\(^{-1}\) by about 100 cm\(^{-1}\). In some cases carbonyl bands of the relevant carboxylic anhydrides were seen and this was taken to be indicative of disproportionation of the mixed carboxylic acid, boric acid anhydrides occurring. For instance, in the spectrum of acetoxy di-n-butylborinite \(\text{Bu}_2\text{BOOCCH}_3\), bands at 1825 and 1757 cm\(^{-1}\) were attributed to the presence of acetic anhydride, and the third carbonyl band at 1603 cm\(^{-1}\) due to the co-ordinated carbonyl in the borinite; the material is therefore an equilibrium mixture and should be represented as:

\[
2\text{Bu}_2\text{BOOCCH}_3 \underset{\text{room temp.}}{\overset{\text{eq}}{\rightleftharpoons}} \text{Bu}_2\text{BOOBu}_2 + (\text{CH}_3\text{CO})_2\text{O}
\]

the intensities of the bands indicated that at room temperature much less than 50% of the borinite was disproportionated. The effect of replacing the acetyl group by trifluoroacetyl was found to give rise to an increase in the carbonyl stretching frequency by 50–70 cm\(^{-1}\) and the tendency of co-ordination to a boron atom by the trifluoroacetyl carbonyl reduced, as compared to an acetyl carbonyl, as shown by trifluoroacetoxy di-n-butylborinite, \(\text{Bu}_2\text{BOOCOF}_3\),
which possesses both a co-ordinated and non-co-ordinated carbonyl (1672 and 1786 cm$^{-1}$) as opposed to the non-fluorinated analogue which only exhibits a co-ordinated (1603 cm$^{-1}$) carbonyl. To distinguish between inter and intra molecular co-ordination the extinction coefficient of the 1608 cm$^{-1}$ co-ordinated carbonyl frequency of acetate di-n-butylborinate in cyclohexane (as opposed to 1603 cm$^{-1}$ of the pure material) was observed to be constant - within 5% - over a concentration range of 0.0244-0.0133M, the slight variation being attributed to hydrolysis of material in imperfectly dried solvent. In compounds based on a $\text{SCH}_2\text{S}$ skeleton chelation to give either a four or a six-membered ring would appear possible but no results to distinguish between them were given.

From the reaction between boron tribromide and a carboxylic acid in benzene Yurev et al. (1960) reported the stable existence of triacetoxyborane, tripropionyloxyborane and tributyryloxyborane.

During investigations of the reactions of boron sulphide Lalancette et al. (1966) proposed a synthetic route to the triacyloxy and triaryloxyboranes from the reaction of either boron sulphide or an orthothioborate ester with carboxylic acids. Preparations of tripropionyloxyborane, tribenzoyloxyborane and tricinnamoyloxyborane were reported but no reference to Yurev’s work was made although the melting point of the tripropionyloxyborane, 110-113°C, differed markedly from Yurev’s value of 87°C. In the case of the reaction between boron sulphide and acetic acid the final product analysed as a mixture of triacetoxyborane and oxybis(diacetoxyborane). Lalancette considered that
the triacetoxy compound was formed first, but that it thermally decomposed to some extent to oxybis(diacetoxyborane) and acetic anhydride. By reacting boric acid with acetic anhydride a solid was obtained, mpt 120°C, which lost weight when kept over potassium hydroxide, its mpt increasing to 145-147°C. From this it was concluded that the previous reports of triacetoxyborane were in fact oxybis(diacetoxyborane) which had retained acetic anhydride upon crystallising.
**B) Dioxaboron Heterocyclics**

**Nomenclature**

As is conventional the nomenclature recommended in 'The Ring Index' (Patterson et al., 1960) will be used. For monocyclic dioxaboron compounds numbering of the ring starts at oxygen then via boron, the size of the ring being specified by the following suffixes:

- 5 membered -olan
- 6 membered -inan
- 7 membered -epan

**e.g.**

![Diagram](image)

2-chloro-1,3,2-dioxaborolan

The only dioxaboron bicyclo-compound which will be discussed, following the standard convention for bicyclo-compounds, is named as follows:

![Diagram](image)
the numbering starting at the bridgehead and passing through the bridge in order of decreasing size, the number of atoms involved in the rings being specified by the equivalent alkane suffix

3-phenyl-2,4-dioxo-3-borabicyclo[3.2.2]nonane

The chemical and physical behaviour of such compounds has been shown to be highly dependent upon the size of the dioxaboron ring. Dale (Hubert et al., 1961) found that the heat of complexing between pyrrolidine and 2-butoxy-1,3,2-dioxaborolan was much greater than in the case of the corresponding six-membered ring and the acyclic tributylborate. Competitive reactions between a mixture of ethane diol and propene-1,3-diol and boric acid in which the five or six-membered dioxaboron cyclic esters may be formed showed that the six-membered ring is formed preferentially. These observations were discussed in terms of the ring strain in the five-membered ring being relieved by the amine co-ordination, thus allowing sp² boron to rehybridize as sp³, the tetrahedral angle being much more compatible with a five-membered cyclic structure than the 120° sp² angle. In the case of the six-membered rings a 120° or 109° 28 angle can exist in a puckered conformation, thus the energy difference between the two six-membered conformations is much less than that between the two five-membered, which gives rise to the variation in heat of amine complexing. It was also noted that the strain energy in the five-membered rings must practically cancel the energy gain on cyclization because although 2-butoxy-1,3,2-dioxaborolan was distillable, on standing it became very viscous, this being attributed to the following type of equilibria
where open chain polymers are formed. In the case of the six-membered 2-butoxy-1,3,2-dioxaborinan such equilibria were much less important, the substance remaining as a liquid indefinitely.

Further work on amine complexes of cyclic boronates (Finch and Lockhart, 1962) in which 2-phenyl-1,3,2-dioxaborolanes and 2-propyl-1,3,2-dioxaborolane and 2-phenyl-1,3,2-dioxaborinanes and 2-propyl-1,3,2-dioxaborinan were studied showed that the five-membered rings formed amine complexes in much higher yield and were more stable with respect to dissociation than the six-membered analogues. No amine adducts were obtained with the six-membered propyl substituted ring although with the phenyl substituted analogues they were. In both cases amine complexes with five-membered rings were obtained. This behaviour was explained by the electrophilic nature of the phenyl nucleus enhancing the Lewis acid strength of these compounds.

Intermolecular association of dioxaboron heterocycles is also very dependent on the ring size and the nature of the substituents as shown in Table 1.1 which lists the degree of association determined for five and six-membered 1,3-dioxaboron and 1,3-dithiaboron cyclic molecules (Finch and Gardner, 1963; Finch et al., 1966).
Table 1.1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Degree of Association</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05M</td>
</tr>
<tr>
<td>O(CH₂)₂OSOCl</td>
<td>1.22</td>
</tr>
<tr>
<td>O(CH₂)₂O₃O(CH₂)₂Cl</td>
<td>1.01</td>
</tr>
<tr>
<td>O(CH₂)₂O₃OB₉</td>
<td>1.01</td>
</tr>
<tr>
<td>O(CH₂)₂O₃C₆H₅</td>
<td>1.0</td>
</tr>
<tr>
<td>O(CH₂)₃O₃Cl</td>
<td>1.12</td>
</tr>
<tr>
<td>O(CH₂)₃O₃O(CH₂)₂Cl</td>
<td>1.03</td>
</tr>
<tr>
<td>S(CH₂)₂SRCl</td>
<td>1.02</td>
</tr>
<tr>
<td>S(CH₂)₂SR₆C₆H₅</td>
<td>0.99</td>
</tr>
<tr>
<td>S(CH₂)₃SRCl</td>
<td>1.08</td>
</tr>
<tr>
<td>S(CH₂)₃SR₆C₆H₅</td>
<td>1.01</td>
</tr>
</tbody>
</table>

The greatest association can be seen to occur in the five-membered 1,3-diazaborolan systems, but this can be reduced to practically zero when a bulky substituent group such as phenyl is linked to boron. Such an effect is not surprising as the mode of association is oxygen to boron, most probably in a stacking arrangement with oxygen donating its lone pair of electrons to boron (Finch and Gardner, 1963).
Recent boron-11 nuclear magnetic resonance spectra of five and six-membered phenyl dioxaboron and dialkylamino dioxaboron rings (Cragg and Lockhart, 1969) showed chemical shifts (relative to trimethyl borate) of 12-13 ppm downfield for phenylborolans and 6-8 ppm downfield for dialkylaminoborolans and 8-9 ppm downfield for phenylborinans. These results indicate more shielding in the six than the five membered rings and from this it was inferred that some intramolecular \( \pi \) electron back donation occurs in the dioxaborinan rings.

A physical property which is influenced markedly by ring size is ring strain. A detailed consideration of this concept is made in Chapter Two, but it is important to note here that such physical measurements relating to this aspect must be made in the gas phase to remove the effects of intermolecular interactions. Previous work in this direction (Finch et al., 1966) in which the 2-chloro-1,3,2-dioxaboron five and six-membered rings were investigated lacked precision because of the difficulty involved in estimating the latent heat of vaporization of the borolan - the substantial association occurring in the pure liquid phase causing the liquid to boil over a wide temperature range.

To eliminate this difficulty it was decided to study cyclic dioxaboron systems in which the substituent on the boron would be such as to reduce the
intermolecular association effect. 2-phenyl-1,3,2-dioxaboron systems
appeared to be promising, but because of the additional electronic effects
associated with the aromatic nucleus, it appeared expedient to consider the
2-n-butyl substituted analogues as well.

Such a programme would require the standard heats of formation $\Delta H_f^\circ$ (gas)
of these compounds to be determined which may be achieved by calorimetric
techniques. If a meaningful interpretation is to be placed on the heat
change afforded by a chemical reaction, then the initial and final states
of reactants and products must be known accurately. When the desired
thermochemical quantity is the standard heat of formation, the calorimetric
reaction must be such as to degrade the compound into certain 'key' compounds
whose standard heats of formation are known. Static oxygen-bath calorimetry
as normally carried out for organic compounds is not generally applicable in
the case of organo-boron compounds because of the non-reproducibility of the
final thermodynamic state, variable quantities of elemental boron, boron
carbide and partially hydrated boric oxide being produced. The B-O bond is
readily susceptible to hydrolytic cleavage and the B-O bond to oxidative attack

e.g. \[(\text{CH}_2\text{O})_2\text{B} + 3\text{H}_2\text{O} \xrightarrow{\text{fast}} 3\text{CH}_2\text{OH} + \text{H}_3\text{BO}_3\]

\[\text{C}_6\text{H}_5\text{B(OH)}_2 + \text{H}_2\text{O} + \text{base} \xrightarrow{\text{fast}} \text{C}_6\text{H}_5\text{OH} + \text{H}_3\text{BO}_3 + \text{base} \] (Finch and Gardner, 1966) so solution reaction calorimetry provides a suitable tool for studying
thermochemically many organo-boron compounds.

In the type of Constant Temperature Environment (C.T.E.) solution
reaction calorimeter developed in this laboratory (F.J. Gardner, 1963;
Finch and F.J. Gardner, 1964) a major source of error is the estimation of
heat losses through the walls of the calorimeter which, in the case of a slow
reaction (> 3 minutes), can become quite serious. To a large extent such
heat losses are circumvented in an adiabatic calorimeter in which the
temperature difference across the walls of the calorimeter is kept constant.
The development of such an instrument is described in detail in Chapter Five.
Chapter One References


Dieroth, C., Ann., 1926, 446, 927.


Schützenberger, M., Compt. Rend., 1861, 22, 338.


Chapter Two. Ring Strain

A major step in the stereochemistry of carbon compounds was taken in the latter part of the nineteenth century when the concept of the tetrahedral carbon atom was proposed independently by van't Hoff (1867) and Le Bel (1874). With the preparations of the four membered carbon ring compound 1,3-cyclobutanedicarboxylic acid by Markownikoff and Krestownikoff in 1881, formed by heating chloropropionic acid with dry sodium ethoxide, and of the three membered cyclopropane by Freund in 1882 by reaction of trimethylene dibromide with sodium, an extension to the tetrahedral carbon theory was required.

Such an extension was provided by the 'Strain Theory' of Meyer in 1885 in which it was assumed that the 'normal' or preferred configuration of carbon was tetrahedral, forming four bonds disposed at an angle of \(109.5^\circ\), but these angles could be altered, the molecule then acquiring a strain energy which would tend to make it unstable. Meyer defined the strain in a cyclic compound as \(\frac{1}{2}(109.5^\circ - \text{bond angle in the ring})\) - the factor \(\frac{1}{2}\) being present because the strain at each carbon atom is divided between two bonds. The major fault in this theory was Meyer's assumption that all carbon rings were planar. On this basis values at strain for various ring sizes are shown in Table 2.1.

<table>
<thead>
<tr>
<th>Ring Size</th>
<th>Bond Angle</th>
<th>Strain</th>
<th>Ring Size</th>
<th>Bond Angle</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>60°</td>
<td>24°44'</td>
<td>8</td>
<td>135°</td>
<td>-12°46'</td>
</tr>
<tr>
<td>4</td>
<td>90°</td>
<td>9°44'</td>
<td>9</td>
<td>140°</td>
<td>-15°16'</td>
</tr>
<tr>
<td>5</td>
<td>108°</td>
<td>0°44'</td>
<td>10</td>
<td>144°</td>
<td>-17°16'</td>
</tr>
<tr>
<td>6</td>
<td>120°</td>
<td>-5°16'</td>
<td>11</td>
<td>147°16'</td>
<td>-19°54'</td>
</tr>
<tr>
<td>7</td>
<td>128°34'</td>
<td>-9°33'</td>
<td>12</td>
<td>150°</td>
<td>-20°16'</td>
</tr>
</tbody>
</table>

Taken from Eliel 1962 'Stereochemistry of Carbon Compounds' P.189
For rings of six members and less, Esenstor's Strain Theory was in qualitative agreement, the increasing strain being paralleled by increasing reactivity. The negative strain of the larger rings corresponding to an increase in the C-C-C angle from tetrahedral was taken as being in agreement with the fact that no rings greater than six had either been prepared or discovered.

That rings larger than five membered could be strainless if the hypothesis of ring planarity was dispensed with while still retaining the tetrahedral carbon concept, was first conceived by Sackee (1890,1892). In the case of cyclohexane, however, two isomers could be constructed, one the 'chair' or rigid form and the other the 'boat' or flexible form. Because two isomers of cyclohexane had not been observed, Sackee's theory lay in disrepute for thirty years until Mohr (1918,1922) showed that both these forms were readily interchangeable, conversion from one to the other requiring only a small amount of distortion at the bond angles at carbon.

Stability of Rings

The most direct approach to the question of energy contained in a cyclic system is afforded by a thermochemical point of view. In the case of the cycloalkanes, the heat of combustion at constant volume at 298.15K per methylene group is a reflection of the internal energy possessed by the ring. If this value is then compared with that derived from differences in the heats of combustion of adjacent longchain n-alkanes, then the difference is a measure of the strain energy per methylene group of the cyclic hydrocarbon as compared to its straight chain analogue. Table 2.2 lists some of these values for cycloalkanes.
### Table 2.2

<table>
<thead>
<tr>
<th>No Atoms in Ring (n)</th>
<th>$\Delta H_n$ (kJ mole(^{-1}))</th>
<th>$\Delta H_n - 37.62$ (kJ mole(^{-1}))</th>
<th>No Atoms in Ring (n)</th>
<th>$\Delta H_n$ (kJ mole(^{-1}))</th>
<th>$\Delta H_n - 37.62$ (kJ mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>39.22</td>
<td>2.20</td>
<td>11</td>
<td>37.86</td>
<td>0.24</td>
</tr>
<tr>
<td>4</td>
<td>38.18</td>
<td>1.56</td>
<td>12</td>
<td>37.69</td>
<td>0.07</td>
</tr>
<tr>
<td>5</td>
<td>37.93</td>
<td>0.31</td>
<td>13</td>
<td>37.72</td>
<td>0.10</td>
</tr>
<tr>
<td>6</td>
<td>37.93</td>
<td>0.00</td>
<td>14</td>
<td>37.62</td>
<td>0.00</td>
</tr>
<tr>
<td>7</td>
<td>37.85</td>
<td>0.21</td>
<td>15</td>
<td>37.64</td>
<td>0.04</td>
</tr>
<tr>
<td>8</td>
<td>37.91</td>
<td>0.29</td>
<td>16</td>
<td>37.64</td>
<td>0.04</td>
</tr>
<tr>
<td>9</td>
<td>37.95</td>
<td>0.33</td>
<td>17</td>
<td>37.57</td>
<td>0.05</td>
</tr>
<tr>
<td>10</td>
<td>37.91</td>
<td>0.29</td>
<td></td>
<td>37.62</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Heats at combustion of the cycloalkanes per methylene group (\(\frac{\Delta H}{n}\)) in the gaseous state at 25°C and 1 atmosphere pressure.

\(\Delta H_n - 37.62\) as the ring size increases from cyclopropane to cyclohexane is due primarily to the increasing ability of the larger rings to accommodate the tetrahedral carbon atom. Reasons for the slight variations in heat of combustion per methylene group of the larger rings will be considered later.

The thermodynamic criterion of stability is a measure of the free energy change in the given reaction, the standard free energy change is also equivalent to the position at equilibrium in the system. So from a thermodynamic point of view, in the case of a cycloalkane, the stability of the ring with respect to the straight chain alkane would be given by the free energy change of the following reaction, all components in the gas phase.

\[
(CH_2)_n + H_2 \rightleftharpoons C_nH_{2n+2}
\]

Unfortunately little information about straight chain/cyclic equilibria is known and practically none of it quantitative. The predominance of
pyrenose over furanose rings in sugars (Eliel, 1962), however, is an indication of the greater thermodynamic stability of a six-membered ring over a five in these compounds. In the reaction of glycerol with formaldehyde (Bibbert and Carter, 1926), the following system occurs.

\[
H_2O + \underset{CH\text{CH}}{\overset{H^+}{\rightleftharpoons}} C\overset{CH\text{OH}}{\overset{CH\text{OH}}{\text{CH}}} + H_2CO \underset{H^+}{\rightleftharpoons} C\overset{CH\text{OH}}{\text{CH}} + H_2O
\]

The five-membered 1,3-dioxolan ring is formed faster than the 1,5-dioxan and is the major product after a short reaction time. If the reaction is allowed to proceed, the 6-membered dioxan ring becomes the major product indicating its thermodynamic stability in this system, the 5-membered ring being kinetically favoured however.

The ease of ring formation is determined principally by the free energy change in going from the reactants to the transition state. Rusicka (1926, 1935) determined the ease of formation of rings by taking the average yields of preparations. If this 'ease of formation' is considered as a function of ring size, the curve in Figure 2.1 is obtained.

Figure 2.1

![Curve showing ease of formation vs. number of C atoms in ring](image)
These observations may be explained by considering the free energy of activation in terms of the enthalpy and entropy of activation.

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

In the case of three methylene groups, the end carbons are necessarily forced into a favourable position for cyclisation resulting in a low entropy of activation, thus the major factor in this case is the distortion required by the bond angles. The end carbons of four methylene groups in the most favourable trans-butane conformation are as far apart as possible, whereas the most favourable conformation for cyclizing is the cis-butane form in which the hydrogens are eclipsed. This cis-butane form has therefore a higher energy and so a relatively low probability of occurring. Hence the entropy of activation in this case is negative. This proves to be the dominant feature and so the free energy of activation in the case of a four-membered ring is more positive than for a three-membered ring. Thus the ease of formation is higher for a three than for a four-membered ring.

For higher-membered rings than these, the strain energy is much less, so making more negative the enthalpy of activation and hence the free energy change. The marked decrease in case of formation up to ring eleven is due to an increase in torsional strain, due to the requirement of eclipsed hydrogens in cycloalkanes of this size with no angle deformation, coupled with a low probability of the ends of the chain meeting; and the steady increase, up to ring fourteen, an indication of the lessening torsional strain.

Larger rings than these are steadily more difficult to form as the probability of the ends of the chain rapidly decreases.

**Bond Energies**

The review by Skinner and Pilcher (1963) on bond energies deals with this topic lucidly and comprehensively so only a brief mention of the basic concepts and relevant schemes will be made here.
In a given molecule properties of the chemical band such as equilibrium band length, or force constant are unique for that particular molecule. The thermochemical band energy is not such an unambiguous concept, being the quantity assigned to each band in the molecule such that the total sum over the entire molecule is equal to the heat of atomization of the molecule. Such an assignment is, of course, useless unless the band energies so derived are transferable from one molecule to another.

Consider a molecule AaBbCc; then the energy change associated with the process carried out in the gas phase (to eliminate binding energies of the condensed states)

$$\text{AaBbCc}(g) \rightarrow aA(g) + bB(g) + cC(g)$$

is composed of not only the internal binding energies of the molecule, but the zero point energies and also (if the temperature at which the process is carried out is greater than OK) thermal energy of translation, rotation and vibration. The logical starting point for the evaluation of bond energies is to consider the ideal process at OK without zero point energy. The consideration of such a process is impractical, however, as in the case of polyatomic molecules estimations of their thermal and zero point energies cannot usually be made with sufficient accuracy (Cottrell, 1956). For most practical applications though this is not important, it being found to make little difference whether reduction to the hypothetically vibrationless state is made or not.

$$\Delta H_{\text{atomization}} \text{ of molecule} = \sum E$$

$$\Delta H_{\text{formation}} \text{ of molecule}$$

$$\Delta H_{\text{atomization}} \text{ of elements}$$

$$\frac{a}{x} aA + \frac{b}{y} bB + \frac{c}{z} cC$$

From the cycle it can be seen that the heat of atomization $\Delta H_{n}(298.15K) =$ sum of bond energy terms $\sum E$
\[ \Delta H^\circ = a \Delta H^\circ(A, \bar{s}) + b \Delta H^\circ(B, \bar{s}) + c \Delta H^\circ(C, \bar{s}) - \Delta H^\circ(A, B, C, \bar{s}) \]

It should perhaps be noted that the quantities \( \Delta H^\circ(A, \bar{s}) \) etc. refer to the ground states of the atoms, which for carbon is the \( 3P, 5s^2p^2 \) state, whereas in a molecule, tetrahedral carbon is in the \( 5s, 5p^3 \) state. This promotion energy into the given valence state should be incorporated into calculations of bond energy terms if strictly meaningful bond energies are to be evaluated (Moore, 1930). Where all that is required, however, is a system which will allow an assessment of the standard heat of formation of a given compound, then such a sophistication is clearly unnecessary.

Consider the specialized case of the \( n \)-alkanes. If only two types of bond are distinguished \( C-C \) and \( C-H \), then the resulting bond energy scheme is in error - in the case of methane - by more than \( 9.2 \text{kJ mole}^{-1} (2.2 \text{Kcal mole}^{-1}) \) (Skinner and Filcher, 1963), that is to say the observed and calculated values of \( \Delta H(298.15) \) differ by this much. In the case of branched chain alkanes the error is even more. Several methods of extending this simple scheme have been proposed and used. One method is to take some account of non-bonded atom interactions or of adjacent bond interactions, as, for instance, in the Allen scheme (Allen, 1959) both these have been shown to be mathematically equivalent. (Wiener, 1947a, 1947b, 1948; Bernstein, 1951, 1952) Another method is to further distinguish between various types of bond, e.g. Laidler (1956; Lovering and Laidler, 1960) considered the \( \Xi(C-C) \) to be constant, but differentiated between three types of \( C-H \) bond, primary - where only one hydrogen was attached to the carbon, secondary - where two hydrogens were attached and tertiary with three attached. This was further extended by Tatevskii et al. (1961) who distinguished between three kinds of \( C-H \) bond and ten kinds of \( C-C \) bond.
Skinner (Skinner and Pilcher, 1963) has reviewed and compared the various bond energy schemes for hydrocarbons.

Mackle and O’Hare (1961) used an updated value of $\Delta H_a$ graphite in Leidler’s scheme together with extra bond energy terms to include aliphatic sulphones with considerable success. They also distinguished between different carbon hybrids (Mackle and O’Hare, 1916).

Cox (1962) extended this approach to include C-X bonds in both aliphatic and benzenoid compounds where X may be fluoro, chloro, bromo, iodo, hydroxyl, oxide (ethers and aldols), carbonyl, carboxyl, thiol, sulphide, sulfoxide, sulphone, primary – amino or cyano and showed that only one other correction was necessary: when oxygen is present a next nearest neighbour correction must be made. By careful exclusion of dubious data, Cox’s scheme is applicable in the majority of cases with an accuracy rarely falling below 8 kJ mol$^{-1}$ Kj mole$^{-1}$ (2 kcal mol$^{-1}$).

The bond energy terms in all the schemes considered here are therefore enthalpy values which contain contributions not only from the chemical binding energies in molecules, but also contributions from translational, rotational and vibrational energies at 298.15K and the effects of this will be considered in detail later.

**Definition of Ring Strain**

In the case of the cycloalkanes considered, the ring strain was taken as the difference in the heats of combustion of the cycloalkane and of a straight chain alkane per methylene group, the n-alkane being sufficiently long so that differences in the heat of combustion per carbon atom had ceased. That is, the n-alkane was taken as an unstrained model of the strained cycloalkane and the two systems compared, the difference being the ‘ring strain’.
Essentially then, the thermochemical concept of ring strain is the difference in internal energy between the cyclic system and an unstrained model. The model is derived from some structurally similar molecule whose configuration is such that it may be considered to be strain free, as, for instance, in the case of the long chain alkanes which provided a model for the cycloalkanes, or the model may be derived, and this is the more usual, having general application, from some bond energy scheme. Neither system takes theoretical preference, (Nelander and Sunner, 1966) but as different methods can give different results it is necessary to try to obtain a detailed, physically meaningful interpretation of the values obtained by different methods.

At present it is generally accepted practice to designate the difference in the standard heat of formation as determined experimentally \( \Delta H^f(g)_{\text{exp}} \) and the value obtained for \( \Delta H^f(g) \) from a bond energy scheme as strain energy. Such a value is, however, an enthalpy term and if cyclic strain is to be discussed as an energy then such an approximation leads to systematic error of \( mRT \), where \( m \) is the number of rings in the cyclic structure (Nelander and Sunner, 1966). Thus, if the ring strain as defined above is taken as \( \Delta E_g = \Delta H^f(g)_{\text{exp}} - \Delta H^f(g)_{\text{calc}} \) a ring strain energy is then obtained as

\[
\Delta E_g^{298.15} = \Delta H_g - mRT
\]

This is equivalent to about \( 2.5 \text{kJ mole}^{-1} (0.6 \text{Kcal mole}^{-1}) \) apparent strain per ring at room temperature if the enthalpy value is taken as the ring strain.

The experimental value for \( \Delta H^f(g) \) contains contributions from translational, rotational and vibrational energies. As has been pointed out before, bond energy terms also include contributions from similar sources so that \( \Delta H^f_{\text{calc}} \) will to some extent contain contributions from energy of nuclear motions. But these have been derived from acyclic
structures, so that there may be expected to be differences between the actual contributions to $\Delta H^\text{ref}$ and the estimated energy contributions by the bond energy scheme. If the ring strain energy is to be discussed in terms of purely electronic energies then such nuclear motion energy differences between the actual molecule and the model must be eliminated.

Sumner has shown how an estimate of the magnitude of these nuclear motion energies can be achieved by the following argument (Nelander and Sumner, 1966).

Consider the atomization of a cyclic alkane containing $m$ rings

$$C_{2n}H_{2n+2-2m} \rightarrow nC + (2n+2-2m)H$$

<table>
<thead>
<tr>
<th>Type of degree of freedom</th>
<th>$3$</th>
<th>$3n$</th>
<th>$6(n+1-m)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Translation</td>
<td>$3$</td>
<td>$3n$</td>
<td>$6(n+1-m)$</td>
</tr>
<tr>
<td>Rotation</td>
<td>$3$</td>
<td>$3n$</td>
<td>$6(n+1-m)$</td>
</tr>
<tr>
<td>Vibration</td>
<td>$9n-6m$</td>
<td>$9n-6m$</td>
<td>$9n-6m$</td>
</tr>
</tbody>
</table>

$9n-6m$ vibrational degrees of freedom have been lost and $9n-6m$ translational and rotational gained (actually all in the form of translation). The energy of atomization associated with this change may be expressed as

$$E_a = E_a^\text{ex} - 9n-6mF(v_1,T) + (9n-6m)\frac{3}{2}RT$$

(where $E_a^\text{ex}$ is the energy of atomization in the hypothetical vibrationless state). By using a two-constant bond energy scheme derived from $n$-alkanes expressions are then obtained representing the bond energy terms $E^\text{ex}$ and $E^\text{co}$. After summing these expressions over the bonds in the cyclic alkane the expression for the 'calculated' heat of atomization $\Delta E_a(\text{ref}) = \Delta E_a^\text{ex} = (mn-m+1) \frac{3}{2}nF(v_1,T) + mn \sum F(v_1,T) + \frac{3}{2}RT$ is obtained. Ring strain energy is obtained as the difference in these two expressions $E_s = (\Delta E_a(\text{ref}) - \Delta E_a) = E_s^\text{ex} - (mn-m+1) \frac{3}{2}nF(v_1,T) - mn \sum F(v_1,T) - \frac{3}{2}RT$ ($E_s^\text{ex}$ is the ring strain energy in the hypothetically vibrationless state).
From this expression it can be seen that the ring strain energy contains contributions from the $F(p, T)$ at any temperature above 0 K, which are dependent on the fundamental vibrational frequencies of the compounds the bond energy terms were derived from, and on the fundamental vibrational frequencies of the cyclic molecule. They are, however, increasingly compensated for by the $5a_{1}RT$ translation and rotation contributions at high temperatures. Not only do the bond energy terms incorrectly estimate the vibrational frequencies but more important, as can be seen from the expression for $E_{r}$, there are effectively $9n(1-n + 1)-(9n-9)n-(9n-6m) = 6m$ extra vibrational degrees of freedom on the cyclic molecule than those allowed for by the bond energy terms.

Nuclear vibration energy may be considered to be made up of two parts, zero-point energy and thermal vibration energy. The zero-point energy is equal to $\frac{3}{4}h = \frac{1}{4}h$ of every fundamental vibration $\nu_{i}$ (the inaccuracy entailed by assuming harmonic motion is very small) and assuming a variation in fundamental vibrational frequency from 200 cm$^{-1}$ to 3000 cm$^{-1}$ this corresponds to a variation of 1.5 to 17.6 kJ mol$^{-1}$ (0.3 to 4.2 kcal mole$^{-1}$) per vibration. The thermal energy associated with this range is 1.5 to $2.5 \times 10^{-5}$ kJ mol$^{-1}$ (0.35 to $6 \times 10^{-5}$ kcal mole$^{-1}$).

From these figures it is apparent that the energy associated with differences in vibrational degrees of freedom of the cyclic molecule and reference molecule are not necessarily small, and it can be seen that the effect of increasing temperature and increasing number of rings is to decrease the apparent strain energy.

The effect of temperature and zero-point energy on the ring strain of three, four, five, and six membered cycloalkanes can be seen in Table 2.3, taken from Sumner's paper (Nelander and Sumner, 1966).
Table 2.4 (Melander and Sumer, 1966) shows the stabilizing effect obtained by fusing more than one ring together.

Thus to estimate the purely electronic contributions to ring strain incurred by a cyclic molecule one must be able to assess the thermal and zero-point nuclear motion energy differences between the given cyclic molecule and the reference molecule. This in turn requires detailed spectroscopic data which, for the majority of compounds, are not available. Determinations of $\Delta H^e_s$, however, are not free from suspicion as different bond energy schemes emphasise different corrections to differing extents. So, although it is probably impossible at present to arrive at an absolute value for electronic strain energy in a cyclic compound of high precision, many of the errors inherent in the absolute value will cancel out to an appreciable extent if the same bond energy scheme is used and compounds with similar structure and the same number of rings are compared.
In this thesis the present convention of defining ring strain as the difference in the experimentally determined standard heat of formation and that calculated by a bond energy scheme \( \Delta H_a = \Delta H^0(\text{exp}) - \Delta H^0(\text{calc}) \) all in the gas phase, will be adhered to. The bond energy scheme used, unless specifically stated otherwise, is the Cox scheme (Cox, 1962; 1963) and values of \( \Delta H^0(\varepsilon) \) obtained by its application are assumed to be within a range of \( \pm 5 \text{kJ mole}^{-1} (\pm 2\text{kcal mole}^{-1}) \).

**Component Parts of Ring Strain**

T. L. Hill (1946) first postulated that it might be possible to assess the steric strain in a molecule by minimizing the energy given as a sum

\[
e^S = U_0\left(\frac{\varepsilon}{\sigma}\right)^{12} - 2U_0\left(\frac{\varepsilon}{\sigma}\right)^{6} + \frac{3k_B}{2}n(1-\Theta)^2 + \frac{3k_B}{2}(\Theta-\Theta_0)^2
\]

that is, he considered the strain energy to be composed of three separable parts:

1) Van der Waals forces given by the Lennard-Jones potential term
2) Energy associated with distortion of the bonds from their equilibrium lengths

Independently, F. H. Westheimer developed similar ideas and applied them to explain the rate of racemisation of biphenyls.

It is general practice at the present time to extend Hill's reasoning and discuss ring strain in terms of

1) Bond length strain
2) Angle strain (Baeyer strain)
3) Torsional strain (Fitzer strain)
4) Non-bonded interaction strain

These will be discussed separately.

1) **Bond Length Strain**

As compared with other methods of deformation, distortion of bond lengths is extremely costly in energy, and it is generally accepted that bond lengths maintain reasonably invariant values. For the C-C and C-H bonds the bond
stretching force constant is about 5 mdyne Å⁻¹. So the change in energy
\( \Delta V \) is given by

\[
\Delta V = 1.5 \times 10^3 \delta x^2 \text{kJ mole}^{-1}
\]

where \( \delta x \) is the displacement from equilibrium length in Angstroms.

Thus for an energy change of 2.4 kJ mole⁻¹ (0.5 kcal mole⁻¹) \( \delta x = 0.04 \text{Å} \)

9.6 kJ mole⁻¹ (2.0 kcal mole⁻¹) \( \delta x = 0.08 \text{Å} \)

2) Bond Angle Strain

The energy required to deform a bond angle can be estimated, to a first
approximation, from the angle bonding force constant. As Hendrickson pointed
out, (Hendrickson, 1961) in the case of tetrahedral carbon, change in one
bond angle will be accompanied by corresponding changes in the other angles
at the same carbon atom. By minimizing the energy during such a change it
was found that for changes of less than 10° the angles bore a substantially
linear relationship to each other. For a 5° change in the methylene angle
the energy change is about 2.1 kJ mole⁻¹ (0.5 kcal mole⁻¹), a 10° change
corresponds to about 6.0 kJ mole⁻¹ (1.2 kcal mole⁻¹).

Garbisch (1965) has made the point that the equilibrium angle is not
necessarily the ideal angle, and most compounds deviate from ideality, e.g.
electron diffraction of n-alkanes gives the average C-C-C angle as 112.4°, and
compounds with structures

\[
\begin{align*}
\text{A} & : R - C - H \\
\text{B} & : R - C - H
\end{align*}
\]

vary over several degrees in their C-C-H angles depending on their \( R, R' \)
substituents, the ideal equilibrium angles of A and B appearing to be about
115° and 117° respectively. Garbisch distinguishes between angle strain,
which is that energy associated with a change in angle from the ideal angle
(corresponding to the hybridization of the atom at the bond angle) and
angle bending strain which is that energy associated with bending an angle from its ideal equilibrium angle in an 'unstrained' acyclic reference system.

3) Torsional Strain

The effect of a torsional barrier along a single bond was first observed by Fitzer (Kemp and Fitzer, 1936; 1937; Fitzer, 1937) in 1936 who found that the entropy of ethane could be rationalized only if a small threefold barrier hindering free rotation about the single bond was postulated. That its origin was not due to any large extent to non-bonded interactions (Wilson, 1959), justified its consideration as a separate potential energy function. Only within the last five years has the nature of the torsional barrier become apparent. In 1964 Perr gave theoretical reasons to show that in a molecule such as ethane the torsional barrier arises from proton-proton repulsions shielded to some extent by the electrons in the vicinity, probably slightly beyond, the ends of the C-H bond. Development of this theory has lead to theoretically useful estimates of the barrier to internal rotation (Lowe and Fitzer, 1966).

Because the potential function for internal rotation is periodic and has certain symmetry properties it may be expanded as a Fourier series of cosine terms (Dauben and Fitzer, 1956),

\[ V(\phi) = \sum_{n=1}^{\infty} \frac{2}{n} V_n (1 - \cos n\phi) \]

For practical applications only one term is usually considered giving

\[ V \text{ torsion} = \frac{V_0}{2} (1 - \cos \phi) \]

where \( V_0 \) is the height of the barrier (usually about 12 kJ mole\(^{-1}\), 3 kcal mole\(^{-1}\)) \( \phi \) is the dihedral angle and \( n \) is the number of maxima (or minima) per revolution.

If spectroscopic data are available then \( V_0 \) may be calculated by first determining quantum mechanically the energy levels of the molecule, using the assumed potential barrier, and then adjusting this until the best fit with the observed energy levels is obtained.
In many cases, internal rotation is inactive spectroscopically but $V_0$ may be calculated from thermodynamic data, if sufficient is known about the other motions of the molecules, by the following general procedure.

For an ethene-like molecule the entropy of translation and rotation of the entire molecule may be calculated by statistical mechanical methods, and from an accurate vibrational analysis of the molecule the vibrational entropy may be assessed. The sum of these two contributions, plus the entropy of internal rotation should then equal the entropy of the molecule derived thermomechanically. Thus the entropy term for internal rotation may be obtained and hence the barrier to internal rotation.

4) Non Bonded Interaction Strain

This potential may be divided into two terms, one a repulsive term and the other attractive. The attractive component arises from London dispersion forces, the Pitzer-Catalano values (Pitzer and Catalano, 1956) usually being taken in the case of numerical estimates, (Gleicher and Schleyer, 1967) varying as the inverse sixth power of the distance. Estimations of the repulsive term are not very satisfactory. These may be based on non-ideal behaviour of the rare gases, but ideal gas deviations at high pressures leads to an evaluation of van der Waals potentials only near the energy minimum, i.e. where the energy is less than 2 kJ mole$^{-1}$ (0.5 kcal mole$^{-1}$) and the compression less than 0.5 Å (Westheimer, 1956). However, steric effects are often large and calculations suggest that it is necessary to know the potential function where the compressional energy is 12 to 17 kJ mole$^{-1}$ (3 to 4 kcal mole$^{-1}$) and the compression 0.5 to 1.0 Å. Work by Andur (Westheimer, 1956) on high velocity molecular beam studies of rare gases allows estimations of the potential functions under conditions of higher compressibility.
Although measurements of this sort allow the potential functions of rare gases to be calculated with reasonable accuracy, for other atoms and molecules this is not the case. Steric factors, for instance, must be taken into account. Whereas rare gases are spherically symmetrical, the H-C moiety is only cylindrically symmetrical. In numerical applications the repulsive potential is usually taken as either an inverse twelfth power of the distance, or an exponential function, (Gleicher and Schleyer, 1967) but in the evaluation of strain energies it seems doubtful if, in fact, a precise knowledge of the van der Waal’s potential is required, as these interactions have the steepest potential gradient of all the causes of strain, thus all other parameters will undergo change before the van der Waal’s radii are affected (Sicher, 1962).

**Ring Strain in Cycloalkanes**

Table 2.5 gives values of $\Delta H^0_f(g)_{\text{exp}}$ and $\Delta H^0_f(g)_{\text{calc}}$ the latter estimated by three bond energy schemes, the Allen scheme, the Allen scheme modified by Skinner (AS) (Skinner and Pilcher, 1963) and the Cox bond energy scheme. Values of ring strain derived from each of these is given.

\[
\text{Ring strain} = \Delta H^0_f(g)_{\text{exp}} - \Delta H^0_f(g)_{\text{calc}}
\]
Table 2.5

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^\circ$ (g) (kJ mole$^{-1}$)</th>
<th>$\Delta H^\circ$ (g) (kcal mole$^{-1}$)</th>
<th>Ring Strain (kJ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Allen</td>
<td>AS</td>
<td>Cox</td>
</tr>
<tr>
<td>Cyclopropane</td>
<td>+53.2</td>
<td>-61.5</td>
<td>-61.9</td>
</tr>
<tr>
<td>Cyclobutane</td>
<td>+26.6</td>
<td>+82.0</td>
<td>+82.5</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>-77.2</td>
<td>-102.5</td>
<td>-103.1</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>-123.1</td>
<td>-123.0</td>
<td>-123.4</td>
</tr>
<tr>
<td>Cyclodecane</td>
<td>-172.5</td>
<td>-143.5</td>
<td>-144.4</td>
</tr>
<tr>
<td>Cyclooctane</td>
<td>-125.6</td>
<td>-164.0</td>
<td>-165.0</td>
</tr>
<tr>
<td>Cyclononane</td>
<td>-134.5</td>
<td>-184.5</td>
<td>-185.6</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>-155.4</td>
<td>-205.0</td>
<td>-206.3</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>-180.4</td>
<td>-225.5</td>
<td>-226.9</td>
</tr>
<tr>
<td>Cyclodecane</td>
<td>-233.6</td>
<td>-246.0</td>
<td>-247.5</td>
</tr>
<tr>
<td>Cyclooctadecane</td>
<td>-248.1</td>
<td>-266.5</td>
<td>-268.2</td>
</tr>
<tr>
<td>Cyclopentadecane</td>
<td>-285.8</td>
<td>-297.0</td>
<td>-298.6</td>
</tr>
<tr>
<td>Cyclohexadecane</td>
<td>-302.3</td>
<td>-307.5</td>
<td>-309.4</td>
</tr>
<tr>
<td>Cycloheptadecane</td>
<td>-522.5</td>
<td>-528.0</td>
<td>-530.6</td>
</tr>
</tbody>
</table>

All values for $\Delta H^\circ$ exp have been taken from the review by Skinner and Pilcher (1963).

Cyclopropane

Although the major part of the large ring strain in cyclopropane, 115 kJ mole$^{-1}$ (27.5 Kcal mole$^{-1}$) is undoubtedly due to angle bending strain, (the normally 111.7° CCC angle of n-propane (Bonham et al., 1959) being distorted to 60°) at least part of the strain must be due to hydrogen interaction as the $\text{H}_{(1)}\text{H}_{(1)}$ distance is only 1.838 ± 0.008 Å, (Bastiansen et al., 1964) whereas the sum of two hydrogen van der Waal's radii is usually taken as 2.4 Å (Kliel, 1962). Torsional strain must be relatively low as the HCH planes are necessarily trigonally disposed.

Molecular orbital calculations by Coulson and Moffitt (1949) showed that the lowest energy is achieved by the carbon orbitals being directed not towards each other, but slightly out from the ring - so called 'bent bonds'. Later Coulson and Goodwin (1962; 1963) incorporated the criterion of maximum
orbital overlap and obtained essentially the same results. More recent
calculations using maximum overlap of Clementi orbitals by Klamkin, Kashaie
and Ramda (1966) have shown that the interorbital C-O-C angle is 105° and
the H-O-H orbital angle 115° (microwave studies give \( \angle \text{HCH} 115.1 \pm 1.0° \)
(Rentzen et al., 1964) the carbon atom assuming an \( \text{sp}^3.36 \) hybridization
for the C-C bond and \( \text{sp}^2.4 \) for the C-H bond.

**Cyclobutane**

Although angle bending strain is minimized when cyclobutane is in a
planar conformation, bond opposition strain is at a maximum — the adjacent
hydrogen being necessarily eclipsed. This is sufficient to cause the
molecule to deviate from planarity in its equilibrium conformation by bending
across the diagonal. Electron diffraction measurements by Buntis and
Scheemaker in 1952 could not determine the dihedral angle more accurately than
20° (+ 10°-20°), but recent infra red work by Ueda and Shimasouki (1968) has
shown the possibility of describing the ring puckering vibration in terms of
a quartic potential \( V(s) = (-0.3348 \pm 0.0044) \times 10^5 s^2 + (0.6253 \pm 0.0128) \)
\( \times 10^6 s^4 \text{ cm}^{-1} \) where \( s \) is the distance between the two lines joining both
diagonals. Such a potential has a double minima (see Fig. 2.2) the barrier
height
being 448.1 ± 18 cm⁻¹ = 5.36 kJ mol⁻¹ (1.26 kcal mol⁻¹) and at the potential minimum the dihedral angle is 34°00' ± 31' and in the ground state the dihedral angle is 35°22' ± 30'.

As with cyclooctane, the C-O bonds of cyclooctane are described as bent the C-CG orbital angle being calculated at 106°45' the carbon atoms being hybridized as sp²47 in the C-C direction and sp²62 in C-O (Klasinc et al., 1966).

Cyclopentane

A regular pentagon has internal angles of 108° so that a planar cyclopentane would possess practically no bond angle strain. Offsetting such a conformation, however, is the torsional strain due to the eclipsing of adjacent carbon hydrogen bonds, which causes cyclopentane to take up a puckered shape. Entropy measurements of cyclopentane were explained by Kilpatrick, Fitzer and Spitzer (1947) by postulating that the puckering rotated around the ring. As no moment of inertia is associated with such a motion it was termed 'pseudorotation', a concept which was refined by Fitzer and Donath in 1959. Pseudorotation results from the near cancellation of angular strain forces with torsional forces due to eclipsing hydrogens along the carbon bonds, the resultant ring being slightly puckered with a potential energy which is practically independent of the phase angle of the puckering (Lafferty et al., 1965). Only recently has any spectroscopic evidence for pseudorotation in cyclopentane been observed. In 1968 Durig and Werta reported a series of pronounced Q branches with 5 cm⁻¹ spacings in the infrared spectrum from 35 to 4000 cm⁻¹ which were shown to be due to the pseudorotation of the ring.

Two basic forms of cyclopentane appear to contain the least strain energy, the envelope and the half chair, (Butcher et al., 1959) (see Fig.2.3) but no substantial potential energy change occurs in converting from one form to the other.
Figures represent distance in Angstrom units above or below the plane (positive or negative). Taken from Miel, 1962 p.290.

Cyclohexane

The strain energy in the cyclohexane system is usually taken as practically zero, but as Sunner (Nelander and Sunner, 1966) has shown some stabilization takes place, due to the ring, which is a function of temperature, amounting to 2 kj mole\(^{-1}\) (0.5 Kcal mole\(^{-1}\)) at 298.15K, although in the hypothetically vibrationless state, i.e. taking zero point and thermal vibrational energy of the molecule into account, the strain energy is 14.6 kj mole\(^{-1}\) (5.5 Kcal mole\(^{-1}\)).

As was shown by Sehme, (1890; 1892) two puckered models of cyclohexane can exist in which all the carbons have tetrahedral bonding, the chair form and the boat. In the chair form no adjacent C-H bonds are eclipsed, whereas
in the boat, however, eclipsing takes place and there is also an especially 
unfavourable 1,4 hydrogen interaction in which the atoms are only 1.8 Å apart. 
Relief of this is, to some extent, obtained in the twist or skew boat 
conformation in which the C-H bonds are staggered and the 1,4 interaction 
reduced.

From systems containing a cyclohexane ring in either a chair or boat 
configuration the enthalpy difference has been estimated experimentally, the 
most recent determinations giving \( \Delta H \) chair \( \rightarrow \) twist boat to be about 23 kJ 
mole\(^{-1}\) (5.5 kcal mole\(^{-1}\)) (Johnson et al., 1949) and 20.0 \( \pm \) 3.9 kJ mole\(^{-1}\) 
(4.79 \( \pm \) 0.94 kcal mole\(^{-1}\)) (Hargrave et al., 1963) agreeing with a previous 
estimate by Allinger and Freiberg (1960) of 24.7 \( \pm \) 2.5 kJ mole\(^{-1}\) (5.9 \( \pm \) 0.6 
kcal mole\(^{-1}\)) obtained from equilibrium studies which also gave \( \Delta S \) chair \( \rightarrow \) boat 
20.5 \( \pm \) 4.2 J mole\(^{-1}\) K\(^{-1}\) (4.9 \( \pm \) 1.0 e.u.). Hendrickson (1961) has computed 
the energy differences for cyclohexane chair \( \rightarrow \) twist boat \( \rightarrow \) full boat 
obtaining 22.5 kJ mole\(^{-1}\) (5.33 kcal mole\(^{-1}\)) and 6.69 kJ mole\(^{-1}\) (1.60 kcal mole\(^{-1}\)), 
the energy barrier between the chair and boat forms being 59 kJ mole\(^{-1}\) (14.13 
kcal mole\(^{-1}\)). This barrier has also been estimated from low temperature nmr 
data to be about 42 kJ mole\(^{-1}\) (10 kcal mole\(^{-1}\)) (Eligil 1962, p.205). Figure 2.4 
expresses this data diagrammatically.

![Figure 2.4](image-url)
Larger Rings

With the seven-membered cycloheptane, two basic forms represent energy minima, the chair form and the boat form. Unlike cyclohexane, however, both chair and boat are flexible, and in their most symmetrical forms each suffers substantial torsional strain from C-H eclipsing and hydrogen-hydrogen interaction. Thus in both conformations the twist forms represent energy minima. Both of these forms undergo pseudorotation with interconversion between each, and this has been dealt with in detail by Hendrickson (1961). However, during the pseudorotation the forms necessarily pass through small strain energy maxima due to eclipsing and hydrogen-hydrogen interaction, and these interactions are relieved to some extent by an expansion of the ring angles which takes the form of a 'breathing' action of the ring.

Strain energy increases from the six-membered cyclohexane up to a maximum at the nine-membered ring, and models of these systems show that up to the seven-membered cycloheptane ring the carbon atoms are surrounded less symmetrically on all sides by hydrogen atoms, the hydrogens keeping out of the ring. Starting with the eight-membered cyclooctane, however, the hydrogens are gradually forced inside the carbon ring so that hydrogen interaction begins to increase, tending to manifest itself as an expansion of the ring angles. X-ray work (Bryan and Danitz, 1960; Ruber-Buser and Danitz, 1960) has shown a large positive deviation in the magnitude of the C-O-C angles in the nine and ten-membered rings from the value found in the n-alkanes being expanded to 117°.

Calculations by Hendrickson (1964) on the lowest energy conformations of the eight, nine and ten-membered cycloalkanes show that several flexible forms of each can occur, each form lying in a small energy minima with ready interconversion between the several types of the same form and between each form into another taking place. In each family of forms the torsional strain remains approximately constant and contributes towards a major part of the strain in the molecule.
As the rings become larger more room is available inside the ring, and x-ray data has shown that above cyclononane there is a large reduction in bond opposition strain indicating that the cycloalkanes are beginning to appear more like the corresponding straight chain alkanes.

**Ring Strain in Cycloalkanes**

Table 2.6 gives values of $\Delta \text{H}^\circ_{(g)}$ for some cycloalkanes together with $\Delta \text{H}^\circ_{(g)}$ for Cox's bond energy scheme and the so derived strain energy.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta \text{H}^\circ_{(g)}$ (kJ mole$^{-1}$)</th>
<th>$\Delta \text{H}^\circ_{(g)}$ calc (kJ mole$^{-1}$)</th>
<th>Ring Strain (kJ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopropene</td>
<td>278.7</td>
<td>35.6</td>
<td>225.1</td>
</tr>
<tr>
<td>Cyclobutene</td>
<td>156.9</td>
<td>35.1</td>
<td>123.8</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>32.3</td>
<td>12.6</td>
<td>19.7</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>-5.36</td>
<td>-7.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Cycloheptene</td>
<td>-6.4</td>
<td>-28.5</td>
<td>20.1</td>
</tr>
<tr>
<td>Cis-cyclooctene</td>
<td>-29.3</td>
<td>-49.0</td>
<td>19.7</td>
</tr>
<tr>
<td>Trans-cyclooctene</td>
<td>-8.4</td>
<td>&quot;</td>
<td>40.6</td>
</tr>
<tr>
<td>Cis-cyclododecane</td>
<td>-35.6</td>
<td>-69.5</td>
<td>33.9</td>
</tr>
<tr>
<td>Trans-cyclododecane</td>
<td>-23.4</td>
<td>&quot;</td>
<td>46.1</td>
</tr>
<tr>
<td>Cis-cyclononone</td>
<td>-69.0</td>
<td>-90.0</td>
<td>21.0</td>
</tr>
<tr>
<td>Trans-cyclononone</td>
<td>-54.4</td>
<td>&quot;</td>
<td>35.6</td>
</tr>
</tbody>
</table>

All exp. values have been taken from Skinner's review (Skinner and Pilcher, 1965) except for cyclobutene.

It is useful to compare the ring strains in the cycloalkanes with those of the cycloalkanes and this is done in Table 2.7.

As might be expected, the strain in cyclopropene is much larger, by about 110 kJ mole$^{-1}$ (26 Kcal mole$^{-1}$), than in the fully saturated three-membered ring, indicating the severe nature of the angle bending strain in cyclopropene. Microwave data (Kasai et al., 1959) give the following angles in cyclopropene: $\angle C-C-C$, $64^\circ 36'$; $\angle C-C-C$, $50^\circ 48'$ which compare with $\angle C-C-C$, $124^\circ 18'$; $\angle C-C-C$, $117^\circ 24'$ in propene and propane respectively.
Table 2.7

<table>
<thead>
<tr>
<th>Size of Ring</th>
<th>Strain in Cycloalkane (kJ mole⁻¹)</th>
<th>Strain in Cycloalkene (kJ mole⁻¹)</th>
<th>Δ strain trans-cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂</td>
<td>115.1</td>
<td>225.1</td>
<td></td>
</tr>
<tr>
<td>C₃</td>
<td>109.0</td>
<td>125.6</td>
<td></td>
</tr>
<tr>
<td>C₄</td>
<td>25.7</td>
<td>19.7</td>
<td></td>
</tr>
<tr>
<td>C₅</td>
<td>0.4</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>C₆</td>
<td>24.6</td>
<td>20.1</td>
<td></td>
</tr>
<tr>
<td>C₇</td>
<td>35.8</td>
<td>19.7</td>
<td></td>
</tr>
<tr>
<td>cis-C₈</td>
<td>50.4</td>
<td>46.1</td>
<td>12.2</td>
</tr>
<tr>
<td>trans-C₈</td>
<td>55.9</td>
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<tr>
<td>cis-C₉</td>
<td>35.9</td>
<td>21.0</td>
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</tr>
<tr>
<td>trans-C₉</td>
<td>50.0</td>
<td>35.6</td>
<td>14.6</td>
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</tbody>
</table>

The difference in strain between cyclobutene and cyclobutane is much reduced, the cyclic olefin being strained by only 15 kJ mole⁻¹ (5.5 kcal mole⁻¹) more than the cycloalkane, the extra angle bending strain now being considerably offset by the decrease in non-bonded hydrogen atom interactions and bond opposition strain.

This trend is observed to be at a maximum in cyclopentene which has about 6 kJ mole⁻¹ (1.4 kcal mole⁻¹) less strain than cyclopentane, presumably bond angle distortion is very slight in this cycloalkane. Calculations by Bocket, Freeman and Pitzer (1948) indicated that the four carbons around the double bond lie in a plane, the fifth atom puckering by up to 0.3 Å without significantly altering the potential energy. Microwave studies by Rathjens (1962) confirm this geometry, also showing that the torsional barrier about the double bond is sufficiently large so as to preclude pseudorotation.

Cyclohexene can exist in two conformations, a chair form and a boat with the four carbon atoms about the double bond lying in a plane. Bocket, Freeman and Pitzer (1948) have shown that the chair form is the more stable
by about 11.3 kJ mole\(^{-1}\) (2.7 kcal mole\(^{-1}\)); even so the molecule is strained
to an extent of 2.5 kJ mole\(^{-1}\) (0.6 kcal mole\(^{-1}\)) on \(\Delta H^f\) data, but if this is
corrected to energy terms as shown by Sunner, \(E_s\)\(_{293.15} = 0.0\) kJ mole\(^{-1}\).

Cycloheptane has less strain than cycloheptene, and this trend continues
with all the higher cis-cycloalkanes, being a feature of the lack of angle
bending strain in these systems. Cyclooctene is the smallest cycloalkane
which has been prepared in a trans configuration and, as might be expected,
shows a considerable ring strain due to its unfavourable conformation. After
the cyclooctenes both the cis and trans forms have less strain energy than the
corresponding cycloalkanes, and models show that the sharp maximum in the
strain at

![Graph](image)

**Figure 2.5**

*Variation of Ring Strain with Ring Size in some Cycloalkanes and Cycloalkenes*
cyclonane is due in the first instance to the inevitable hydrogen atoms crowding inside the ring which presumably is relieved by widening of the C-C-C angles in the ring. Nevertheless, the fewer hydrogens in the unsaturated compound is generally reflected in a lessening of strain energy.

The Effect of Further Unsaturation in the Ring

Generally speaking insufficient experimental data is available to detect trends in the effect on ring strain of more than one double bond in the ring. Frequently the situation is complicated by the effects of interaction of the π electrons in the system.

Four Membered Ringes

The relative lack of change in ring strain in going from cyclobutane to cyclobutene has been commented on. The situation is, however, completely changed by further unsaturation. Cyclobutadiene has 4 π electrons, and, as predicted by molecular orbital theory, should be antiaromatic, incurring extra instability and zero delocalization. In its free state it has never, as yet, been synthesised, but some empirical estimation of the destabilization energy may be obtained by consideration of molecules containing the cyclobutadiene structure. One such molecule is biphenylene, but the idea that the strain energy in cyclobutadiene may be assumed equal to that of biphenylene, as has been done in the past (Dewar and Gleicher, 1965), must be treated with caution.

Figure 2.6
as the canonical forms which are the major contributors to the resonance hybrid of biphenylene are dimethylenecyclobutane type structures (II) rather than the cyclobutadiene type (I) (Cava, 1967).

\[ \Delta H^0_{f(g)} \text{biphenylene} = 353.1 \text{ kJ mole}^{-1} \] (84.4 kcal mole\(^{-1}\)) (Bedford et al., 1962), \[ \Delta H^0_{f(g)} \text{calc (from Cox's bond energy scheme)} = 341.4 \text{ kJ mole}^{-1} \] (81.6 kcal mole\(^{-1}\)) giving a strain energy of 11.7 kJ mole\(^{-1}\) (2.8 kcal mole\(^{-1}\)).

By the same procedure for biphenyl using \( \Delta H^0_{f(g)} \) biphenyl = 95.7 kJ mole\(^{-1}\) (23.1 kcal mole\(^{-1}\)) (Parks and Vaughan, 1951), the resonance energy in biphenyl is 249.8 kJ mole\(^{-1}\) (59.7 kcal mole\(^{-1}\)). Thus by comparison with biphenyl, biphenylene has a strain energy of 261.5 kJ mole\(^{-1}\) (62.5 kcal mole\(^{-1}\)).

Whether such a procedure is entirely justifiable is debatable. If, instead of biphenyl, benzene was used as a reference then the strain energy is calculated to be 195.8 kJ mole\(^{-1}\) (46.8 kcal mole\(^{-1}\)), but presumably biphenyl provides a better reference system, possessing a closer configuration to biphenylene than two isolated benzene rings.

Probably the major fault in this assessment of the strain energy in cyclobutadiene is that biphenylene is representative more of dimethylenecyclobutane which would presumably be a more stable molecule than a cyclobutadiene, possessing no antiaromatic character. Thus these strain estimates may be expected to be low and detailed molecular orbital calculations by Coulson and Moffitt (1949) assessed the total strain energy of cyclobutadiene to be about 310 kJ mole\(^{-1}\) (74 kcal mole\(^{-1}\)) which tends to support this conclusion.

**Five Membered Rings**

From heat of hydrogenation figures corrected to 298K (\( \Delta H_{\text{hydrogen}} \) 298K \( \text{C}_2\text{H}_6 \) = 210.5 \pm 1.6 kJ mole\(^{-1}\) (50.3 \pm 0.4 kcal mole\(^{-1}\))) combined with

\[ \Delta H^0_{f(g)} \text{cyclopentane} = 123.2 \text{ kJ mole}^{-1} \] (31.84 kcal mole\(^{-1}\)) (Turnbull, 1967). Cox's bond energy scheme gives \( \Delta H^0_{f(calc)} \) cyclopentadiene = 112.1 kJ mole\(^{-1}\) (26.8 kcal mole\(^{-1}\)). Thus strain energy of cyclopentadiene = 21.1 kJ mole (5.0 kcal mole\(^{-1}\)).
Comparing this value with the strain energies of cyclopentane and cyclohexane, i.e. 25.7 kJ mol\(^{-1}\) (61 kcal mol\(^{-1}\)) and 19.7 kJ mol\(^{-1}\) (47 kcal mol\(^{-1}\)) the striking thing is the similarity of these strains, indicating that the slight but progressive angle bending strain which occurs in moving towards the more unsaturated systems is almost entirely offset by the decrease in torsional strain.

**Larger Rings**

Little experimental data is available for determining the ring strains in diene rings larger than five membered, but as a major part of the ring strain in the fully saturated cycloalkanes is as a result of torsion due to C-H bond eclipsing (Hendrickson, 1964), it would seem most probable that unless unfavourable trans configurations were observed, then the ring strain would decrease with unsaturation, as has been observed with the cycloalkanes.

**Heterocyclics**

Some thermochemical data for heterocyclic molecules up to six-membered containing oxygen, sulphur and nitrogen are available, and will be considered here. Table 2.3 summarises this information. \(\Delta H^\circ_f(g)\) has been estimated by Cox's bond energy scheme.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta n^0 F_e^{(g)}$ (kJ mole(^{-1}))</th>
<th>$\Delta n^0 F_e^{(g)}$ (kJ mole(^{-1}))</th>
<th>$\Delta H_0$ (kJ mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>△</td>
<td>-52.6(^a)</td>
<td>-166.9</td>
<td>114.3</td>
</tr>
<tr>
<td>△</td>
<td>-30.5(^a)</td>
<td>-187.4</td>
<td>106.9</td>
</tr>
<tr>
<td>△</td>
<td>-184.2(^a)</td>
<td>-207.9</td>
<td>23.7</td>
</tr>
<tr>
<td>△</td>
<td>-223.8(^a)</td>
<td>-228.4</td>
<td>4.6</td>
</tr>
<tr>
<td>△</td>
<td>-302.1(^b)</td>
<td>-332.2</td>
<td>30.1</td>
</tr>
<tr>
<td>△</td>
<td>-341.0(^c)</td>
<td>-352.7</td>
<td>11.7</td>
</tr>
<tr>
<td>△</td>
<td>-318.0(^c)</td>
<td>-334.3</td>
<td>16.3</td>
</tr>
<tr>
<td>△</td>
<td>-505.4(^d),(^e)</td>
<td>-495.0</td>
<td>-10.4</td>
</tr>
<tr>
<td>△</td>
<td>82.3(^d),(^e)</td>
<td>2.9</td>
<td>79.4</td>
</tr>
<tr>
<td>△</td>
<td>61.3(^a)</td>
<td>-18.0</td>
<td>79.3</td>
</tr>
<tr>
<td>△</td>
<td>-33.5(^a),(^e)</td>
<td>-38.5</td>
<td>5.0</td>
</tr>
<tr>
<td>△</td>
<td>-63.1(^a),(^e)</td>
<td>-59.0</td>
<td>-4.1</td>
</tr>
<tr>
<td>△</td>
<td>125.8(^h),(^k)</td>
<td>14.6</td>
<td>111.2</td>
</tr>
<tr>
<td>△</td>
<td>-3.6(^i),(^m)</td>
<td>-26.8</td>
<td>23.2</td>
</tr>
<tr>
<td>△</td>
<td>-48.0(^p),(^q)</td>
<td>-47.3</td>
<td>-0.7</td>
</tr>
</tbody>
</table>

\(^a\) Fell and Pilcher, 1965  \(^b\) Nelson and Jeansup, 1952  
\(^c\) Fletcher et al., 1959  \(^d\) Bury and Good, 1956  
\(^e\) Snelson and Skinner, 1961  \(^f\) Hildenbrand et al., 1959  
\(^g\) Skinner, 1963  \(^h\) McCullough et al., 1959  
\(^i\) Guthrie et al., 1952  \(^j\) Bury et al., 1963  
\(^k\) McCullough and Good, 1961  \(^l\) Bedford et al., 1963  
\(^m\) Mccullough and Good, 1961  \(^n\) Cox, 1963  
\(^o\) updated by Cox, 1963  
\(^p\) Hubbard et al., 1952  
\(^q\) Hubbard et al., 1952
Comparison of the strain energies of the three, four, five and six
membered cyclic alkanes, -ethers, -sulphides and -imines, (see Table 2.9)
is instructive.

Table 2.9

<table>
<thead>
<tr>
<th>No. atoms in ring</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alkane</td>
</tr>
<tr>
<td>3</td>
<td>115.1</td>
</tr>
<tr>
<td>4</td>
<td>109.0</td>
</tr>
<tr>
<td>5</td>
<td>25.7</td>
</tr>
<tr>
<td>6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

It is apparent that substitution of CH₂ in a cycloalkane by either O
or NH has little effect on the ring strain and this is not surprising
considering that the principal cause of strain in these small rings is due
to angle bending and the \( \angle \text{COS}, \angle \text{COS}, \angle \text{CNC} \) angles and C-O, C-N
bond length are not very different, the angles lying within two degrees of
110°, and the bond lengths ranging from 1.4 to 1.5Å in acyclic compounds
(Sutton, 1958). The reason for the substantial strain reduction in the
sulphur compounds must be due largely to the reduction in the \( \angle \text{CSC} \) angle
which is about 105° (Sutton, 1958) in acyclic compounds. The longer C-S
bond length, about 1.8Å (Sutton, 1958) also has the effect of increasing the
COC angle in the ring so reducing this angle strain as well.

Further substitution of oxygen into the cyclohexane ring results, in
the first instance, in an increase in strain energy, see Table 2.10. Possibly

Table 2.10

<table>
<thead>
<tr>
<th>Compound</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KJ mole⁻¹</td>
</tr>
<tr>
<td>0.4</td>
<td>4.6</td>
</tr>
</tbody>
</table>

this is due to a gradual increase in angle bending strain. The stabilization
energy observed for 1,3,5-trioxan might be accounted for if the system was reduced to the hypothetically vibrationless state, and a decrease in strain in going from the mono and dioxa substituted rings can be explained by the observation that three symmetrically disposed -O-O- linkages can cyclize with no angle strain (see Appendix I).

**Ring Puckering Motions of Small Rings**

The two principal causes of strain in four and five membered rings, as has previously been pointed out, are 1) angle bending strain, which tends to keep the molecule planar by achieving maximum ring angle, and 2) torsional strain, which arises from carbon hydrogen bond interactions and is minimal when the molecule is puckered.

In 1945, Bell suggested that the out of plane bending mode of the four membered rings should be quartic. This follows directly from the geometry of the molecule if the assumption is made that the angle bending potential function is purely quadratic, i.e. harmonic. The effect of torsion is to cause a quadratic term to be added to the ring puckering potential, thus the final form of the ring puckering potential may be expressed as

$$V(x) = a(x^4 + bx^2) \text{ cm}^{-1}$$

where x is the ring puckering coordinate. That the ring puckering potential can be treated separately like this is a consequence of there being no low frequency vibrations in the molecule except ring puckering (Darig and Lord, 1966). The sign of b is found to depend on whether or not there are eclipsed protons in the ring. If b is negative, then the torsional forces are quite large and the ring puckering potential has a double minimum with a barrier to the planar configuration (Green, 1969). If b is positive then there is a single minimum at the planar configuration.
Barrier heights for the planar configuration of some four-membered cyclic molecules are given in Table 2.11.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Barrier Height</th>
<th>cm⁻¹</th>
<th>kj mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclobutane</td>
<td></td>
<td>449.12</td>
<td>5.420.2</td>
</tr>
<tr>
<td>Trimethylene oxide</td>
<td></td>
<td>15.350.5</td>
<td>5.18</td>
</tr>
<tr>
<td>Trimethylene sulphide</td>
<td></td>
<td>274.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Trimethylene selenide</td>
<td></td>
<td>373.124</td>
<td>4.5</td>
</tr>
<tr>
<td>1,1-difluorocyclobutane</td>
<td></td>
<td>241.25</td>
<td>2.9</td>
</tr>
</tbody>
</table>

The reduction in potential barrier in going from trimethylene selenide to trimethylene sulphide to trimethylene oxide is a reflection on the increasing bond angle strain, the acyclic angles $\angle$CSeC, $\angle$CSC and $\angle$COO being about 95°, 105° and 111° respectively.

When a five-membered ring contains a double bond then the system can be treated similarly to the four-membered rings as far as the ring puckering vibration is concerned because the ethylenic linkage tends to behave as a single unit (Green, 1969). Two out of plane ring bending modes occur which are fairly well separated in frequency and may be described as a double bond twist, or torsional motion occurring in the region of 400 cm⁻¹, and the pseudo four-membered ring puckering vibration. As such there is a

\[ \text{Figure 2.7} \]

Twist about the double bond

Ring puckers with $\times$ acting as a single unit
potential barrier to the planar configuration, the magnitude of which is an indication of the relative strengths of the angle bending strain and the torsional forces. Table 2.12 lists such potential barriers which have so far been assessed.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Barrier Height</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>235.5ᵃ, 244.6ᵇ</td>
</tr>
<tr>
<td>2,5-dihydrofuran</td>
<td>planarᵇ</td>
</tr>
<tr>
<td>2,5-dihydrothiophene</td>
<td>planarᵇ</td>
</tr>
<tr>
<td>2,3-dihydrofuran</td>
<td>36.8ᵇ</td>
</tr>
<tr>
<td>2,3-dihydrothiophene</td>
<td>medium barrierᵃ</td>
</tr>
</tbody>
</table>

ᵃ Leane and Lord, 1967
ᵇ Ueda and Shimanouchi, 1967
ᶜ Green, 1969

In the case of the 2,3- and 2,5-isomers, to a first approximation the angle bending strains should be equal, so the differences in potential barrier height must be due primarily to differences in torsional strain. The 2,3-isomers have two pairs of eclipsed hydrogen atoms whereas the 2,5-have none, thus the 2,3-must be expected to possess the greater barrier to planarity and the 2,5-little or none. As can be seen from Table 2.12, this is the case, and furthermore cyclopentene, with four pairs of eclipsed hydrogen atoms, possesses a much larger barrier to planarity.

**Bridge Compounds**

Compounds with two rings joined so as to share at least one carbon atom may be either spiro, fused or bridged. Unfortunately, however, of the numerous possible compounds very little thermochemical data, even of hydrocarbons, is available. One series of which sufficient data has been obtained to observe trends is that of two fused hydrocarbon rings, one of
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_f^\circ (g)$ \ _{exp} (kJ mole$^{-1}$)</th>
<th>$\Delta H_f^\circ (g)$ \ _{calc} (kJ mole$^{-1}$)</th>
<th>$\Delta H_g$ (kJ mole$^{-1}$)</th>
<th>Sum of $\Delta H_g$ of both rings</th>
<th>Extra Strain \ $\Delta H_g - \Sigma \Delta H_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bicyclo[1,1,0]butane</td>
<td>217.6$^a$</td>
<td>-50.2</td>
<td>267.8</td>
<td>230.2</td>
<td>37.6</td>
</tr>
<tr>
<td>bicyclo[2,1,0]pentane</td>
<td>154.0$^a$</td>
<td>-70.7</td>
<td>225.5</td>
<td>241.1</td>
<td>1.4</td>
</tr>
<tr>
<td>bicyclo[3,1,0]hexane</td>
<td>38.1$^a$</td>
<td>-91.2</td>
<td>129.3</td>
<td>140.8</td>
<td>-11.5</td>
</tr>
<tr>
<td>bicyclo[4,1,0]heptane</td>
<td>1.3$^a$</td>
<td>-111.7</td>
<td>113.0</td>
<td>115.5</td>
<td>-2.5</td>
</tr>
<tr>
<td>bicyclo[5,1,0]octane</td>
<td>-16.3$^a$</td>
<td>-152.2</td>
<td>115.9</td>
<td>159.7</td>
<td>-23.8</td>
</tr>
<tr>
<td>bicyclo[6,1,0]nonane</td>
<td>-31.0$^a$</td>
<td>-152.7</td>
<td>121.7</td>
<td>153.9</td>
<td>-32.2</td>
</tr>
</tbody>
</table>

Est. error usually ± 3 kJ mole$^{-1}$

$^a$ Boyd et al., 1967

$^b$ Wiberg and Fenoglio, 1968
When a fused ring hydrocarbon is formed there are two principal stabilizing effects, 1) stabilization due to an effective change in the number of vibrational degrees of freedom and 2) a reduction in the number of hydrogen atoms thereby reducing non-bonded interactions. In the case of two fused six membered rings, Sumner (Melander and Sumner, 1966) showed that decalin is about kj mole⁻¹ (Kcal mole⁻¹) stabilized with respect to cyclohexane, but this figure is not transferable to other fused ring systems being a function of the fundamental vibrational frequencies and hence of the structure of the molecule. Opposing these stabilizing effects, however, is the strain incurred by bonding two incompatible (from the point of view of bond directions) systems together and this must, in certain cases, be quite severe.

A useful method of considering the strain in a fused system is to compare it with the sum of the strains of the individual rings, see Table 2.13. Bicyclobutane, not surprisingly, is much more strained than two cyclopentane rings reflecting the large magnitude of the angle bending strain that must be present. The very low extra ring strain for bicyclo[2,1,0]pentane indicates that the stabilizing effects must be quite large because it would seem that a substantial amount of extra angle bending strain must be present in this molecule. What the significance is of the apparent minimum in the extra ring strain at bicyclo[3,1,0]hexane is difficult to assess, and to try to rationalize it without knowing more about the nuclear motion stabilization in this series would be pointless as this stabilization could amount to far more than 6 x 1.3 = 8 kj mole⁻¹ (2 Kcal mole⁻¹) (Melander and Sumner, 1966). In the case of bicyclo[4,1,0]heptane it is possible to make an apparently reasonable estimation of the non-bonded and torsional strains which must occur. This bicycloheptane consists of a cyclohexane ring with two hydrogens replaced by a bridged methylene group. Now, in effect, to remove
two hydrogens from cyclohexane and replace with a carbon requires that the hydrogens are in the same plane, that is, eclipsed, and the only cyclohexane conformation which has eclipsed hydrogens is the full boat. It would appear, therefore, that the cyclohexane conformation in bicycle[4,1,0] heptane is the boat. The boat conformation possesses about 29.5 kJ mole\(^{-1}\) (7 kcal mole\(^{-1}\)) more energy than the chair making (together with 0.4 kJ mole\(^{-1}\) ring strain in the chair) altogether about 30 kJ mole\(^{-1}\) strain. But in forming the bicycloheptane, one pair of eclipsed hydrogen atoms is removed.

If the torsional strain in ethane, with three pairs of eclipsed hydrogens, is taken to be about 12 kJ mole\(^{-1}\) (3 kcal mole\(^{-1}\)) (Beuben and Fitzke, 1956), i.e. 4 kJ mole\(^{-1}\) per pair, then the remaining strain in the cyclohexane ring in bicycloheptane is about 26 kJ mole\(^{-1}\) (6 kcal mole\(^{-1}\)). Such a line of reasoning ignores any changes in geometry of the boat due to the adjoined cyclopropane ring and as such is admittedly crude, but it must place a lower limit to the strain energy (ignoring nuclear motions) in such a system because no account has been taken of the added angle bending strain. As the observed extra ring strain is about -2.5 kJ mole\(^{-1}\) then the stabilizing effect due to nuclear vibrations must be in the region of 26 + 2.5, i.e. around 30 kJ mole\(^{-1}\) (7 kcal mole\(^{-1}\)) and this value does not appear to be unreasonable.

The larger bicyclic compounds in this series exhibit an increased extra stabilization. Models of these molecules show that a similar situation to the bicycloheptane occurs where, because of the requirement of one pair of eclipsed hydrogens in the large ring, other hydrogen atoms are forced into eclipsed and unfavourably close positions. Extra angle bending strain must occur at the bridged positions adding up to a not insignificant amount of angle bending, torsional and interaction strain, so the marked degree of extra stabilization which is observed indicates the seemingly large effect which nuclear vibration stability has on these systems.
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Chapter Three

Results and Discussion

A) Acetoxyboranes

As was shown in Chapter One, the literature reports of acetoxyboranes are often conflicting, especially with regard to its molecular structure. From the work of Carpenter et al. (1954) in particular it appears that various acetoxyboranes exist with the oxybis(acetoxyborane) structure being the most representative. Certainly it seems to be clear that triacetoxyborane is highly unstable and may not have an isolated existence, it disproportionating rapidly into higher molecular weight acetoxyboranes and acetic acid, a reaction which may conveniently be regarded as being:

\[ 2(CH_2COO)_3 → (CH_2COO)_2BOH(OCOCH_3)_2 + (CH_2CO)_2O \]

In going from acetoxyborane to propionoxyborane and higher the existence of stable triacetoxyboranes seems to be more definite although no determinations of their kinetic or thermodynamic stability, with respect to the above type of disproportionation, have been made. It might be noted here that H.U. Kibbel (1965a,b) prepared compounds of the type \( H(OOCCH_3) \_2 B - 3(OOCCH_3) \_2 \)

\[ \text{possibly } (CH_2COO)_2 B(OOCCH_3) \_3 \cdot H^+ \] \( \text{where } H = \text{Li, Na, K, Tl, Ag, and} \)

\[ \text{and } \] \( B(OOCCH_3) \_3 \cdot K = K, Rb, Cs, Tl, \) and showed that in the hydrolyses of these latter compounds together with \( \text{N} \cdot (OOCCH_3) \_3 \cdot H = \text{N}(CH_3) \_2 H \) and \( \text{N}(CH_3) \_2 \) and also \( \text{CH}_2\text{COO} \_2 B - 3 \cdot \text{H} \) (Kibbel, 1968a) it is the dissociation of the complexes which is the rate determining step, the reaction being first order. Thermogravimetric analysis indicated that thermal decomposition of these complexes was by the following four steps:
As an approach to the question of thermodynamic stability it was decided, as a first step, to determine standard heats of formation of triacyloxyboranes and oxybis(diacyloxyboranes) for a homologous series with acyloxy groups
\[ \text{CH}_3\text{(CH}_2\text{n} \text{COO)}_n \text{ n = 1 to 4.} \]

Initial experiments involving the reaction between propionic anhydride and boric acid in various proportions produced undefined products which did not analyse to give a propionate:boron ratio in any simple proportion and which proved to be quite insoluble in diethyl ether. A change of reaction to that between boric acid and propionyl chloride gave no better results, so the preparation of butyryloxyborane was then attempted. It was quickly found that the reaction between boric acid and butyryl chloride was the most convenient synthesis, and a white crystalline compound, highly soluble in diethyl ether, was produced. An accurate 2:1 ratio for the butyrate:boron analysis was obtained and the structure, corresponding to oxybis(dibutyloxyborane) was confirmed by elemental analysis and molecular weight determinations, the reaction proceeding as
\[ \text{Butyryloxide + Heat} \text{ } \rightarrow \text{Butyraldehyde + Acetic Acid} \]

Heat of hydrolysis were determined by reacting the butyryloxyborane with water in the calorimeter, a reaction which was quite rapid proceeding as
\[ \text{Butyryloxyborane} + \text{Water} \text{ } \rightarrow \text{Acetic Acid + Butyaldehyde + Heat} \]

(heats of mixing being assumed negligible).
The results of five such determinations are given in Table 3.1. $\Delta H^\circ$ is the enthalpy of reaction for which the reactants and products of the reaction are in their standard state, obtained by use of the ancillary data given in Table 3.2.

\[
\left[ \left( \text{C}_9\text{H}_{15}\text{COO} \right)_2 \text{B} \right] \text{O} \, (s) + \text{H}_2\text{O} \, (l) \rightarrow \text{H}_2\text{B}_2\text{O}_5\, (l) + 2\text{B(OH)}_3\, (s) \quad \Delta H^\circ
\]

### Table 3.1

<table>
<thead>
<tr>
<th>Amount of hydrolysis 298K (moles)</th>
<th>$\Delta H$ hydrolysis 298K (kJ mole$^{-1}$)</th>
<th>$\Delta H$ hydrolysis 298K (cal mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.740 x 10$^{-3}$</td>
<td>53.293</td>
<td>12.503</td>
</tr>
<tr>
<td>3.578 x 10$^{-3}$</td>
<td>106.739</td>
<td>25.037</td>
</tr>
<tr>
<td>2.902 x 10$^{-3}$</td>
<td>53.736</td>
<td>12.571</td>
</tr>
<tr>
<td>4.537 x 10$^{-3}$</td>
<td>106.506</td>
<td>25.047</td>
</tr>
<tr>
<td>4.035 x 10$^{-3}$</td>
<td>53.666</td>
<td>12.569</td>
</tr>
</tbody>
</table>

Hydrolyses carried out using 200 ml, 11.4 moles H$_2$O

Mean $\Delta H$ hydrolysis 298K = $38.75 \pm 0.10$ kJ mole$^{-1}$ (9.26 $\pm 0.02$ kcal mole$^{-1}$)

Giving $\Delta H^\circ = 75.87 \pm 0.61$ kJ mole$^{-1}$ (18.14 $\pm 0.2$ kcal mole$^{-1}$)

$\Delta H^\circ \left[ \left( \text{C}_9\text{H}_{15}\text{COO} \right)_2 \text{B} \right] \text{O} \, (s) = 2813.9 \pm 1.9$ kJ mole$^{-1}$ (-673.72 $\pm 0.50$ kcal mole$^{-1}$)

### Table 3.2

<table>
<thead>
<tr>
<th>Quantity, 298K</th>
<th>kJ mole$^{-1}$</th>
<th>kcal mole$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$al B(OH)$_3$ in H$_2$O</td>
<td>21.09</td>
<td>5.04</td>
<td>Stiller, 1964</td>
</tr>
<tr>
<td>$\Delta H$al C$_9$H$_7$COOH in H$_2$O</td>
<td>-1.6720.21</td>
<td>-0.4020.05</td>
<td>Aveyard &amp; Mitchell, 1963</td>
</tr>
<tr>
<td>$\Delta H^\circ$ B(OH)$_3$ (s)</td>
<td>-1.094.1240.3</td>
<td>-261.540.2</td>
<td>Good and Monson, 1966</td>
</tr>
<tr>
<td>$\Delta H^\circ$ C$_9$H$_7$COOH (s)</td>
<td>-533.924.59</td>
<td>-122610.14</td>
<td>Lebedeva, 1964</td>
</tr>
<tr>
<td>$\Delta H^\circ$ H$_2$O (l)</td>
<td>-239.15</td>
<td>-58.315</td>
<td>Updated circ. 500</td>
</tr>
</tbody>
</table>
The reaction between valeryl chloride and boric acid proceeded as the previous reaction using butyryl chloride. A white crystalline product was obtained which proved to be highly soluble in diethyl ether and analysed accurately for a 2:1 ratio of valeraterboron. Elemental analysis confirmed that oxybis(divaleryloxyborane) had been prepared, and Table 3.3 gives heat of hydrolysis data for the reaction

$$\left[\left(\text{C}_4\text{H}_9\text{COO}\right)_2\text{B}\right]_2^0(\text{c}) + 5\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{C}_4\text{H}_9\text{COOH}(\text{aq}) + 2\text{B(OH)}_3(\text{aq}) \Delta \text{Hydrol}$$

From the data in Table 3.2 together with $\Delta H^\circ$ valeric acid in $\text{H}_2\text{O}$, 298K = $-0.50 \pm 0.21$ kJ mole$^{-1}$ ($-0.12 \pm 0.05$ kcal mole$^{-1}$) (Aveyard and Mitchell, 1968) and $\Delta H^\circ$ of $\text{C}_4\text{H}_9\text{COOH}$(L) = $-96.24 \pm 0.67$ kJ mole$^{-1}$ ($-135.90 \pm 0.16$ kcal mole$^{-1}$) (Lebedeva, 1969).

$\Delta H^\circ$ the enthalpy of hydrolysis for reactants and products in their standard state, and $\Delta H^\circf\left[\left(\text{C}_4\text{H}_9\text{COO}\right)_2\text{B}\right]_2^0(\text{c})$ is calculated.

<table>
<thead>
<tr>
<th>Amount oxybis(divaleryloxyborane) (moles)</th>
<th>$- \Delta H$ hydrolysis 298K (kJ mole$^{-1}$ kcal mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.843 x 10$^{-4}$</td>
<td>35.932 8.937</td>
</tr>
<tr>
<td>8.693 x 10$^{-4}$</td>
<td>35.162 8.409</td>
</tr>
<tr>
<td>1.598 x 10$^{-3}$</td>
<td>37.120 8.872</td>
</tr>
<tr>
<td>1.023 x 10$^{-3}$</td>
<td>36.075 8.622</td>
</tr>
<tr>
<td>9.742 x 10$^{-4}$</td>
<td>36.219 8.696</td>
</tr>
</tbody>
</table>

Hydrolysis carried out using 200 mL, 11.1 moles $\text{H}_2\text{O}$

Mean $\Delta H$ hydrolysis = $36.10 \pm 0.31$ kJ mole$^{-1}$ ($8.63 \pm 0.09$ kcal mole$^{-1}$)

Giving $\Delta H^\circ$ = $77.90 \pm 0.90$ kJ mole$^{-1}$ ($18.63 \pm 0.22$ kcal mole$^{-1}$)

$\Delta H^\circf\left[\left(\text{C}_4\text{H}_9\text{COO}\right)_2\text{B}\right]_2^0(\text{c}) = 2922.15 \pm 3.1$ kJ mole$^{-1}$ ($693.39 \pm 0.08$ kcal mole$^{-1}$)

The reaction between a carboxylic acid and an orthothioborate ester to produce a triacyloxyborane as reported by Lalancette et al. (1966) was attempted by using valeric acid and anythioboranes, a valerate:boron
analysis gave a ratio of 1:1.6 indicating that the trivalentxyloxyborane had not been produced.

In its behaviour oxybis(divaleryloxyboranes) appeared to be even more moisture sensitive than oxybis(dibutylxyloxyboranes) it hydrolysing in a dry-nitrogen filled glove bag in the presence of phosphorus pentoxide. This increased moisture sensitivity is probably the reason for the rather larger scatter of hydrolysis results.

Preparation of hexylxyloxyborane by reaction of hexyl chloride and boric acid gave rise to a diethyl ether soluble white crystalline compound with a melting point of ca. 40-50°C (cf 83-89°C for oxybis(dibutylxyloxyboranes). This compound also proved to be intensely moisture sensitive and analysed for a 3:2 ratio of hexate:boron. Cryoscopic molecular weight determination, which proved to be quite difficult because of this compound's extreme hydroscopic nature, gave a value of 581 but as hydrolysis had taken place, rendering the material quite slushy, this value is substantially low. These data coupled with C,H analysis figures indicate that a hexa-hexylxyloxyborane had been formed

![Structure of Hexylxyloxyborane](image)

MW 782.5; found 581
hexate:boron 3:2; found 3:2
C 55.3%; H 9.5%; found C 55.9%, H 9.1%.

To summarise so far, it appears that if triacyloxyboranes exist, then they must be highly unstable with respect to oxybis(diacyloxyboranes) and the carboxylic anhydride, or more polymeric molecules as in the case of hexylxyloxyborane. This type of behaviour is in marked contrast to the trialkylborate, which are quite stable with regard to disproportionation
reactions of the type described here. A major factor in the stability of
the trialkylborates arises out of the ability of the oxygen lone pair
electrons to back donate into the empty boron $p_z$ orbital thus forming a
substantial amount of double bond character.

![Diagram](attachment:image.png)

The partial filling of the empty boron $p_z$ orbital has the effect of reducing
the ability of boron in this environment to be a Lewis acid, although in the
case of trimethylborate, which has the least steric requirements of any
trialkylborate, a 1:1 addition compound with ammonia $(\text{CH}_3\text{O})_3\text{B.H}_2$ which
sublimes at $45^\circ\text{C}$ and is stable up to at least $375^\circ\text{C}$, may be formed (Steinberg,
1964). From the absence of heat of mixing of tri-$\alpha$-butylborate with pyridine
and an observed heat of mixing of $71 \text{ kJ mole}^{-1}$ (17 kcal mole$^{-1}$) of
trialkylborate and pyridine in the gas phase, H.C. Brown and R.A. Fletcher
(1951) estimated the resonance energy of tri-$\alpha$-butylborate with canonical
forms such as

![Diagram](attachment:image.png)

to be at least $71 \text{ kJ mole}^{-1}$.

If the alkyl groups in trialkylborates are replaced by acyl groups,
however, an entirely different situation exists because of the electron
withdrawing effect of the carbonyl group which causes the ability of the
oxygen attached to boron to back donate electrons to be much reduced.
In consequence the following type of four-centre mechanism leading to the elimination of carboxylic anhydride would seem possible.

This type of mechanism depends upon the existence of an electron deficient \( sp^2 \) hybridized boron atom; however it has been shown (Duncanson et al., 1958) that intramolecular co-ordination exists in acyloxyboranes, possibly of the two types A and B, thereby increasing

the \( sp^3 \) hybridization of the boron. It seems logical to suppose that type B involving a six-membered ring would be much more stable than type A in which a necessarily strained four-membered ring is formed, so, as type A is the only way in which triacyloxyboranes may intramolecularly co-ordinate, intermolecular reaction leading to elimination of carboxylic anhydride and formation of oxybis(diacyloxyborane) would readily occur which would then allow B type co-ordination to take place. If for some reason type B is not favourable, then this would be indicated by increased susceptibility to nucleophilic attack at the \( sp^2 \) boron.
Also repeated intermolecular reaction could take place leading to the formation of higher polymeric species with liberation of carboxylic anhydride. This type of increased susceptibility to hydrolytic attack and the formation of higher polymeric species has been noted as the size of the acyl group is increased, indicating that steric interaction to prevent type B co-ordination from taking place exists.
The importance of this type of intramolecular co-ordination is demonstrated by the existence of compounds I and II (Kibbel, 1963b).

![Chemical structures of compounds I and II](image)

In an attempt to determine whether the reaction

\[
(RCOO)_2BOB(OCOR)_2 + (RCO)_2O \rightarrow 2(RCOO)_3B
\]

would proceed, the heat of solution of oxybis(dibutyloxoyborane) in a solution of butyric anhydride in benzene was determined

\[
\left[ (C_3H_7COO)_2B \right]_2O(c) + (C_3H_7COO)_2O(\text{benzene}) \rightarrow \Delta H_1
\]

Because it was anticipated that complexing of the anhydride via the carbonyl oxygen to boron would take place, a similar heat of solution using methyl ethyl was determined

\[
\left[ (C_3H_7COO)_2B \right]_2O(c) + \text{M.E.K.}(\text{benzene}) \rightarrow \Delta H_2
\]

These two heats of solution together with \( \Delta H_3 \) defined by

\[
\left[ (C_3H_7COO)_2B \right]_2O(c) + \text{benzene} \rightarrow \Delta H_3
\]

serve to determine the reactions.
\[
\left[\left(\text{C}_2\text{H}_5\text{OO}\right)\text{B}ight]_2\text{O}^0(\text{benzene}) + \left(\text{C}_3\text{H}_7\text{OO}\right)\text{B}_2\text{O}^0(\text{benzene}) \longrightarrow \Delta H_1 = \Delta H_3
\]

and
\[
\left[\left(\text{C}_3\text{H}_7\text{OO}\right)\text{B}_2\text{O}^0(\text{benzene}) + \text{M.S.K.}(\text{benzene}) \longrightarrow \Delta H_2 = \Delta H_3
\]

The results are given in Tables 3.3, 3.4 and 3.5. All determinations refer to reaction at 298K using 200 al s dry benzene and \(\Delta H\) values are with respect to a mole of oxybis(dibutylxyloxyborane).

### Table 3.3

<table>
<thead>
<tr>
<th>Amount of oxybis(dibutylxyloxyborane) (moles)</th>
<th>Amount of butyric anhydride (moles)</th>
<th>(\Delta H_1) (kJ mole(^{-1}))</th>
<th>(\text{cal mole}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.208 x 10(^{-3})</td>
<td>1.52 x 10(^{-3})</td>
<td>14.43</td>
<td>3.45</td>
</tr>
<tr>
<td>1.452 x 10(^{-3})</td>
<td>1.68 x 10(^{-3})</td>
<td>13.54</td>
<td>3.24</td>
</tr>
<tr>
<td>1.427 x 10(^{-3})</td>
<td>1.67 x 10(^{-3})</td>
<td>14.90</td>
<td>3.56</td>
</tr>
</tbody>
</table>

Heat of solution of oxybis(dibutylxyloxyborane) in benzene + butyric anhydride giving \(\Delta H_1 = 14.39 \pm 0.36 \text{kJ mole}^{-1} (3.42 \pm 0.32 \text{cal mole}^{-1})\)

### Table 3.4

<table>
<thead>
<tr>
<th>Amount of oxybis(dibutylxyloxyborane) (moles)</th>
<th>Amount of M.S.K. (moles)</th>
<th>(\Delta H_2) (kJ mole(^{-1}))</th>
<th>(\text{cal mole}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.726 x 10(^{-3})</td>
<td>4.51 x 10(^{-3})</td>
<td>15.60</td>
<td>3.63</td>
</tr>
<tr>
<td>1.521 x 10(^{-3})</td>
<td>3.89 x 10(^{-3})</td>
<td>13.25</td>
<td>3.17</td>
</tr>
</tbody>
</table>

Heat of solution of oxybis(dibutylxyloxyborane) in benzene + M.S.K. giving \(\Delta H_2 = 14.33 \pm 2.14 \text{kJ mole}^{-1} (3.43 \pm 0.51 \text{cal mole}^{-1})\)
Table 3.5

<table>
<thead>
<tr>
<th>Amount of oxybis(dibutyryloxyborane) (mole)</th>
<th>ΔH₂</th>
<th>kcal mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.338 x 10⁻³</td>
<td>18.99</td>
<td>4.54</td>
</tr>
<tr>
<td>1.449 x 10⁻³</td>
<td>17.34</td>
<td>4.26</td>
</tr>
</tbody>
</table>

Heat of solution of oxybis(dibutyryloxyborane) in benzene

Giving \( \Delta H_3 = 13.42 \pm 1.15 \text{ kj mole}^{-1} (4.44 \pm 0.38 \text{ kcal mole}^{-1}) \)

Thus for the reaction with reactants and products in benzene solution

\[
\left[ (C_3H_7COO)_{2}H \right]_2^0 \text{(benzene)} + (C_3H_7COO)_2^0 \text{(benzene)} \rightarrow \Delta H_1 = \Delta H_3
\]

\[-4.15 \pm 1.78 \text{ kj mole}^{-1} \quad (-0.93 \pm 0.42 \text{ kcal mole}^{-1})\]

and \[
\left[ (C_3H_7COO)_{2}H \right]_2^0 \text{(benzene)} + N.H.H. \text{(benzene)} \rightarrow \Delta H_2 = \Delta H_3
\]

\[-4.09 \pm 2.43 \text{ kj mole}^{-1} \quad (-0.97 \pm 0.53 \text{ kcal mole}^{-1})\]

From these two results whose difference \((\Delta H_2 = \Delta H_3) - (\Delta H_2 = \Delta H_3)\) amounts to \(-0.05 \pm 2.54 \text{ kj mole}^{-1} (-0.01 \pm 0.60 \text{ kcal mole}^{-1})\) it is seen that there is no effective difference in the enthalpy change between the two reactions and from the very small (ca. \(-4 \text{ kj mole}^{-1}\)) entropy change it may be inferred that no bond breaking reactions are taking place because the reaction

\[
\begin{align*}
\text{RCOO} & \quad \text{O} \\
\text{B} & \quad \text{O} \\
\text{RCOO} & \quad \text{O}
\end{align*} 
\]

is not a redistribution reaction if the boron-oxygen, \(\text{BO} - \text{O}\) bond is considered to be different to a boron-oxygen, \(\text{B} - \text{O}\) bond.

If the alkyl group in an acyloxyborane has strongly electron withdrawing
properties such as \(-\text{CF}_2\), then its effect on the carbonyl group will be to reduce the charge on the oxygen

\[
\begin{array}{c}
\text{C} \\
\text{O} \\
\text{O} \\
\text{O} \\
\hline
\text{O} \\
\text{C} \\
\text{CF}_2 \\
\end{array}
\]

The Lewis base property of the carbonyl oxygen will thus be reduced so preventing oxbyl(di-trifluorocetatoxyborane) from deriving as much stabilization from intramolecular co-ordination with respect to tri-trifluorocetatoxyborane as in the case of the non-fluorinated analogues. On this basis, therefore, it may be expected that both these fluorinated molecules will have a stable existence as was reported by Gerrard et al. (1953) although two carbonyl stretching frequencies attributed to a co-ordinated and non-co-ordinated carbonyl oxygen (Bumsenson et al., 1953) in both these compounds were noted showing that the trifluoromethyl group is not a sufficiently strongly electron-withdrawing species to completely eliminate the Lewis base properties of the carbonyl group in this environment.

If one of the acyloxy groups in an acyloxyborane was substituted by a group which would allow back donation to the boron atom - such as phenyl - then it would seem possible that dicetoxyphenyborane would have a stable existence. Such a compound was reported by Gerrard et al. (1953), but when the preparation was repeated, after recrystallization from acetic anhydride, a compound with a very similar melting point 172-173°C (Gerrard et al. 172-174°C) was obtained which analysed for a 1:1 acetate:bromine ratio. No method of purification was mentioned in Gerrard’s paper and it would appear most likely that the compound prepared in both instances was

\[
\left[(\text{CH}_3\text{COO})_2\text{B}^+\text{F}_2\right]^2\text{O}
\]

which in Gerrard’s case had retained acetic anhydride on crystallizing, this being driven off in the melting point apparatus. The reported titrimetric analytical procedure is also suspect, because when repeated extremely poor end points were observed. Chemical analysis was the only method of structural determination used.
As tribenzozylxoyborane was reported to have been prepared (Lalancette et al., 1966) the preparation of this compound was attempted by reaction of benzoyl acid with boron trichloride, it being considered that the aryl groups might have the effect of increasing the electron density on the boron atoms, so reducing the tendency for intramolecular co-ordination and hence the difference in stability between tribenzozylxoyborane and oxybis(dibenzozylxoyborane). The compound obtained was analysed for a 2:1 benzoylboron ratio indicating that oxybis(dibenzozylxoyborane) had been prepared. The melting point, 203-206°C, compares to 195-197°C obtained by Lalancette et al. for the tribenzozylxoyborane. It seems unlikely that tribenzozylxoyborane and oxybis(dibenzozylxoyborane), respective molecular weights 378.2 and 522.1, would have such similar melting points.

In no instance in this work was the existence of a triacylcyloxyborane noted, all evidence indicating oxybis(dicylcyloxyborane) structures, or higher polymeric molecules. While this does not exclude the existence of triacylcyloxyborane it does reflect a measure of their instability. From the reaction between acetoxylborane and pyridine in boiling acetic anhydride, Kibbel (1968b) obtained the triacylcyloxyborane, pyridine complex \((\text{CH}_3\text{COO})_2\text{B}.\text{NC}_5\text{H}_5\)\(_2\). The tripropoxyxylxoyborane, pyridine complex was similarly obtained. This was explained by means of the reactions:

\[
\begin{align*}
(\text{CH}_3\text{COO})_2\text{B}(\text{COO})_2 + (\text{COO})_2\cdot \text{B} \quad \xrightarrow{\text{L}} \quad 2\text{B}(\text{COO})_3
\end{align*}
\]

\[
\begin{align*}
(\text{COO})_2\cdot \text{B} + \text{L} \quad \rightarrow \quad (\text{COO})_2\cdot \text{B}.\text{L} \quad \text{L} = \text{Ligand}
\end{align*}
\]

or \[
\begin{align*}
(\text{CH}_3\text{COO})_2\text{B}(\text{COO})_2 + (\text{COO})_2\cdot \text{B} \quad \xrightarrow{\text{L}} \quad 2(\text{COO})_3\cdot \text{B}.\text{L}
\end{align*}
\]

either of which could occur. At lower temperatures (below 50°C) the 1:2 and 1:1 complexes \(\left[(\text{CH}_3\text{COO})_2\text{B}\right]_2\cdot \text{L}_2\) and \(\left[(\text{CH}_3\text{COO})_2\text{B}\right]_2\cdot \text{L}_1\) (where \(\text{L} = \text{pyridine or trimethylamine and L}_1 = \text{quinoline}\)) were formed.

Stabilization of triacylcyloxyborane can therefore be achieved if boron is
$sp^3$ hybridized by complexing with a Lewis base. It would be of value therefore to determine the thermodynamic stability of such systems using Lewis bases of varying strength.
3) Diababoron Heterocycles

The ring strains of the following compounds, 2-n-buty1-1,5,2-dioxaborolan, 2-n-buty1-1,3,2-dioxaborinan, 2-n-buty1-1,3,2-dioxaborapen and the 2-phenyl analogues together with 3-phenyl-2,4,5-trim-5-borabicyclo[3,2,2]nonane - this latter compound being the phenylboronate of cyclohexane-1,4-diol \( \text{OCH(CH}_2\text{CH}_2\text{CH}_2\text{H}_2 \text{CH}_2\text{CH}_2\text{H}_2 \text{CH}_2\text{CH}_2\text{H}_2 \text{CH}_2\text{CH}_2\text{O}_2\text{H}) \text{ and will be referred to as the 'bicycle-compound'} - were determined by the methods.

1) Comparison of experimentally determined \( \Delta H^\circ \text{(g)} \) with that calculated directly from the Cox bond energy scheme (Cox, 1962, 1963) or, as in the case of \( H(S - 0) \) and \( H(S - 5) \) with bond energies incorporated into the scheme.

2) By using the acyclic n-butyldihexyloxyborane and phenylidencyclohexane analogues together with the Cox bond energy scheme.

In all cases \( \Delta H^\circ \text{(standard state) at 298K (referred to as } \Delta H^\circ \text{(as of the compounds was determined by oxidative hydrolysis in the calorimeter using aqueous } 0.1M \text{ NaOH), } 0.1M \text{ H}_2\text{O}_2 \text{ solution (to be referred to afterwards as } \text{aeb aqueous excess base).}

Heats of mixing of products are assumed to be negligible.

With the exception of the bicycle compound, the oxidative hydrolysis proceeded smoothly according, in the case of the cyclic molecules, to the general equation,

\[
\text{[CH}_2\text{]}_n \text{OCH}_2\text{H}_2\text{O}_2\text{(as)} + \text{H}_2\text{O}_2\text{(aeb)} + 2\text{H}_2\text{O}\text{(aeb)}
\]

\[
\text{\text{\rightarrow H}_2\text{CH}_2\text{H}_2\text{O}_2\text{(aeb)} + ROH\text{(aeb)} + \text{H}_2\text{BO}_3\text{(aeb)} \quad \Delta H_{\text{obs}}}
\]

and in the case of the acyclic molecules

\[
\text{[CH}_2\text{]}_n \text{OCH}_2\text{H}_2\text{O}_2\text{(as)} + \text{H}_2\text{O}_2\text{(aeb)} + 2\text{H}_2\text{O}\text{(aeb)}
\]

\[
\text{\text{\rightarrow 2CH}_2\text{H}_2\text{O}_2\text{(aeb)} + ROH\text{(aeb)} + H_2\text{BO}_3\text{(aeb)} \quad \Delta H_{\text{obs}}}
\]

Where \( n = 2, 3 \) or 4

\( R = \text{either } \text{C}_6\text{H}_5 \) or \( n-\text{C}_6\text{H}_5 \)

The bicycle compound tended to float on the surface in the calorimeter
generating local thermal inhomogeneities and dissolving very slowly, so it was dissolved in dry, 1,4-dioxane before reacting it in the calorimeter, a procedure which served to disperse it in the calorimeter fluid, allowing it to react quickly and uniformly. The necessary ancillary reactions to this procedure were also undertaken.

Using the data given in Table 3.6 values for $\Delta H^\circ$, the enthalpy of reaction with all reactants and products in their standard states, i.e.,

$$
\frac{O(CH_2)_nOH}{2\text{ mol}} + H_2O_{(l)} + 2H_2O_{(l)} \rightarrow MO(\text{CH}_2)_nOH_{(as)} + ROH_{(as)}
$$

was calculated. Values thus obtained of $\Delta H^\circ$ are given in Tables 3.3 and 3.9.

<table>
<thead>
<tr>
<th>Table 3.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity (298K)</td>
</tr>
<tr>
<td>$\Delta$ Enol $\text{H}_2\text{O}$ in ag $\text{NaCl}$</td>
</tr>
<tr>
<td>$\text{H}(\text{CH}<em>2\text{OH})</em>{(l)}$</td>
</tr>
<tr>
<td>$\Delta$ Enol $\text{H}_2\text{O}$ in $\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\Delta$ Enol $\text{C}_2\text{H}_4\text{OH}$ in $\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\Delta$ Enol $\text{C}_2\text{H}_4\text{OH}$ in $\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\Delta$ Enol $\text{H}_2\text{O}$ in $\text{H}_2\text{O}$</td>
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<tr>
<td>$\Delta$ Enol $\text{H}_2\text{O}$ in $\text{H}_2\text{O}$</td>
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<tr>
<td>$\Delta$ Enol $\text{H}_2\text{O}$ in $\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\Delta$ Enol $\text{C}_2\text{H}_4\text{OH}$ in $\text{H}_2\text{O}$</td>
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</tbody>
</table>

In cases where heat of solution in water data were available, this was taken as being the same as the corresponding heat of solution in aeb.

To reduce the reaction involving the bicyclo-compound to an equation involving reactants and products in their standard states the following ancillary data were needed.

$\Delta H$ solution $\text{HOSCH(CH}_2\text{CH}_2\text{)CHOH}$ in aeb 1.209 ± 0.003 KJ mol$^{-1}$

(0.259 ± 0.002 kcal mol$^{-1}$) (This work)
\[ \Delta H \text{ solution} \text{ of CH}_2(\text{CH}_3)_2\text{CHOH} \cdot \text{H}_2 \text{O} \text{ in dioxan, } 20.67 \pm 0.4 \text{ kJ mole}^{-1} \]

\[ (4.94 \pm 0.1 \text{ kcal mole}^{-1}) \text{ (This work)} \]

\[ \Delta H \text{ solution dioxan in aeb, } -9.6 \text{ kJ mole}^{-1} (\pm 2.3 \text{ kcal mole}^{-1}) \]

(Finch et al., 1967)

The method of calculating \( \Delta H^0 \) for the bicycle compound is as follows.

Consider the reaction between \( n_1 \) moles of the bicycle compound dissolved in \( n_2 \) moles of dioxan reacting with aeb. Then

\[ n_1 \text{ CH}_2(\text{CH}_3)_2\text{CHOH} \cdot \text{H}_2\text{O} (\text{aeb}) + 2n_1\text{H}_2\text{O} (\text{aeb}) + n_1\text{H}_2\text{O} (\text{aeb}) \]

\[ \rightarrow n_1 \text{ HOCH}(\text{CH}_3)_2\text{CH(OH)} \cdot \text{H}_2\text{O} (\text{aeb}) + n_1\text{H}_2\text{O} (\text{aeb}) + n_1\text{H}_2\text{O} (\text{aeb}) + n_2\text{D} (\text{aeb}) \]

where \( q \) is the heat of reaction observed in joules (same sign convention as for enthalpy changes).

\( n_2\text{D} \) refers to \( n_2 \) moles of dioxan.

Thus by addition of the following two equations

\[ n_1 \text{ CH}_2(\text{CH}_3)_2\text{CHOH} \cdot \text{H}_2\text{O} (\text{aeb}) + \rightarrow n_1 \text{ HOCH}(\text{CH}_3)_2\text{CH(OH)} \cdot \text{H}_2\text{O} (\text{aeb}) + n_1\text{H}_2\text{O} (\text{aeb}) \]

and \( n_2 \text{D} + \text{aeb} \rightarrow n_2\text{D} (\text{aeb}) \]

and by division of \( n_1 \), the equation

\[ n_1 \text{ HOCH}(\text{CH}_3)_2\text{CH(OH)} \cdot \text{H}_2\text{O} (\text{aeb}) + \rightarrow n_2\text{D} \text{aeb} \]

\[ \Delta H = \Delta H_1 + \Delta H_2 \]

\[ \Delta H_3 = \Delta H_1 + \Delta H_2 \]

Where \( \Delta H_3 \) corresponds to \( \Delta H\text{obs} \) of the previous reactions; the additional heat effects due to the presence of dioxan being effectively removed.

Four sets of data were used in the calculation of \( \Delta H_3 \) and these are given in Table 3.7. The \( \Delta H_3 \) values are listed under \( \Delta H\text{obs} \) in Table 3.9, and from these \( \Delta H^0 \) is calculated.
### Table 3.7

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount (moles) x 10(^4)</th>
<th>(\Delta N_{\text{obs}}) (kj mole(^{-1}))</th>
<th>(\Delta N_{\text{Calc}}) (kcal mole(^{-1}))</th>
<th>(\Delta H^\circ) (kj mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_2)_2\text{O})</td>
<td>5.647</td>
<td>-408.99</td>
<td>-408.82</td>
<td>-374.52</td>
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<td>-361.82</td>
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### Table 3.8

<table>
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<tr>
<th>Compound</th>
<th>Amount (moles) x 10(^4)</th>
<th>(\Delta N_{\text{obs}}) (kcal mole(^{-1}))</th>
<th>(\Delta N_{\text{Calc}}) (kcal mole(^{-1}))</th>
<th>(\Delta H^\circ) (kcal mole(^{-1}))</th>
</tr>
</thead>
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<td>((\text{CH}_2)_2\text{O})</td>
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</tr>
<tr>
<td>Compound</td>
<td>Amount (mole) x 10^4</td>
<td>∆ H° (kJ mole^-1)</td>
<td>∆ H° (kcal mole^-1)</td>
<td>∆ H°</td>
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</table>
To obtain values for $\Delta H_f^{\circ}(s)$ from $\Delta H_f^{\circ}$ the ancillary data listed in Table 3.10 were used and these

Table 3.10

<table>
<thead>
<tr>
<th>quantity</th>
<th>Values at kJ mole$^{-1}$</th>
<th>298K kcal mole$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_f^{\circ}(g) \ H_2BO_3$</td>
<td>-1094.12±0.8</td>
<td>-261.52±0.2</td>
<td>Good and Hanson, 1966</td>
</tr>
<tr>
<td>$\Delta H_f^{\circ}(aq) \ H_2O$</td>
<td>-295.03</td>
<td>-69.515</td>
<td>Wagner et al., 1965</td>
</tr>
<tr>
<td>$\Delta H_f^{\circ}(aq) \ H_2O_2$</td>
<td>-487.78±0.06</td>
<td>-119.38±0.02</td>
<td>Wagner et al., 1965</td>
</tr>
<tr>
<td>$\Delta H_f^{\circ}(aq) \ C_2H_5OH$</td>
<td>-277.65±0.4</td>
<td>-66.36±0.1</td>
<td>Nonsini et al., 1952</td>
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<tr>
<td>$\Delta H_f^{\circ}(aq) \ CH_3SH$</td>
<td>-326.72±0.53</td>
<td>-78.09±0.13</td>
<td>Sundry et al., 1962</td>
</tr>
<tr>
<td>$\Delta H_f^{\circ}(aq) \ CH_3$</td>
<td>-165.19±0.39</td>
<td>-39.66±0.08</td>
<td>Green, 1961</td>
</tr>
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<td>$\Delta H_f^{\circ}(aq) \ HO(CH_2)_2OH$</td>
<td>-498.05±0.7</td>
<td>-108.35±0.07</td>
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</tr>
<tr>
<td>$\Delta H_f^{\circ}(aq) \ HO(CH_2)_4OH$</td>
<td>-465.17±0.8</td>
<td>-110.7±0.2</td>
<td>Gardner &amp; Hussain, 1969</td>
</tr>
<tr>
<td>$\Delta H_f^{\circ}(aq) \ HO(CH_2)_4OH$</td>
<td>-500.62±1.3</td>
<td>-119.65±0.3</td>
<td>Gardner &amp; Hussain, 1969</td>
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<tr>
<td>$\Delta H_f^{\circ}(aq) \ C_8H_8O_2$</td>
<td>-548.5±2.1</td>
<td>-131.4±0.5</td>
<td>Rothstein, 1930</td>
</tr>
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</table>

are given in Table 3.15.

Heats of transition $\Delta H_{liq} \rightarrow \text{gas} (298K)$ were estimated from logT vs $\frac{1}{T}$ plots obtained by means of a dynamic distillation method. The $\Delta H_{liq}$ data so obtained was reduced to 298K by means of Watson's equation (Watson, 1931)

$$\frac{\Delta H_{liq}}{\Delta H_{g}} = \left( \frac{1 - T_2}{1 - T_1} \right)^{0.53}$$

where $\Delta H_{liq}$ and $\Delta H_{g}$ are the two enthalpies of vaporization at $T_1$ and $T_2$, and $T_{1}$ and $T_{2}$ refer to the two reduced temperatures corresponding to $T_1$ and $T_2$. This required an estimation of the critical temperature, $T_c$, of each compound which was obtained from the empirical equation

$$T_c = 1.027 T_B + 199 \quad (\text{see Jans, 1967})$$
$T_B$, the normal boiling point, was obtained by extrapolation of the
log $p$ vs $\frac{1}{T}$ graphs to $p = 760$ mm Hg.

The constants $A$ and $B$ in the equation $\log_{10} p$(mm Hg) = $A - \frac{B}{T}$ together
with the mean temperature $T$, at which these values apply, and $T_B$ and $T_C$,
the normal boiling point and critical temperature are given in Table 3.11.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$A$</th>
<th>$B$</th>
<th>$T$ (K)</th>
<th>$T_B$ (K)</th>
<th>$T_C$ (K)</th>
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<tr>
<td>$\text{O(CH}_2\text{)}_2\text{OCH}_2\text{CH}_2\text{O}$</td>
<td>7.750</td>
<td>2472</td>
<td>427</td>
<td>307</td>
<td>680</td>
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<tr>
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<td>8.650</td>
<td>3000</td>
<td>443</td>
<td>320</td>
<td>693</td>
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<tr>
<td>$\text{O(CH}_2\text{)}_2\text{OCH}_2\text{CH}_2\text{O}$</td>
<td>8.574</td>
<td>3057</td>
<td>419</td>
<td>335</td>
<td>709</td>
</tr>
<tr>
<td>$\text{OCH}(\text{CH}_2\text{CH}_2\text{)}_2\text{OCH}(\text{CH}_2\text{CH}_2\text{)}_2\text{O}$</td>
<td>8.265</td>
<td>3560</td>
<td>432</td>
<td>339</td>
<td>733</td>
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<tr>
<td>$\text{C}_2\text{H}_4\text{C}_2\text{H}_4\text{O}$</td>
<td>10.767</td>
<td>3539</td>
<td>333</td>
<td>447</td>
<td>618</td>
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<td>7.729</td>
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<td>434</td>
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<tr>
<td>$\text{O(CH}_2\text{)}_2\text{OCH}_2\text{CH}_2\text{O}$</td>
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<td>2250</td>
<td>351</td>
<td>454</td>
<td>629</td>
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<tr>
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<td>8.155</td>
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<td>333</td>
<td>433</td>
<td>604</td>
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</table>
Values of $\Delta H_{\text{liquid}} \rightarrow \text{gas}$ (78%) are given in Table 3.12 together with $\Delta H_{\text{liquid}} \rightarrow \text{gas}$ (298K).

### Table 3.12

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<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_{\text{liquid}} \rightarrow \text{gas (78%)}$</th>
<th>$\Delta H_{\text{liquid}} \rightarrow \text{gas (298K)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O(CH}_2\text{)}_2\text{OCH}_2\text{H}_2$</td>
<td>47.33 kcal mole$^{-1}$</td>
<td>55.24 kcal mole$^{-1}$</td>
</tr>
<tr>
<td>$\text{O(CH}_2\text{)}_2\text{OCH}_2\text{H}_2$</td>
<td>58.55 kcal mole$^{-1}$</td>
<td>66.73 kcal mole$^{-1}$</td>
</tr>
<tr>
<td>$\text{OCH(CH}_2\text{CH}_2\text{)}_2\text{OCH}_2\text{H}_2$</td>
<td>68.16 kcal mole$^{-1}$</td>
<td>78.29 kcal mole$^{-1}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{O}_2\text{OCH}_2\text{H}_2$</td>
<td>67.57 kcal mole$^{-1}$</td>
<td>70.61 kcal mole$^{-1}$</td>
</tr>
<tr>
<td>$\text{O(CH}_2\text{)}_2\text{O} \text{O} \text{C} \text{H}_2\text{H}_2$</td>
<td>40.27 kcal mole$^{-1}$</td>
<td>42.36 kcal mole$^{-1}$</td>
</tr>
<tr>
<td>$\text{O(CH}_2\text{)}_2\text{O} \text{O} \text{C} \text{H}_2\text{H}_2$</td>
<td>43.08 kcal mole$^{-1}$</td>
<td>46.05 kcal mole$^{-1}$</td>
</tr>
<tr>
<td>$\text{O(CH}_2\text{)}_2\text{OCH}_2\text{H}_2$</td>
<td>76.59 kcal mole$^{-1}$</td>
<td>83.02 kcal mole$^{-1}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{O}_2\text{O} \text{C} \text{H}_2\text{H}_2$</td>
<td>43.77 kcal mole$^{-1}$</td>
<td>46.05 kcal mole$^{-1}$</td>
</tr>
</tbody>
</table>

The errors in these values at 298K are taken as ± 2.1 kcal mole$^{-1}$, ± 0.5 kcal mole$^{-1}$.

For the two solids at 298K, the bicycle compound and 2-phenyl-1,3,2-dioxaborinane, $\Delta H_{\text{solid}} \rightarrow \text{liquid}$ was taken to be the same as $\Delta H_{\text{solution}}$ in an inert solvent. $\Delta H_{\text{sol}}$ in 1,4-dioxan being taken for the bicycle-compound (26.07 ± 0.4 kcal mole$^{-1}$, 10.94 ± 0.1 kcal mole$^{-1}$) and $\Delta H_{\text{sol}}$ in dry benzene for the dioxaborinane (21.55 ± 0.29 kcal mole$^{-1}$, 5.15 ± 0.09 kcal mole$^{-1}$; this work).
Values of $\Delta h_f^{\circ}$ (as) and $\Delta h_f^{\circ}$ (g) are given in Table 3.13.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta h_f^{\circ}$ (as)</th>
<th>$\Delta h_f^{\circ}$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kj mole$^{-1}$</td>
<td>kcal mole$^{-1}$</td>
</tr>
<tr>
<td>O(CH$_2$)$_2$OOC$_6$H$_5$</td>
<td>572.95±1.7</td>
<td>136.8±0.4</td>
</tr>
<tr>
<td>O(CH$_3$)$_2$OOC$_6$H$_5$</td>
<td>609.15±1.7</td>
<td>145.6±0.4</td>
</tr>
<tr>
<td>O(CH$_2$)$_2$OOC$_6$H$_5$</td>
<td>649.30±2.1</td>
<td>155.3±0.5</td>
</tr>
<tr>
<td>OCH(CH$_2$CH$_3$)$_2$OOC$_6$H$_5$</td>
<td>669.68±4.2</td>
<td>158.6±1.0</td>
</tr>
<tr>
<td>C$_2$H$_3$O$_2$C$_6$H$_5$</td>
<td>672.68±2.1</td>
<td>160.2±0.5</td>
</tr>
<tr>
<td>O(CH$_2$)$_2$OBn-C$_4$H$_9$</td>
<td>741.95±2.7</td>
<td>177.3±2.4</td>
</tr>
<tr>
<td>O(CH$_3$)$_2$OBn-C$_4$H$_9$</td>
<td>761.37±2.1</td>
<td>182.8±2.5</td>
</tr>
<tr>
<td>O(CH$_2$)$_2$OBn-C$_4$H$_9$</td>
<td>805.12±2.1</td>
<td>192.4±2.5</td>
</tr>
<tr>
<td>(C$_2$H$_5$)$_2$Br-C$_4$H$_9$</td>
<td>871.90±2.7</td>
<td>208.4±2.4</td>
</tr>
</tbody>
</table>
Estimation of $\Delta H^0_{i}^{(g)}$ by the Cox Bond Energy Scheme

All the data used in these calculations are given in Table 3.14.

### Table 3.14

<table>
<thead>
<tr>
<th>Quantity (gaseous)</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ mol$^{-1}$</td>
<td>kcal mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta H^0_{i}^{(g)}$</td>
<td>715.0</td>
<td>170.9420.05</td>
</tr>
<tr>
<td>$\Delta H^0_{ii}^{(g)}$</td>
<td>215.025.004</td>
<td>52.120.001</td>
</tr>
<tr>
<td>$\Delta H^0_{i0}^{(g)}$</td>
<td>299.202.12</td>
<td>59.360.05</td>
</tr>
<tr>
<td>$\Delta H^0_{iB}^{(g)}$</td>
<td>344.621.32</td>
<td>132.324.0</td>
</tr>
<tr>
<td>$\Delta H^0_{iC}^{(g)}$</td>
<td>301.727.1</td>
<td>72.422.7</td>
</tr>
<tr>
<td>$\Delta H^0_{iD}^{(g)}$</td>
<td>712</td>
<td>1722</td>
</tr>
</tbody>
</table>

**a)** Cox, 1962


c) From (C$_3$H$_2$)$_3$B$_2$ + B$_2$ using $\Delta H^0_{i}^{(g)}$=B$_2$+B$_2$

d) Estimated by addition of $\Delta H^0_{i}^{(g)}$ of B$_2$ and B$_2$.

e) Estimated by addition of $\Delta H^0_{i}^{(g)}$ of B$_2$ and B$_2$.

143.1 kJ mol$^{-1}$ (34.2 kcal mole$^{-1}$), Finch et al., 1967, but with

$\Delta H^0_{i}^{(g)}$ corrected to 295°C by Watson's equation.

d) From (n-C$_4$H$_7$)$_3$B$_2$ using $\Delta H^0_{i}^{(g)}$(n-C$_4$H$_7$)$_3$B$_2$=B$_2$+B$_2$.

-343.9 kJ mol$^{-1}$ (-82.4 kcal mole$^{-1}$) mean value from Viktorov and

Zagorukhin, 1967 and Johnson et al., 1964, together with $\Delta H^0_{i}^{(g)}$(n-C$_4$H$_7$)$_3$B$_2$.

61.9 kJ mol$^{-1}$ (146 kcal mole$^{-1}$) from Skinnor, 1966.

e) JANAF Thermochromac tables, Dow Chemical Co., Midland, Michigan, 1964,
distributed by GIFSTI, Springfield, Virginia.

Addenda. PB 168 370-1 1966

PB 168 370-2 1957

f) Kerr, 1966
Values of $\Delta H^\circ_{f(g)}$ calculated from these data are given in Table 3.15 together with the strain energy values obtained by comparing the calculated $\Delta H^\circ_{f(g)}$ values with the observed $\Delta H^\circ_f$ values from Table 3.13.

### Table 3.15

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-\Delta H^\circ_{f(g)}$ calculated</th>
<th>Ring Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ mole$^{-1}$</td>
<td>kcal mole$^{-1}$</td>
</tr>
<tr>
<td>$\text{O}$(CH$_2$)$_2$OCH$_3$H$_9$</td>
<td>540.6-13.4</td>
<td>129.9±9.4</td>
</tr>
<tr>
<td>$\text{O}$(CH$_2$)$_3$OCH$_2$H$_9$</td>
<td>661.5±19.2</td>
<td>154.6±14.6</td>
</tr>
<tr>
<td>$\text{O}$(CH$_2$)$_4$OCH$_2$H$_9$</td>
<td>531.4±19.7</td>
<td>129.1±9.7</td>
</tr>
<tr>
<td>O(2H$_2$O)CH$_2$CH$_2$CH$_2$H$_5$</td>
<td>609.0±21.8</td>
<td>145.6±9.2</td>
</tr>
<tr>
<td>$\text{O}$(CH$_2$)$_2$OEt-OCH$_2$H$_9$</td>
<td>633.9±19.2</td>
<td>163.5±14.6</td>
</tr>
<tr>
<td>$\text{O}$(CH$_2$)$_3$OEt-OCH$_2$H$_9$</td>
<td>704.3±19.7</td>
<td>168.4±14.7</td>
</tr>
<tr>
<td>$\text{O}$(CH$_2$)$_4$OEt-OCH$_2$H$_9$</td>
<td>724.7±20.1</td>
<td>173.5±14.8</td>
</tr>
</tbody>
</table>

Estimation of $\Delta H^\circ_{f(g)}$ by using the Acyclic Analogues

Consider the reaction

$$\text{(C}_2\text{H}_2\text{O})_2\text{B}_{10}\text{H}_{12} \rightarrow 4\text{H} + 10\text{H} + \text{C}_6\text{H}_6\text{B}_{10} \quad \Delta H_1$$

Then $\Delta H_1 = 28\text{(C=O)} + 4\text{B(0-H)}_{11} + 68\text{(C=H)}_{111} + 23\text{(C=O)}$

$$= 5939.8 \text{ kJ mole}^{-1} (1394.1 \text{ kcal mole}^{-1})$$

Also $\Delta H^\circ_{f(g)}[\text{C}_6\text{H}_6\text{B}_{10}^2] = \Delta H^\circ_{f(g)}[\text{(C}_2\text{H}_2\text{O})_2\text{B}_{10}\text{H}_{12}] - 4 \Delta H^\circ_{f(g)}[\text{C}]$

$$- 10 \Delta H^\circ_{f(g)}[\text{H}] + \Delta H_1$$

which gives $\Delta H^\circ_{f(g)}[\text{C}_6\text{H}_6\text{B}_{10}^2] = -10293.8 \text{ kJ mole}^{-1} (-2442.4 \text{ kcal mole}^{-1})$

Thus in the case of 2-phenyl-1,3,3-dioxaborolan
\[
\begin{align*}
\text{O(CH}_2\text{)}_2\text{OCH}_2\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_2\text{BO}_2 \cdot 2\text{H} + 2\text{H} & \quad \Delta H \\
\end{align*}
\]

Where \( \Delta H = 2\text{H}(\text{C} = \text{O}) + \text{H}(\text{C} = \text{C}) + 4\text{H}(\text{C} = \text{H}) \)

\[
= 2\times 716.8 \text{ kJ mole}^{-1} (649.3 \text{ kcal mole}^{-1})
\]

And

\[
\Delta H^0_{f(g)}\left[\text{O(CH}_2\text{)}_2\text{OCH}_2\text{C}_6\text{H}_5\right] = \Delta H^0_{f(g)}\left[\text{C}_6\text{H}_2\text{BO}_2\right] + 2\Delta H^0_{f(g)}\left[\text{H}\right]
\]

\[
+ 4\Delta H^0_{f(g)}\left[\text{H}\right] = \Delta H
\]

which gives

\[
\Delta H^0_{f(g)}\left[\text{O(CH}_2\text{)}_2\text{OCH}_2\text{C}_6\text{H}_5\right] = -1516.8 \text{ kJ mole}^{-1} (-123.5 \text{ kcal mole}^{-1})
\]

By a similar reasoning

\[
\Delta H^0_{f(g)}\left[\text{n-C}_4\text{H}_9\text{BO}_2\right] = -1516.8 \text{ kJ mole}^{-1} (-123.5 \text{ kcal mole}^{-1})
\]

The values of all \( \Delta H^0_{f(g)} \) calculated by this method are given in Table 3.16.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(-\Delta H^0_{f(g)}) calculated</th>
<th>Ring Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{kJ mole}^{-1} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{kJ mole}^{-1} )</td>
<td>( \text{kcal mole}^{-1} )</td>
</tr>
<tr>
<td>( \text{O(CH}_2\text{)}_2\text{OCH}_2\text{C}_6\text{H}_5 )</td>
<td>516.8 ( \pm ) 4.5</td>
<td>123.5 ( \pm ) 1.3</td>
</tr>
<tr>
<td>( \text{O(CH}_2\text{)}_2\text{OCH}_2\text{C}_6\text{H}_5 )</td>
<td>537.1 ( \pm ) 1.1</td>
<td>128.1 ( \pm ) 1.0</td>
</tr>
<tr>
<td>( \text{O(CH}_2\text{)}_2\text{OCH}_2\text{C}_6\text{H}_5 )</td>
<td>559.2 ( \pm ) 3.3</td>
<td>133.3 ( \pm ) 2.1</td>
</tr>
<tr>
<td>( \text{O(CH}_2\text{)}_2\text{OCH}_2\text{C}_6\text{H}_5 )</td>
<td>585.1 ( \pm ) 4.1</td>
<td>139.9 ( \pm ) 2.0</td>
</tr>
<tr>
<td></td>
<td>( \text{kJ mole}^{-1} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{kJ mole}^{-1} )</td>
<td>( \text{kcal mole}^{-1} )</td>
</tr>
<tr>
<td>( \text{O(CH}_2\text{)}_2\text{OCH}_2\text{C}_6\text{H}_5 )</td>
<td>740.2 ( \pm ) 1.0</td>
<td>177.0 ( \pm ) 1.0</td>
</tr>
<tr>
<td>( \text{O(CH}_2\text{)}_2\text{OCH}_2\text{C}_6\text{H}_5 )</td>
<td>760.9 ( \pm ) 2.0</td>
<td>181.9 ( \pm ) 2.0</td>
</tr>
<tr>
<td>( \text{O(CH}_2\text{)}_2\text{OCH}_2\text{C}_6\text{H}_5 )</td>
<td>781.7 ( \pm ) 2.5</td>
<td>186.5 ( \pm ) 2.0</td>
</tr>
</tbody>
</table>
From Tables 3.15 and 3.16 it can be seen that the two procedures used to calculate the ring strain in the \( \text{2-butyl} \) and \( \text{3-phenyl} \) heterocycles lead to sets of values differing in absolute magnitude by \(-56.6\) \(\text{kJ \ mole}^{-1}\) \((-13.5\) \(\text{kcal \ mole}^{-1}\)) in the case of the \( \text{2-butyl} \) molecules and \(25.9\) \(\text{kJ \ mole}^{-1}\) \((5.8\) \(\text{kcal \ mole}^{-1}\)) in the case of the \( \text{phenyl} \) analogues. This requires some comment.

For a given set of compounds the differences in ring strain are constant, independent of the method of calculation. The change in absolute magnitude is therefore a reflection on the nature of the model which has been used, in one case of a self-consistent bond energy scheme and in the other a model based on the assumption that \( \text{HNB}(\text{C}_{2}H_{5})_{2} \cdot \text{X} = \text{C}_{2}H_{5} \) or \( n-C_{4}H_{9} \), are strainless reference molecules. If \( \Delta H^0f(g) \) of the two diethoxy compounds are estimated by using the same bond energy scheme (i.e. the Cox bond energy scheme) and are compared with the experimental values, i.e.

\[
\begin{align*}
\text{a) } & \Delta H^0f\left( \text{C}_{2}H_{5}O\right)_{2} \text{C}_{6}H_{5}(g) = -626.0\text{ \text{kJ \ mole}^{-1}} (-149.7\text{ \text{kcal \ mole}^{-1}}) \\
\text{cf. } & \Delta H^0f\left( \text{C}_{2}H_{5}O\right)_{2}n-C_{4}H_{9}(g) = -769.3\text{ \text{kJ \ mole}^{-1}} (-143.9\text{ \text{kcal \ mole}^{-1}}) \\
\text{and b) } & \Delta H^0f\left( \text{C}_{2}H_{5}O\right)_{2}n-C_{4}H_{9}(g) = -602.1\text{ \text{kJ \ mole}^{-1}} (-143.9\text{ \text{kcal \ mole}^{-1}}) \\
\text{cf. } & \Delta H^0f\left( \text{C}_{2}H_{5}O\right)_{2}n-C_{4}H_{9}(g) = -325.9\text{ \text{kJ \ mole}^{-1}} (-197.4\text{ \text{kcal \ mole}^{-1}})
\end{align*}
\]

it may be noted that the differences between these two sets of values \(-56.6\) \(\text{kJ \ mole}^{-1}\) \((-13.5\) \(\text{kcal \ mole}^{-1}\)) for \( \text{C}_{2}H_{5}O\) \(\text{B}_{2}n-C_{4}H_{9}\)

\(-56.6\) \(\text{kJ \ mole}^{-1}\) \((-13.5\) \(\text{kcal \ mole}^{-1}\)) are the same as the differences in ring strains obtained by the two procedures described above. So that a reasonable estimation of the absolute magnitude of the ring strains may be made it is important to consider the reasons for this discrepancy. Basically it is a question of the nature of the bonding of a boron atom in various environments. Boron chemistry is dominated by the ability of the empty \( p_2 \) orbital in \( \text{sp}^2 \).
hybridized boron to be filled to varying extents, either rehybridizing to sp$^3$
as in F-B.O(C$_2$H$_5$)$_2$ or by increasing the B-X bond order in BX$_3$, as occurs when
X = aryl or alkoxy, donation from the oxygen lone pairs or the arenic
delocalized π electron system readily taking place. The mean bond
dissociation energies $\overline{D}(B - C_6H_5)$ and $\overline{D}(B - C_4H_9)$ used in the bond energy
scheme were values obtained by a consideration of the reactions

$$\text{B}(n - C_4H_9)_3(g) \rightarrow \text{B}(g) + 3n - C_4H_9(g)$$

and

$$\text{B}(C_6H_5)_3(g) \rightarrow \text{B}(g) + 3C_6H_5(g)$$

that is to say the bond energies obtained are strictly applicable only to the
compounds tri-n-butylborane and triphenylborane. Similarly $\overline{D}(B - O)$ was a
mean value obtained from the trialkyl borates $[O(CH_2)_nCH_3]_3$ $n = 0$ to $3$
by considering the reactions

$$[O(CH_2)_nCH_3]_3 \rightarrow \text{B} + 3O + 3(n+1)C+3(2n+3)H$$

That these bond energy values do not remain constant in a different
environment can be seen from the following redistribution reactions

$$\text{HB}(C_6H_5)_3(g) + \frac{1}{2}(O_2) \rightarrow (C_6H_5)_2BOH_5(g) \ \Delta H_1$$

and

$$\frac{3}{2}\text{HB}(n-C_4H_9)_3(g) + \frac{1}{2}(O_2) \rightarrow (C_4H_9)_2B(n-C_4H_9)(g) \ \Delta H_2$$

Using the values of $\Delta H^0_1$ and $\Delta H^0_2$ given in Table 3.17, $\Delta H_1$ and $\Delta H_2$ may be
calculated to be 22.1 kJ mole$^{-1}$ (5.3 kcal mole$^{-1}$) and -58.3 kJ mole$^{-1}$
(-13.9 kcal)$^{-1}$ respectively.
Table 3.17

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H^\circ_{298} ) (kJ mole(^{-1}))</th>
<th>( \Delta H^\circ_{298} ) (kcal mole(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Si}(\text{CH})_2 \text{Cl}_2 )</td>
<td>143.12 2.9</td>
<td>34.320.7</td>
<td>Ref. 4, Table 3.14</td>
</tr>
<tr>
<td>( \text{Si}(\text{CH})_2 \text{Cl}_2 )</td>
<td>-207.0</td>
<td>-48.6</td>
<td>Table 3.14</td>
</tr>
<tr>
<td>( \text{Si}(\text{CH})_2 \text{Cl}_2 )</td>
<td>-1007.921.7</td>
<td>-240.920.4</td>
<td>Table 3.13</td>
</tr>
<tr>
<td>( \text{Si}(\text{CH})_2 \text{Cl}_2 )</td>
<td>-632.122.9</td>
<td>-143.320.7</td>
<td>Table 3.13</td>
</tr>
<tr>
<td>( \text{Si}(\text{CH})_2 \text{Cl}_2 )</td>
<td>-825.922.6</td>
<td>-197.420.6</td>
<td>Table 3.13</td>
</tr>
</tbody>
</table>

a From updated values of Charnley et al., 1952

Using the value of \( \Delta H^\circ_{298} \left[ \text{Si}(\text{CH})_2 \text{Cl}_2 \right]_g \) in Table 3.17 the bond energy \( B(\text{Si}-\text{O}) \) in triethylborate is 319.6 kJ mole\(^{-1}\) (124.2 kcal mole\(^{-1}\)) which compares with the value of \( B(\text{Si}-\text{O}) \) used in the bond energy scheme of 521.3 kJ mole\(^{-1}\) (124.6 kcal mole\(^{-1}\)) obtained by averaging the \( B(\text{Si}-\text{O}) \) values in the trialkylborates \( \left[ \text{Si}(\text{CH})_2 \text{CH}_3 \right]_n \), \( n = 0 \) to 3. It is this difference in these two \( B(\text{Si}-\text{O}) \) values of 1.7 kJ mole\(^{-1}\) (0.4 kcal mole\(^{-1}\)) which accounts for the discrepancy between the difference in \( \Delta H^\circ_{298} \left[ \text{Si}(\text{CH})_2 \text{CH}_3 \right]_n \) obtained by the bond energy scheme and the experimentally determined value (23.9 kJ mole\(^{-1}\), 5.3 kcal mole\(^{-1}\)) compared with \( \Delta H^\circ_{298} \text{ from the redistribution reaction (22.1 kJ mole\(^{-1}\), 5.3 kcal mole\(^{-1}\))} \). Similarly the difference in \( \Delta H^\circ_{298} \left[ \text{Si}(\text{CH})_2 \text{Cl}_2 \right]_n \) obtained by the two methods (-56.6 kJ mole\(^{-1}\), -13.5 kcal mole\(^{-1}\)) compared with \( \Delta H^\circ_{298} \text{ from the redistribution reaction (-58.3 kJ mole\(^{-1}\), -19.9 kcal mole\(^{-1}\))} \) is accounted for in the same manner.

Consideration of the diethoxyphenylboronate redistribution reaction shows that the \( \text{O}-\text{Si} \) and \( \text{O}-\text{O} \) bonds in this molecule are destabilized by 22.1 kJ mole\(^{-1}\) with respect to triethylborate and triphenylborane. By comparison with diethoxy-n-butylboronate, the corresponding bonds of which are stabilized with respect to triethylborate and tri-n-butylborane by 58.3 kJ mole\(^{-1}\), this might at first sight seem surprising, but a consideration of the molecular geometry of diethoxyphenylborane shows that if maximum overlap of the oxygen
Severe hydrogen hydrogen interactions take place if the skeleton is planar, the hydrogen van der Waals radius being ca. 1.2 Å (Pauling, 1960)
lone pair electrons and the phenyl \( \pi \) electrons with the empty boron \( p_z \)
orbital is to occur, necessitating as will be shown later a planar
\[
\begin{align*}
0 & \rightarrow 0 \\
C - B
\end{align*}
\]
system, then severe hydrogen-hydrogen interactions will take
\[
\begin{align*}
0 & \rightarrow 0 \\
C - C
\end{align*}
\]
place, as can be seen from Figure 3.1.

These steric interactions may be reduced only at the expense of decreased
orbital overlap, so in effect diethoxyphenylboronate is 'strained' or
destabilized because of these steric and reduced conjugation effects. The
value of \( \Delta H_{1} \) from the redistribution reaction may be taken to be a measure
of the strain in diethoxyphenylboronate with respect to triphenylborane and
triethylboronate, but this is not the desired destabilization enthalpy being
merely the change in enthalpy of the redistributed bonds. The required
destabilization enthalpy may be defined as \( -\Delta H \) hypothetical from the
transition
\[
\begin{align*}
(\text{C}_2\text{H}_5\text{O})_2\text{B} = \text{H}_2(g) & \rightarrow (\text{C}_2\text{H}_5\text{O})_2\text{B} = \text{H}_2(g, \text{with maximum } \pi \text{ overlap}) \\
-\Delta H_{\text{steric interactions}} = \Delta H \text{ hypothetical}
\end{align*}
\]
\( \Delta H \) hypothetical is thus the stabilization enthalpy given by gaseous
diethoxyphenylboronate going to a planar conformation in which the effects of
steric interactions which must take place (as shown previously) have been
removed. The required model by which to compare the strained 8-phenyl
heterocyclics is therefore \( (\text{C}_2\text{H}_5\text{O})_2\text{B} = \text{H}_2(g, \text{with maximum } \pi \text{ overlap and no}
steric interactions) \). In the case of diethoxy-n-butylboronate the corresponding
\( \Delta H_{\text{hypothetical}} = 0 \) because no similar steric interactions take place when
maximum \( \pi \) overlap is achieved. Thus in this case diethoxy-n-butylboronate
in a suitable unstrained reference molecule.

The previous statement that the value of \( \Delta H_{1} \) of the redistribution
reaction between triphenylboronate and triethylboronate going to diethoxyphenyl-
boronate is 'merely the change in enthalpy of the redistributed bonds"
implies that the nature of the boron-oxygen and boron-phenyl bonds changes substantially from one molecule to another. Some evidence of this is afforded by accurate self-consistent field MO calculations (Armstrong and Perkins, 1967a,b) which give the boron-phenyl bond orders in phenylboronic acid $\text{H}_3\text{B(OH)}_2$ and triphenylborane $\text{B}_3\text{H}_9$ to be 0.199 and 0.172 respectively. The change in bond strength of boron-phenyl bonds has also been determined thermochromically (Finch et al., 1967) for triphenylborane, diphenylboron chloride and phenylboron dichloride, the values obtained being given in Table 5.16. By subtracting $E(\text{B}-\text{C})$ in tricyclohexylborane for which pure $\sigma$-boron-carbon bonds were assumed, $E(\text{B}-\text{C})_\pi$ the boron-carbon $\pi$ bond energy was obtained. For these calculations $E(\text{B}-\text{C})$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E(\text{B}-\text{C})$</th>
<th>$E(\text{B}-\text{C})_\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[kJ mole$^{-1}$]</td>
<td>[cal mole$^{-1}$]</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_9$</td>
<td>443.9 ± 9.6</td>
<td>106.6 ± 2.3</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_9\text{Cl}$</td>
<td>ca. 469</td>
<td>ca. 115</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_9\text{Cl}_2$</td>
<td>434.5 ± 9.6</td>
<td>115.6 ± 2.3</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_9\text{Cl}_2$</td>
<td>359.9 ± 14.2</td>
<td>88.4 ± 3.4</td>
</tr>
</tbody>
</table>

was required and this was assumed to have a constant value, being equal to that in boron trichloride, the constancy of the $\text{B}-\text{Cl}$ bond lengths in boron trichloride, 1.753 ± 0.03Å and in phenylboron dichloride, 1.750 ± 0.05Å (Sutton, 1953) implying constancy of boron-chlorine bond order. The decrease in $E(\text{B}-\text{C})_\pi$ observed with increasing numbers of phenyl groups was taken to be due to the steric interactions of the phenyl groups causing them to rotate out of the $\text{B}_3\text{H}_9$ plane and thus reducing phenyl $\pi$ electron overlap with the empty boron $p_2$ orbital. A further indication of the variation in the nature of boron-carbon and boron oxygen bonds with environment is given by $\Delta H_2$ in the dihydroxy-dihydroxymethylboronate redistribution reaction in which no
steric interactions will take place, but the negative $\Delta H^\circ$ implies a substantial stabilization - as mentioned before - of the boron-oxygen and boron-carbon bonds in diethoxy-m-butylboronate with respect to tri-butylborane and triethylborate.

The important point to be made is, that, except for the distortions caused by the steric restrictions of the ring atoms - which is considered to be a part of the ring strain - the diethoxy-m-butylboronate molecule provides a logical strainless reference model because its atoms are disposed in the same manner as in the heterocyclics. In the case of diethoxyphenylboronate, however, because of steric interactions present in the acyclic molecule, but not in the heterocyclic analogues, this molecule does not provide a good strainless reference model unless this destabilizing factor can be independently assessed.

As has been noted previously, the stabilization achieved by donation of the oxygen lone pair to the empty boron $p_z$ orbital is of major importance.

It is therefore necessary to appreciate how the oxygen lone pairs are directed so that the changes in oxygen donation induced by changing the geometry of the heterocycle may be anticipated.

Accurate self consistent field molecular orbital calculations for the water molecule (Peters, 1963; Peters, 1967), in which localized molecular orbitals corresponding to two electron bond and lone pairs have been introduced, indicate that the bonding oxygen atomic orbitals are practically pure $2p_x$ and one lone pair is close to pure $2p_y$, the other being pure $2p_z$.

Thus one lone pair is only slightly directed away from the hydrogens, the other is directed perpendicular to the OBO plane. If this is extended to oxygen in a COB environment, then the directed lone pair in oxygen is perpendicular to the COB plane, whereas the empty boron $p_z$ orbital is perpendicular to the COB plane, therefore for maximum oxygen electron donation in a dimerboron the entire COBOC skeleton must be coplanar. Consideration of
the 501 angle in trimethylborate, 113°24' (Sutton, 1958) indicates that some sp\(^2\) hybridisation of the oxygen probably occurs where one lone pair orbital lies in the 501 plane and the other perpendicular to this plane.

**2-ethyl-1,3,2-dioxaborolane**

Microwave data of 1,3,2-dioxaborolanes give the following structural details (Hend and Schwendeman, 1966)

<table>
<thead>
<tr>
<th></th>
<th>OCB</th>
<th>OCC</th>
<th>OBC</th>
<th>OCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.5412(2) 0.009 &amp;</td>
<td>OCB 114.24(0.5)°</td>
<td>OCC 107.35(0.5)°</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>1.435(2) 0.010 &amp;</td>
<td>OCB 104.91(0.5)°</td>
<td>OCB 107.35(0.5)°</td>
<td></td>
</tr>
<tr>
<td>BO</td>
<td>1.366(2) 0.010 &amp;</td>
<td>OCC 105.91(0.5)°</td>
<td>OCB 107.35(0.5)°</td>
<td></td>
</tr>
<tr>
<td>CB</td>
<td>1.075(2) 0.010 &amp;</td>
<td>OCC 109.25(0.5)°</td>
<td>OCC 112.52(0.7)°</td>
<td></td>
</tr>
<tr>
<td>BB</td>
<td>1.22(2)(assumed) OCC 112.52(0.7)°</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The dihedral angle between the OCC and the OBO planes is 7.1°.

The dihedral angle between the C\(_1\)C\(_2\)O\(_2\) and the C\(_3\)O\(_4\) planes is 11.8°.

The decrease of every ring angle in the borolane by approximately 5° from their undistorted values is the most significant feature, from the point of view of ring strain, in this molecule, and as the ring angles in 2-ethyl-1,3,2-dioxaborolane must be very similar to those of 1,3,2-dioxaborolanes, the large ring strain (as compared to other five-membered cyclic molecules) of 41 kJ mol\(^{-1}\) (10 kcal mol\(^{-1}\)) may be attributed primarily to this factor.

It is interesting to compare the series of five-membered rings cyclopentane, 1,3-dioxolane and 2-ethyl-1,3,2-dioxaborolane. The ring strains in these molecules increase progressively, being respectively 23.7 kJ mol\(^{-1}\) (5.7 kcal mol\(^{-1}\)), 29.1 kJ mol\(^{-1}\) (6.9 kcal mol\(^{-1}\)) and 41 kJ mol\(^{-1}\) (10 kcal mol\(^{-1}\)). The major features account for this trend; firstly the increasing angle bending strain and secondly the decreasing torsional strain. It is apparent that the former is the most dominant factor of the two. A consequence of the opposition of these two forces is
the ring puckering vibration which takes the form of a pseudorotation in
cyclopentane (see Chapter Two). Spectroscopic evidence (Junge and Venter,
1963) indicates that pseudorotation also takes place in 1,3-dioxane, the
potential barrier to the planar conformation hindering this ring vibration
being estimated at 0.3 kJ mol$^{-1}$ (0.13 kcal mol$^{-1}$). The further reduction
in eclipsed hydrogens in going to 1,3,2-dioxaborolane (and thus to
2-n-buty1-1,3,2-dioxaborolane) has the effect of reducing the ring warping
vibration to one in which only a torsion about the CC bond occurs with a
simultaneous motion of the carbon atom, one above and one below the CC
plane. Although no quantitative estimate of the barrier to the planar
conformation could be made (Land and Schendeman, 1956) it was concluded
that it must be very low, probably lying below the lowest vibrational level.

2-n-Buty1-1,3,2-Dioxaborinane
The increase in ring strain in moving from 2-n-buty1-1,3,2-dioxaborolane
to 2-n-buty1-1,3,2-dioxaborinane, i.e. from 43.2$^{\pm}$5.0 kJ mol$^{-1}$ to 45.6$^{\pm}$4.2
kJ mol$^{-1}$ is quite unique in simple five and six-membered cyclic molecules
of the same type (see Table 2.8 Chapter Two). Although the structure of
any 1,3,2-dioxaborinane has not been experimentally determined, considerations
of the geometry of such rings shows that least angle bending strain occurs in
a puckered chair or boat conformation. This is in opposition to the
requirement of a coplanar COSOC skeleton for maximum pi orbital overlap, a
situation which did not occur in the five-membered analogue. Thus a
compromise between two extremes of destabilization, one involving angle
bending and torsional strain for a coplanar COSOC skeleton, and the other
reduced pi orbital overlap for a puckered conformation, will be achieved.
Severe ring strain still occurs in the equilibrium conformation, however,
to the extent of 45.6$^{\pm}$4.2 kJ mol$^{-1}$. 
2-n-Butyl-1,3,2-Dioxaboropan

The trend observed in the previous two members of this series of increasing steric strain brought about by a planar COBOC skeleton, is maintained with this molecule.

In such a conformation the 4,7-hydrogen-hydrogen internuclear distance is only 0.8Å and two pairs of hydrogens on the 5,6 carbon atoms are eclipsed. Relief of these strains leads to decreased π orbital overlap and to the associated electronic destabilization and the strain energy minimum which achieved is higher than either the five or six-membered analogues.

The 2-Phenyl-1,3,2-Dioxaboron Heterocycles

The outstanding feature of these molecules is the very small variation in ring strain throughout the series, the 2-phenyl-1,3,2-dioxaborolan ring being approximately 3 kJ mole⁻¹ more strained than the other two. From the previous discussion of the acyclic molecules the point was made that diethoxyphenylboronate must be considered to be strained, so values of ring strain given in Table 3.16 for the phenyl rings must be increased by this amount. It seems logical to suppose that the factors contributing to the ring strain of 2-phenyl-1,3,2-
dioxaborolanes and 2-α-buty1-1,3,2-dioxaborolane must be quite similar, being predominantly due to angle bending and torsional strains, optimum π orbital overlap being achieved in both cases. It will therefore be assumed that both these five-membered rings have the same ring strain, i.e. approximately 41 kJ mole⁻¹ (10 kcal mole⁻¹) implying that dichlorophenyl boronate is strained by approximately this amount, the ring strain of 2-phenyl-1,3,2-dioxaborolanes as compared to its acyclic analogue being 0.5 kJ mole⁻¹ (-0.1 kcal mole⁻¹) (see Table 3.15). On this basis the ring strains of all the phenyl rings must be increased by 41 kJ mole⁻¹ (10 kcal mole⁻¹) with respect to those values given in Table 3.16. The values as obtained are given in Table 3.19 and the ring strains of these molecules will be discussed in terms of these values.

Table 3.19

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ring Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ mole⁻¹</td>
</tr>
<tr>
<td>O(CH₂)₂OC₆H₅</td>
<td>41</td>
</tr>
<tr>
<td>O(CH₃)₂OC₆H₅</td>
<td>37</td>
</tr>
<tr>
<td>O(CH₃)₂OC₆H₅</td>
<td>38</td>
</tr>
<tr>
<td>O(CH₂)₂OC₆H₅</td>
<td>60</td>
</tr>
</tbody>
</table>

It has been proposed that the principal feature in the five, six and seven-membered α-buty1 dioxaborolene heterocycles causing a steady increase in ring strain with ring size has been the conflicting requirements of a planar C₆B₄OOC skeleton for maximum π orbital overlap, and the angle bending, torsional and non-bonded interactions such a requirement imposes. In the case of the phenyl dioxaborolene heterocycles, however, back donation of electrons from the phenyl group to the boron atom may take place thereby reducing the importance of the oxygen-boron back donation, the aromatic nucleus acting as an electron source which will tend to maintain the electron
density, born constant irrespective of the born-oxygen orbital overlap. It is proposed, therefore, that the requirement of a planar C0H0H0 skeleton in the phenyl rings is much less important than in the case of the n-butyl analogues and so the angle bending, torsional and non-bonded interaction strains may be more readily relieved in these molecules by the packing of the ring atoms. It is instructive at this stage to consider the ring strains in the five, six and seven-membered cyclic alkanes, 1,3-dioxane and 2-phenyl-1,3,2-dioxaborin compounds. These are given in Table 3.20. It can be seen that with increasing hetero-atom substitution in the rings not only do the ring strains of the five-membered and six-membered rings increase, but the difference in ring strains between the five and six and the six and seven-membered rings decreases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ring Strain</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25.7 kJ mol^{-1}</td>
<td>0.4 kJ mol^{-1}</td>
<td>24.6 kJ mol^{-1}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.1 kcal mol^{-1}</td>
<td>0.1 kcal mol^{-1}</td>
<td>5.9 kcal mol^{-1}</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ring Strain</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>39.1 kJ mol^{-1}</td>
<td>11.7 kJ mol^{-1}</td>
<td>23.5 kJ mol^{-1}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.2 kcal mol^{-1}</td>
<td>2.8 kcal mol^{-1}</td>
<td>5.7 kcal mol^{-1}</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ring Strain</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>41 kJ mol^{-1}</td>
<td>37 kJ mol^{-1}</td>
<td>38 kJ mol^{-1}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 kcal mol^{-1}</td>
<td>9 kcal mol^{-1}</td>
<td>9 kcal mol^{-1}</td>
<td></td>
</tr>
</tbody>
</table>

See Table 2.5 Chapter Two for the cyclic alkanes and Table 2.8 Chapter Two for 1,3-dioxane and 1,5-dioxin.

The ring strain of 1,3-dioxane was derived from heat of combustion data (Kanatzov et al., 1957) together with the C-C bond energy scheme.
The first of these observations is rationalized by the increasing angle-bending strain imposed by the hetero-atoms, and this effect also reduces the stability – with respect to acyclic molecules – of the six-membered rings so causing the difference in ring strain between the five and six-membered rings to decrease. The major cause of strain in cycloheptane is due to hydrogen-hydrogen interaction, this is reduced in 1,3-dioxepan so an increase in ring strain with additional hetero-atoms is not observed. There is an increase in ring strain in going to the 2-phenyl-1,3,2-dioxaboropan, however, and this is due to the relatively smaller hydrogen-hydrogen interaction in going from the 1,3-dioxaboropan than from cycloheptane, coupled with the reduced pi orbital overlap which, although a less important effect than in 2-n-butyl-1,3,2-dioxaboropan, must still be present.

2-Phenyl-2,4-bis(3-hexabicyclo[3.2.2]octane

This molecule is simplest to visualize as a cyclohexane ring, the 1,4-positions being bridged by OOC-. Geometric considerations show that its most stable structure is when the cyclohexane ring assumes a twist-boat conformation, a full boat structure requiring the two oxygen atoms to be only about 1.8 Å apart – similar to the unfavourably disposed 1,4-hydrogens in a boat form cyclohexane. As a first approximation the strain energy in the bicyclic-compound may be considered to be the sum of two 2-phenyl-1,3,2-dioxaboropan rings plus a cyclohexane chair to twist boat enthalpy minus the reduced non-bonded hydrogen interactions (i.e. the 1,4-interactions in the twist boat and also two 4,7-hydrogen interactions in each of the dioxaboropan rings). This does not take into account the change in angle bending and torsional strain in the seven-membered heterocycles due to the steric requirements of the bicycle-system. It also does not take into account the stabilization associated with forming a bicyclic molecule – a stabilization which has been shown in Chapter 12 to be quite significant.
The cyclohexene chair $\rightarrow$ boat transition enthalpy is accepted as being 25.0 kJ mole$^{-1}$ (5.9 kcal mole$^{-1}$), and the boat $\rightarrow$ twist boat enthalpy to be about -6.7 kJ mole$^{-1}$ (-1.6 kcal mole$^{-1}$) (see Chapter Two) giving the chair $\rightarrow$ twist boat transition enthalpy 16.3 kJ mole$^{-1}$ (3.9 kcal mole$^{-1}$).

From Table 3.19 ring strain in 2-phenyl-1,3,5-triazabicyclo[4.4.0]decanes = 38 kJ mole$^{-1}$ (9 kcal mole$^{-1}$) and that of the bicycle-compound 60 kJ mole$^{-1}$ (15 kcal mole$^{-1}$). Thus 2x(ring strain in 2-phenyl-1,3,5-triazabicyclo[4.4.0]decanes) + chair $\rightarrow$ twist boat enthalpy = 2x38 + 16 = 93 kJ mole$^{-1}$ (22 kcal mole$^{-1}$) leaving 32 kJ mole$^{-1}$ (7 kcal mole$^{-1}$) of stabilization in the bicycle-compound to be accounted for in other ways. These are, changes in the angle bending strain, torsional strain and hydrogen-hydrogen interactions, but the principal stabilizing factor is probably due to the differences in nuclear action energy between the acyclic model (also inherent in the bond energy terms) and the bicyclic system. This stabilizing factor has been discussed in detail in Chapter Two and, as can be seen from Table 3.13 which compares the ring strain in a bicyclic molecule with the sum of the two acyclic molecules, this factor is very important, but it can only be estimated from a knowledge of the fundamental vibrational frequencies of the bicyclic molecule. It is also worth pointing out that all the ring strains discussed so far in this chapter have been enthalpy values.

If converted to the more correct energy values - by allowing 32 kJ mole$^{-1}$ per ring - this reduces the ring strain of the bicycle-compound by 3.4 kJ mole$^{-1}$ (0.8 kcal mole$^{-1}$) per ring.


Chapter Three: References


Con, J.D., Tetrahedron, 1962, 18, 1597; 1963, 19, 1175.


Green, J.A.S., Quart., Rev., 1961, 15, 125.


Rothstein, B., Ann., 1930, 14, 492.


CHAPTER FOUR

Solution Reaction Adiabatic Calorimetry

Introduction

The reasons for developing a solution reaction adiabatic calorimeter were outlined in Chapter One and the principles involved in such a system will be described here.

Ideally, the heat change of a reaction in solution is confined entirely within the calorimeter thus causing the total enthalpy change of the system to be zero. This heat of reaction is measured by determining the amount of work (usually electrical) needed to give the same temperature change inside the calorimeter.

In practice such an apparatus takes the form of a reaction vessel surrounded by an adiabatic shield whose temperature is maintained at the same value as the temperature inside the reaction vessel. This has been accomplished by various workers in different ways and some designs of adiabatic solution calorimeters will now be briefly mentioned.

One of the first adiabatic solution calorimeters was described by A.S. Carson, K. Hartley and H.A. Skinner (1949) and consisted of a glass reaction vessel which fitted inside a Dewar vessel, the intervening space being filled with water; the Dewar vessel was placed in a heavily lagged copper tank filled with oil. The heat of reaction was determined by measuring the temperature rise of the Dewar and the oil bath and maintained at this same temperature by means of a heater. Thermocouples were used to detect the temperature difference between inside and outside the Dewar, the potential generated being displayed as the movement of a galvanometer spot which was detected by means of a photocell which in turn activated the heating system via relays. The deflection of the galvanometer spot equivalent to a temperature difference of 0.05°C was sufficient to activate the heaters, the output of which being controlled by a Variac transformer.
could be adjusted so that the spot scarcely moved from zero.

A modification of this system was described by Skinner and Tees (1953), the central reaction vessel having a lower compartment filled with mercury for ballast, the whole floating on a pool of mercury inside the surrounding Dewar. This arrangement allowed the inner reaction vessel to be rotated during operation as a means of stirring. The adiabatic shield consisted of a metal can filled with oil and the adiabatic temperature control were similar to that described previously by Carsen et al., (1949).

A rather different system was described by Coops et al. (1956), the calorimeter consisting of a glass Dewar (250 ml capacity) fitted with an evacuated glass head by means of a ground joint. The whole calorimeter was filled with fluid and the flow of liquid was directed to circulate along the calorimeter walls by means of inner concentric walls thus maintaining the calorimeter walls at a uniform temperature. All temperature changes were determined by thermistors and adiabatic control was achieved by means of a thermistor bridge, the out of balance potential activating a proportional control device so that the output of the heaters connected to this was proportional to the temperature difference between inside and outside the calorimeter. The slight loss of adiabatic control observed at the initiation of a reaction was recorded photographically from the deflection of a galvanometer spot, but it was found that the necessary heat loss correction for this was less than the precision of the apparatus. By determining the energy equivalent of the calorimeter for several 240 sec heating periods, the precision of the apparatus was reported as 0.1%.

This system was later modified (Carsen et al., 1963) in the following respects. The adiabatic temperature detection bridge was replaced by an a.c. thermistor bridge which allowed amplification of the out of balance potential. After rectification this potential was passed to the heater via a magnetic amplifier to achieve proportional control thereby, for small imbalances of
the bridge, the rate of heating is proportional to the temperature difference. By this means fluctuations in the temperature difference between inside and outside the calorimeter were reduced to below $10^{-5} \, ^{\circ}{\text{C}}$. The temperature detection system also utilized an a.c. Wheatstone bridge allowing temperature differences of $0.25 \times 10^{-5} \, ^{\circ}{\text{C}}$ to be detectable. For the heat of solution of KCl in water (total temperature change 0.03 to 0.04$^{\circ}$C) a precision of 0.03$^{\circ}$C was achieved.

Because the sources of heat inside a calorimeter are not distributed perfectly evenly, temperature gradients exist which in turn result in temperature gradients across the walls of the calorimeter. Such temperature gradients between the calorimeter and shield cause a net heat exchange during an experiment. Variation of the heating rate during a calibration has often been used as a test of precision of such systems; as a slower heating rate will lead to smaller temperature gradients and so reduce the rate of heat exchange between calorimeter and adiabatic shield. This line of reasoning has been challenged (West and Ginnings, 1953) by the following lines of reasoning. During the heating period there are gradients between the calorimeter and the adiabatic shield. These gradients, and therefore the effective temperature difference between them, are very nearly proportional to the rate of heating. Consequently the rate at which heat is lost from the calorimeter by transfer to the shield is directly proportional to the rate of heating. In any given experiment the heating rate is virtually constant, so that energy lost from the calorimeter is directly proportional to the product of the heating rate and the time of heating. Since this product is equal to the change in the calorimeter temperature, the energy lost is the same in any two experiments provided the initial and final temperatures are the same.

A rather more involved argument is presented in Appendix Five which shows that under the working conditions of the calorimeter described in
this thesis heat exchanges between the calorimeter and shield must, to a
large extent, cancel out between reaction and calibration.

In combustion calorimetry it is convenient to calibrate the apparatus
using the heat of combustion of a sample of benzoic acid, the value of which
has been very accurately determined in a standards laboratory. This is not
the case in solution calorimetry, however, where electrical standardisation
is generally used. The reasons for this difference are as follows. Firstly,
for combustion calorimetry:

a) The heat capacity of the benzoic acid and oxygen is only a very small
part of the heat capacity of the apparatus and hence this is altered only
very slightly in changing from the experimental to the calibrating system.
b) The reaction in the combustion calorimeter is very rapid so the heat
distribution is primarily a function of the stirring and design of the
apparatus, this being the same for both experiment and calibration.

In solution reaction calorimetry, however, the reacting system is a
major part of the heat capacity of the apparatus, and also the heat
distribution is dependent upon the kinetics of the reaction. Because of
this electrical calibration of such instruments is usually undertaken.
Difficulties with this procedure are that a) the source of heating is in the
one case localized at the heater surface whilst during reaction it may be
diversified over the entire solution volume and also at the surface of
undissolved reactants, depending on the nature of the reaction being carried
out.
b) The rate of heating during calibration and reaction may be markedly
different.

Electrical calibration is, therefore, not strictly comparable with
reaction and so it is highly desirable to have a test reaction whose reaction
heat is known precisely so that the accuracy of the system may be assessed.
Desirable characteristics for a rapid test reaction have been suggested by S.R. Cunn (1955) as

1. The process should consist of mixing a weighed amount of a standard substance - liquid or solid - in a frangible bulb or other sample chamber with a large volume of liquid.

2. The liquid should preferably be pure water; if not, then aqueous solution, preferably of neutral pH.

3. The process should be rapid and complete.

4. An exothermic process would be more desirable than an endothermic one.

5. The temperature change should be about 1 degree, but the heat process should be known with little loss of accuracy under conditions giving considerably smaller changes of temperature.

6. The heat should be defined at 298K, but the temperature coefficient should be small.

7. The heat should be fairly insensitive to the ratio of standard substance to liquid, and to the concentration of solutes, if any, in the initial liquid.

8. Exposure of the liquid to the atmosphere should have a negligible effect on the heat.

9. The heat should be the same in closed or open calorimeters, or the difference should be readily calculable.

10. No gases should be evolved.

11. The change in volume of the liquid should be small.

12. The change in vapour pressure of the liquid should be small.

13. The volume required of the sample chamber should be no more than 5% of the liquid and preferably less.

14. The mass of the standard substance should be large enough for convenient and accurate weighing.
15) The heat capacity of the standard substance should be small (and this is important in isothermally jacketed calorimeters where the temperature of the standard substance may lag significantly behind the liquid during the forced drift; it is unimportant in adiabatic calorimeters). Point 15 is generally in conflict with Point 14.

16) The standard substance should be available in high purity or be readily purifiable.

17) The standard substance should be non-hidrosopic and non-volatile and non-reactive with the atmosphere.

18) The standard substance should not be subject to significant energy perturbations from crystal defects or surface energy effects.

A test reaction for solution reaction calorimeters which was rapid was recommended by Nieschke and Kagansvich (1949) as being the dissolution of KCl in water. Since then numerous determinations of this heat of solution have shown a significant variation (in the order of 1%). Sumner and Wadsö in 1959 and Gunn in 1969 in particular have therefore recommended that its use as a standard reaction be discontinued.

The heat of solution of THAM or TRIS (trishydroxymethyl)aminomethane in 0.1M HCl was proposed by Irving and Wadsö (1964) as a test reaction and at present this appears to be universally accepted. Values of this heat of reaction obtained on various samples of THAM is given in Table 4.1.
At the present time therefore a suitable rapid test reaction for solution calorimeters is available. In the case of slow reactions, however, no such standards exist, the only published suggestion being due to Gunn (1965) who considered briefly the possibility of using the reaction between magnesium and dilute hydrochloric acid. This, and other possible reactions, will be considered later in this thesis.

### Table 4.1

<table>
<thead>
<tr>
<th>kJ mol⁻¹</th>
<th>kcal mol⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.736±0.004</td>
<td>7.107±0.001</td>
<td>Gunn, 1965</td>
</tr>
<tr>
<td>29.752±0.004</td>
<td>7.113±0.001</td>
<td>Gunn and Wadsø, 1966</td>
</tr>
<tr>
<td>29.757±0.008</td>
<td>7.112±0.002</td>
<td>Øjeland and Wadsø, 1967</td>
</tr>
<tr>
<td>29.744±0.003</td>
<td>7.109±0.001</td>
<td>Hill, Øjeland and Wadsø, 1969</td>
</tr>
</tbody>
</table>

Heats of solution of THAM in 0.1M HCl at 25°C

\[ \text{H}_2\text{O}:\text{THAM} = 500 \text{ to } 2000 \]
Chapter Four References


Chapter Five

The Adiabatic Solution Reaction Calorimeter

Essentially the adiabatic calorimeter described here is a development of the constant temperature environment (C.T.E.) calorimeter described by Gardner (1964) and Finch and Gardner (1964), but because of the various modifications required, the design of this apparatus will be described in detail.

The Adiabatic Control Unit

By detecting the temperature difference between the inside and outside of the calorimeter this unit automatically switches on heaters which heat the water bath outside the calorimeter thereby maintaining it at the same temperature, or at the same constant temperature difference, with respect to inside the calorimeter. The design of this is the same (with minor modifications) as the automatic adiabatic control unit used in the Calenkaup Adiabatic Bomb Calorimeter (Raymond et al., 1957). Figure 5.1 shows the circuit diagram and it functions essentially as follows. Two matched f23 (Standard Telephone and Cable Ltd) thermistors are the temperature sensing elements and these are incorporated in the arms of an a.c. Wheatstone bridge, one being located inside the calorimeter and the other outside. The output voltage from the bridge decreases as the balance point is approached and it undergoes a phase reversal when the two resistances are equal. After amplification this out of balance bridge potential is passed to V3 a tetrode which, being supplied with an alternating anode voltage, is phase-sensitive and fires when the grid voltage is in phase with the anode voltage. The output from this valve operates a relay which is coupled to a blackened 25w light bulb which serves as a heater. Under steady operating conditions and for a slow reaction the rapid switching of this heating device is sufficient to maintain the outer bath at a constant temperature differential with respect to inside the calorimeter. The tetrode V4 operates only when the out of
Figure 5.1

Circuit Diagram of the Adiabatic Control Unit
| R_1 | 220 ohm | C_1 | 0.1 μF |
| R_2 | 90 ohm  | C_2 | 0.3 μF |
| R_3 | 330 ohm | C_3 | 10 μF  |
| R_4 | 100 ohm | C_4 | 0.02 μF |
| R_5 | 100 ohm | C_5 | 50 μF  |
| R_6 | 10K ohm | C_6 | 4nF    |
| R_7 | 1M ohm  | C_7 | 4nF    |
| R_8 | 220K ohm| C_8 | 20 μF  |
| R_9 | 22K ohm | C_9 | 16 μF  |
| R_{11} | 100 ohm | C_{10} | 90 μF |
| R_{12} | 10M ohm | C_{11} | E_{12} = 8 μF |
| R_{13} | 1M ohm  | C_{12} | 50 μF  |
| R_{14} | 270 ohm | C_{13} | 50 μF  |
| R_{15} | 4.7% ohm| A Relay, Post-office 5000 type to boost heater |
| R_{16} | 3.7% ohm| B Relay, Post-office 5000 type to monitor heater |
| R_{17} | 1M ohm  | V_1 | EF86   |
| R_{18} | 1M ohm  | V_2 | EF91   |
| R_{19} | 47K ohm | V_3 | 2D21   |
| R_{20} | 4.7K ohm, 2 watt | V_4 | 2D21   |
| R_{21} | 5K ohm, 5 watt | R_1 = R_2 = 0.1μF |
| R_{22} | 5K ohm, 5 watt | T_1 = T_2 = F23 Thermistors |
balance potential is rather larger, and triggers a 250W heater wired through a Variac transformer to allow more delicate control.

A change in the rate of heating inside the calorimeter requires, correspondingly, a change in the rate of heating of the adiabatic shield to maintain the same temperature differential between inside and out. But an increased rate of heating of the adiabatic control unit in turn requires an increased temperature differential (there being no feedback circuit) thus, when there is an alteration in the rate of temperature change inside the calorimeter the adiabatic unit cannot maintain a constant temperature differential. In practice this is corrected for by adjusting manually a control on the adiabatic unit, which corresponds to R, thereby altering the temperature difference needed for the adiabatic unit to operate the heaters. Such adjustments are normally required only a few times during the entire operation.

The Calorimeter

The calorimeter consists of a pyrex Dewar vessel internal diameter 2 inches and depth 6½ inches with a rounded bottom. The capacity of this vessel is about 250 ml and under working conditions contains 200 ml of liquid. To restrict heat conduction through the walls, the 3/8 inch wide insulating gap is evacuated to \(10^{-6}\) cm Hg. The lid fits the calorimeter via a flanged ground glass collar, the joint being lightly greased during operation to provide a gastight seal, and it is through the lid that the inserts project via standard 8/4 and 8/0 ground glass sockets, the ground joints sealing on P.T.F.E. sleeves which prevent movement of the inserts when in operation, but allow easy removal.

The Stirrer

This takes the form of a small double bladed propeller attached to the end of a precision bore glass rod which enters the calorimeter through a
precision bore tube mounted in the central 1/4 inlet of the lid (see Figure 5.2). Lubrication of the precision rod/tube with a light oil is sufficient to maintain the stirrer functioning perfectly. In practice it is found that the positioning of the stirrer blades inside the colorimeter is very important, operating best about 1/2 inch from the bottom, the total depth of colorimeter fluid being 4 inches. The pitch of the blades is downwards, but perhaps surprisingly, this was found to have little effect on the direction of flow of the liquid, the major factor here being the outward flow from the stirrer blades, due to centrifugal force, which in turn sets up a flow down the stirrer shaft. Stirrer blades which were too large caused a deep vortex around the stirrer shaft which in extreme cases was found to rupture the liquid surface – an effect which just be prevented as it causes large and irregular heat of stirring effects.

To maintain a constant stirring speed the stirrer is driven by a Favalux 1/30 H.P. motor operating at 1370 r.p.m., transmission being via a flexible drive cable.

**Ampoules**

Original designs of ampoule were based on a simple thin glass bulb arrangement which could be shattered by lowering into the stirrer blades. With this type of design, however, it was found that frequently a steady after-period was impossible to attain. Possible reasons for this appeared to be, a) interaction of broken ampoule glass with the temperature sensing thermistor b) interaction of broken ampoule glass with the stirrer blades. Shielding the thermistor tip with glass wool did nothing to alleviate unsteady after-period readings so it seemed that the design of the ampoule was at fault.

To be satisfactory, an ampoule must therefore liberate, at the most, very small amounts of broken glass, it must rupture readily and not cause too great a change in the geometry of the system after rupture. A design which was found to work perfectly and have the added advantage of not requiring
Figure 5.2

Calorimeter and Lid

Heater

Stirrer

Thermistor

Ampoule
any change in design of the calorimeter is shown in Figure 5.2. It takes
the form of a thin walled glass tube up to 2 inches long and about 3/8 inch
in diameter fitted with a standard B7 socket. Two extremely thin glass
bubbles preferably not more than 3/16 inch in diameter are blown, one at the
bottom and the other in the side near the top. Such an ampule will hold
about 1 to 1.5 ml of sample and fragmentation of the bubbles in the stirrer
blades and against the side of the calorimeter produces no detectable heat
of breaking. The two openings in the ampule allow a flow of calorimeter
fluid through, thus allowing complete dissolution of the sample. It was
found that such ampules could be blown reasonably readily after a little
practice and a good empirical rule to gauge the thinness of the bubbles is to
tap them very lightly with a piece of glass rod or tube, adequate thinness
being signified by absolutely no detectable sound from the tapping. Generally
a slight elasticity of the bubble is experienced.

The ampules are sealed by means of a B7 ground glass cone onto which is
mounted a B5 socket, this socket fitting onto a corresponding cone on the
ampule holder. A small rubber band, or in the case of an organic calorimeter
fluid, a loop of nichrome wire was found adequate to maintain the ampule in
position on the ampule holder.

The ampule holder is made of precision bore glass rod which seats in
precision tube mounted in a B10 cone in the calorimeter lid. During operation
this is clamped from outside the calorimeter lid. During operation this is
clamped from outside the calorimeter to prevent any movement, but will allow
vertical movement required when the ampule is lowered into the stirrer
blades and a bend in the rod allows lateral movement (by rotation of the
shaft) required to break the side bubble against the walls of the calorimeter
(see Figure 5.2).
Temperature Detection

Three thermistors are used inside the calorimeter for temperature detection, one coupled to the adiabatic control unit, another in conjunction with an external matched thermistor allowing the temperature difference between inside and outside the calorimeter to be displayed on a galvanometer, and the third used to measure the temperature changes inside the calorimeter.

The thermistor bridge circuit used to give readings of the temperature difference inside and outside the calorimeter is shown in Figure 5.5. A temperature difference of 0.001°C is readily observable as a deflection in the light spot of the Scalemp 1400 ohm Galvanometer (W.G. Pye & Co. Ltd.) and in a steady state the adiabatic system holds this temperature difference to within a few thousandths of a degree. During a fast reaction this temperature difference may increase briefly by two orders of magnitude, but control can quickly be restored in a few seconds. Such deviations from a perfect adiabatic system have negligible effect if they are corrected for within about ten seconds. For slow reactions, for which the system is much better suited, the temperature difference between inside and out is maintained automatically quite accurately. During operation it is found that no correction is necessary for any loss of adiabatic control due to a rapid reaction.

The thermistor used for measuring the temperature of the calorimeter is an F53 (Standard Telephone & Cable Ltd.). It is incorporated in a simple optimised Wheatstone bridge circuit (see Figure 5.4) powered by a 2V accumulator. The galvanometer is a 1400 ohm Scalemp Galvanometer (W.G. Pye & Co. Ltd.).

At 25°C the thermistor has a resistance temperature coefficient of about 130 ohms per degree. With a full-scale deflection of about 20 ohms on a 14 cm scale, 0.001°C corresponds to 0.18 ohms which is about 0.16 cm deflection. Thus a one thousandth of a degree temperature change is easily observable.
Figure 5.3

Temperature Differential Thermistor Bridge

Figure 5.4

Temperature Detection Thermistor Bridge
As the smallest resistance unit on the Decade (Hairhead & Co. Ltd.) resistance box is one tenth of an ohm, readings are taken to the nearest one tenth ohm.

The sensitivity of a Wheatstone bridge circuit (see Figure 5.4) in terms of the deflection of the galvanometer is given by

\[
\text{Sensitivity } S = \frac{G E}{R_1 R_2 + R_2 R_3 + R_3 R_4 + R_4 R_1} \left( \frac{R_1}{R_2} + 2 \frac{R_2}{R_1} \right)
\]

where \( G \) is the sensitivity of the galvanometer measured in terms of deflection per current

- \( R_1, R_2, R_3, R_4 \) are resistances of the bridge arms
- \( R_g \) is the galvanometer resistance
- \( E \) is the potential applied across the bridge

Now for \( ig = 0 \)

\[
\frac{R_1}{R_2} = \frac{R_3}{R_4}
\]

so if \( R_1 = R_3 \) then \( R_2 = R_4 \)

and for maximum sensitivity \( R_2 = R_1 \sqrt{\frac{R_g}{R_1 + R_2}} \)

See, for instance, Page and Adams (1931).

As the temperature change inside the calorimeter is measured directly in terms of resistance change, it is far more convenient to consider at all times the change of temperature as a change of resistance.

The variation in thermistor resistance as a function of temperature may be expressed as \( R = R_0 e^{AT} \), where \( R \) is the resistance in ohms, \( T \) is the absolute temperature and \( A \) and \( B \) are constants which depend on the particular thermistor. Typical values of the constants are \( A = 0.05 \) ohms, \( B = 3 \times 10^3 \).

If the above expression for resistance is expressed as a power series expansion about \( T = 300^\circ \mathrm{C} \) in terms of \( \theta^\circ \mathrm{C} \) the difference in temperature from \( T \) (see Appendix Two).

Then \( R = R_0 \left( 1 + 0.0333 \theta + 0.007 \theta^2 + 0.0001 \theta^3 \right) \)

where \( R_0 \) is the thermistor resistance at \( 300^\circ \mathrm{C} \).
Thus to a fairly good approximation for any $0 < 1^\circ C$, the change in resistance is a linear function of the change in temperature.

This is a justification of a linear graphical extrapolation of the resistance time graph, which must be performed for the afterperiod readings, instead of the more theoretically correct temperature time extrapolation.

To determine the amount of heat liberated or absorbed inside the calorimeter during a reaction essentially one compares the resistance change during reaction with a similar resistance change caused by a known amount of heat delivered by the electrical heater.

As shown in Appendix Three

\[
\frac{\text{Heat of Reaction}}{\text{Heat of Calibration}} = \frac{\log \frac{R_2}{R_1}}{\log \frac{R_3}{R_4}}
\]

where $R_1 > R_2$ and $R_3 > R_4$

For an exothermic reaction $R_1$ is initial resistance, $R_2$ is final resistance
For an endothermic reaction $R_2$ is initial resistance, $R_1$ is final resistance
For calibration $R_3$ is initial resistance, $R_4$ is final resistance.

This expression is accurate to better than $99.9\%$ during normal operating conditions.

**Calibration Heater**

The function of the heater is to convert a precisely known quantity of electrical work into heat, inside the calorimeter. To prevent chemical reaction, heaters are typically encased in a thin glass sheath, but because glass is not a good thermal conductor a relatively high temperature is built up inside the heater which promotes thermal losses up the electrical conduction wires. The design of a heater which was found to work satisfactorily is shown in Figure 5.2, its essential points are as follows.
The heater element is made from 42 S.W.G. constantan wire of length about 12 inches giving a total resistance of approximately 13 ohms. This is wound on a small brass cross-piece and soldered to relatively thick copper leads. The heater element is of such dimensions as to provide a good fit in the thin glass sheath, and in position is covered to a height of 1\(\frac{1}{2}\) inches with transformer oil to provide good thermal contact. To promote heat flow outwards from the copper leads rather than upwards, the wires are bent so as to lie along the glass sheath. With such a system it was observed that a slow, long-term ageing took place, causing a steady change in resistance of up to almost a tenth of an ohm over a period of several months. So that this should not go undetected, thin leads were soldered across the heater element for the purpose of measuring the potential drop across the heater during every calibration. As the potential difference across the heater is approximately 4.6 volts in the circuit given it is not possible to read this directly by means of the potentiometer (maximum potential ca. 1.3 volts), so the circuit shown in Figure 5.3 was designed. Using short, thick connecting wires all wire resistances are considered zero unless designated \(R_e\).

From the Figure it can be seen that

\[ I_2 + I_3 = \frac{V_3}{R_s} \]

and

\[ I_3 = \frac{V_1}{10} \]

so

\[ I_2 = \frac{V_3}{R_s} - \frac{V_1}{10} \]

\[ P_1, P_1^{I1}, P_2^{I}, P_2^{I1} \] are values of potential at the points shown, with \(P_1\) and \(P_2\) the respective potential differences.

Because of \(R_{II} \), \(P_1^{II}\) is more positive than \(P_1^{I}\)

so

\[ P_1^{II} = P_1^{I} + P_1 \]
Figure 5.5

Heater Circuit

- $R_{ll}$ and $R_{22}$ leads resistances
- $R_H$ Heater Resistance  
  (ca 18 ohms)
- $R_S$ Standard resistance  
  0.9932 ohms
- $R_1$ 100 ohms
- $R_2$ 10 ohms
- $T$ Timer
Because \( \frac{R_{21}}{R_{21} + R_{11}} < \frac{10}{100} \), \( P_{211} \) is more positive than \( P_{21} \)

so \( P_{211} = P_{21} + P_2 \) \hspace{1cm} (2)

Now \( P_{21} = P_2 + 100 i_2 \)

\( a = P_1 + 107_1 \)

Subst in eq (2)

\( P_{211} = P_1 + P_2 + 107_1 \) \hspace{1cm} (3)

so the potential difference across \( R_1 \), i.e., \( P_2 = P_{21} \)

is given by

\[
P \cdot R_1 = 107_1 + P_2 = P_1
\]

Thus, potential difference across heater = \( 107_1 + P_2 = P_1 = V \)

Current through heater \( = \frac{V}{R_1} = \frac{V_1}{10} \) = i

Power by heater = VI and its resistance \( \frac{V}{I} \) should be constant at all times.

When set up as described, the calorimeter is then clamped in position inside a clear cylindrical Dewar vessel which contains approximately 3.5 litres of water when filled. The outer thermistor arms of the adiabatic bridge circuit and of the temperature difference circuit are held in position and the 25w and 250w heaters from the adiabatic unit mounted close to the stirrer. It was found expedient to incorporate a small cooling coil, operating from a constant head device to ensure a slow but steady flow of cooling water.

It is convenient to tabulate at this stage results obtained for the heat of solution of TRAP in 0.1M HCL.
Table 5.1

<table>
<thead>
<tr>
<th>wt (gm)</th>
<th>Kj mole⁻¹</th>
<th>kcal mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8908</td>
<td>29.83</td>
<td>7.13</td>
</tr>
<tr>
<td>0.8016</td>
<td>29.71</td>
<td>7.10</td>
</tr>
<tr>
<td>0.9130</td>
<td>29.75</td>
<td>7.11</td>
</tr>
<tr>
<td>1.0249</td>
<td>29.66</td>
<td>7.09</td>
</tr>
<tr>
<td>0.9647</td>
<td>29.83</td>
<td>7.13</td>
</tr>
<tr>
<td>1.1754</td>
<td>29.75</td>
<td>7.11</td>
</tr>
<tr>
<td>0.1368</td>
<td>29.75</td>
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</tr>
<tr>
<td>1.0175</td>
<td>29.66</td>
<td>7.09</td>
</tr>
<tr>
<td>0.8134</td>
<td>29.83</td>
<td>7.13</td>
</tr>
<tr>
<td>0.6092</td>
<td>29.71</td>
<td>7.10</td>
</tr>
</tbody>
</table>

Mean 29.75 ± 0.02 7.11 ± 0.005

Heat of solution of THAM in 0.1M HCl at 25°C.

M[H₂O:THAM] = 11.55 to 22.27
Chapter Five References


Electrolytes may be considered to be exceptionally high conductivity solutions. In the immediate vicinity of the conducting electrodes, the electrolyte is necessarily a highly concentrated solution, with concentrated electrolytes at the electrodes. In this section we shall consider the electrolyte behavior at the electrodes and the interface between the electrolyte and the electrode. This is done in order to bring out the reactions taking place in the electrolyte. Certain precautions are taken in order to obtain results that are independent of the conditions prevailing in the electrolyte. Although this section is of importance for electrolytic processes, the solution to determining the conductance of water depends on the conditions prevailing in the electrolyte. However, this section is of importance for water electrolysis, as a general rule, and for other electrolytic processes. Some of the electrolyte behavior at the electrode and interface are considered in this section.
CHAPTER SIX

Slow Reactions

The purpose of this part is to consider in detail some slow reactions from the possibility of their being used as standard reactions in adiabatic solution calorimetry.

1) Reaction Between a Metal and a Dilute Acid

Many metals may be obtained in an extremely high state of purity; in this case magnesium crystals (Holwood Chemicals Ltd., Stanwell Moor, Staines, Middx.) with a purity of 99.99% were reacted with 0.1M HCl. One disadvantage of this reaction is that the evolved hydrogen forces gas saturated with water vapour from the calorimeter. This in turn requires a heat correction due to the corresponding evaporation of water. Certain previous workers had estimated for this effect by collecting the evolved gas, drying it, and so determining the amount of water evaporated (see for example Johnson et al., 1961). Although this sort of procedure was tried several times, no reproducible results could be obtained. A more convenient method of estimating the required heat effect is to assume that the evolved gas becomes saturated with the calorimeter fluid vapour - in this case water vapour, hydrogen chloride gas exerting a negligible vapour pressure under these conditions (Shomate and Huffman, 1943) - and so calculate the heat effect as follows (Maso, 1966):

\[ V, P, H_2O, 23^\circ C = 24\text{mm} Hg, \Delta H_{vap} H_2O, 25^\circ C = 43.9\text{kJ mole}^{-1}(10.5\text{kcal mole}^{-1})\]

So heat effect = \[\frac{2\times43.9}{750} = 1.19\text{kJ mole}^{-1}(0.33\text{kcal mole}^{-1})\]

Experimental values of the required standard heats of formation for the reaction

\[ \text{H}_2(\text{g}) + 2\text{HCl}(0.1\text{m}) \rightarrow \text{H}_2\text{Cl}_2(\text{aq}) + \text{H}_2(\text{g} \text{sat with H}_2\text{O}) \Delta \text{H}^{\circ} \text{obs} \]

are available in the literature (Rossoni et al., 1952), so the expected heat of reaction, \( \Delta \text{H}^{\circ} \text{obs} \), may be readily calculated. In the first instance determinations of \( \Delta \text{H}^{\circ} \text{obs} \) gave persistently high values until it was realised
that the magnesium fragments were interacting with the stirrer blades giving an anomalously high heat of stirring during the reaction period.

**Correction of this Heat of Stirring Effect**

As a first approximation it was assumed that the heat evolved due to interactions between the magnesium particles and the stirrer blades was proportional to the mass of magnesium present. This follows from the assumption that the particles are hit by the stirrer with the same frequency irrespective of their size, the transfer of energy then being proportional to their mass. A knowledge of the rate of dissolution of the magnesium particles is then required so that their mass can be estimated at all times.

Referring to Figure 6.1, if the final heat of stirring \( \frac{dH}{dt} = H_f \) i.e. when no magnesium particles are present and the heat of stirring due only to the particles be \( H \) and this takes the value \( H_0 \) when the particles are in their original form, i.e. at the start of the reaction, then it is shown (see Appendix Four) that if the rate of dissolution of magnesium is proportional to its surface area, i.e. first order with respect to the surface area, then

\[
\frac{T_f - T_0}{T_f - T_i} = H_0 + \% \Delta H
\]

where \( T_i \) and \( T_f \) are the initial and final temperatures at the start and finish of the reaction, and \( T_0 \) and \( T_1 \) are the corresponding times.

As a justification of the above first order rate assumption then it is also shown that \( T \propto (t_f - t)^3 \). Thus a plot of \( H_0(t_f - t)^3 \) should also be nearly linear (the error involved by considering resistance \( R \) instead of temperature \( T \) amounting to about 2% over a 1°C temperature change). Such a plot is shown in Figure 6.2.

Thus if the time of reaction is known \( (t_f - t_i) \) and \( H_0 \) and \( \% \Delta H \) are known then the heat of stirring correction may readily be calculated. The first two of these observations are straightforward, but to estimate \( H_0 \) the
Figure 6.1

Heat of stirring with dissolving particles
(zero heat of reaction)
Figure 6.2

Plot of resistance change \( x (\text{time})^3 \)
following procedure was reported to.

A weighed amount of magnesium crystals were liberated from an ampoule into the calorimeter full of water; this gives heat of stirring \( H' \). Next sufficient concentrated hydrochloric acid was added to dissolve the magnesium and then the heat of stirring \( H_1 \) was determined. The difference \( (H_1 + H_0) - H_0 \) is the heat of stirring due to magnesium particles alone. Eight such determinations as shown in Table 6.1 were carried out.

<table>
<thead>
<tr>
<th>Number</th>
<th>Rate Stirring Mg (ohms min(^{-1}))</th>
<th>Rate Magnesium (g)</th>
<th>Rate of Stirring (ohms min(^{-1}) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0859</td>
<td>0.0134</td>
<td>4.47</td>
</tr>
<tr>
<td>2</td>
<td>0.0242</td>
<td>0.0135</td>
<td>4.84</td>
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<td>3</td>
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<td>0.0233</td>
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</tr>
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<td>4</td>
<td>0.0539</td>
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</tr>
<tr>
<td>5</td>
<td>0.0617</td>
<td>0.0126</td>
<td>4.89</td>
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<td>6</td>
<td>0.0683</td>
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<tr>
<td>7</td>
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<tr>
<td>8</td>
<td>0.0323</td>
<td>0.0352</td>
<td>2.34</td>
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</table>

Ignoring the two lowest values Nos. 3 and 7, these results give a mean value of \( 4.7 \pm 0.9 \text{ ohms min}^{-1} \text{ g}^{-1} \) where the range is taken as twice the standard deviation of the mean. Because, during reaction, the liberated hydrogen causes the magnesium particles to float rather higher in the calorimeter than under the conditions described above with deionised water present, the particles tend to interact with the stirrer blades to a lesser extent. This, rather arbitrarily, it was decided to reduce this stirring correction by one half.

The actual stirring correction needed, therefore, is equal to \( \frac{4.7}{2} \times 8 \times t \times m \) where \( t \) is the time of reaction (min) and \( m \) is the original mass of magnesium (g).
Table 6.2 gives the results of ten heats of solution of magnesium in 0.1M HCl at 25° C

\[
\text{Mg}(s) + 2\text{HCl}(0.1\text{Maq}) \rightarrow \text{H}_2(g) + \text{MgCl}_2(aq) \quad \Delta H \text{ reaction}
\]

<table>
<thead>
<tr>
<th>Number</th>
<th>(\Delta H \text{ obs} ) (kJ mole(^{-1}))</th>
<th>Stirring correction (kJ mole(^{-1}))</th>
<th>(\Delta H \text{ reaction} ) (kJ mole(^{-1}))</th>
<th>Mg Magnesium (g)</th>
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<tr>
<td>7</td>
<td>-463.19</td>
<td>5.96</td>
<td>-453.62</td>
<td>0.01078</td>
</tr>
<tr>
<td>8</td>
<td>-453.09</td>
<td>4.94</td>
<td>-449.14</td>
<td>0.01181</td>
</tr>
<tr>
<td>9</td>
<td>461.90</td>
<td>5.03</td>
<td>-457.86</td>
<td>0.01312</td>
</tr>
<tr>
<td>10</td>
<td>-473.44</td>
<td>6.09</td>
<td>-460.74</td>
<td>0.01492</td>
</tr>
</tbody>
</table>

\(\Delta H \text{ reaction} = \Delta H \text{ obs} + \text{stirring correction} -1.39 \text{ kJ mole}^{-1}\)

These reactions took from 30 to 120 minutes each. The two anomalously low values Nos. 5 and 8 are probably due to an incorrect assessment of the heat of stirring correction and are ignored in the mean figure which is 

\(-463.8 \pm 1.8 \text{ kJ mole}^{-1} (-110.59 \pm 4.55 \text{ kcal mole}^{-1})\). Over the same range of concentrations the literature value (Masini et al., 1952) is 

\(-467.71 \pm 0.21 \text{ kJ mole}^{-1} (-110.59 \text{ kcal mole}^{-1})\).

2) Hydrolysis of Acetic Anhydride

in a large excess of water acetic acid hydrolyses according to first order kinetics with a half life of 4.44 min (see later). Previous estimates of the heat of this reaction

\[
(\text{CH}_3\text{CO}_2\text{O})(\text{L}) + \text{H}_2\text{O}(\text{L}) \rightarrow 2\text{CH}_3\text{COOH}(\text{L}) \quad \Delta H^0
\]
have been made by considering the reaction of acetic anhydride with sodium hydroxide solution, which is quite rapid, together with the relevant ancillary data (Cook et al., 1942; Wadee, 1962).

Purification of the acetic anhydride was carried out by fractional distillation at atmospheric pressure, but considerable difficulty was experienced in attempts to determine the purity of the sample by G.L.C. due, presumably, to decomposition of the anhydride at the heated metal inlet. Potentiometric titration of the hydrolysed acetic anhydride was finally resorted to and the small amount of impurity observed attributed to the presence of acetic acid.

The sample analysed according to a mixture (CH₃COO)₂O + (0.0133 ± 0.0072) CH₃COOH and from this true values of amounts of acetic anhydride present in the weighed samples were calculated. These values, together with ΔHhydrolysis are given in Table 6.3 for the reaction

\[(\text{CH}_3\text{COO})_2\text{O}(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightarrow 2\text{CH}_3\text{COOH}(\text{aq})\]

<table>
<thead>
<tr>
<th>Number</th>
<th>ΔHhydrolysis (kJ mole⁻¹)</th>
<th>Amount Acetic Anhydride (moles)</th>
<th>Moles water</th>
<th>Moles acetic acid</th>
<th>Half Life (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>61.410</td>
<td>4.270 x 10⁻³</td>
<td>1.3 x 10⁻³</td>
<td>4.39</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>61.470</td>
<td>4.831 x 10⁻³</td>
<td>1.2 x 10⁻³</td>
<td>4.35</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>60.993</td>
<td>4.732 x 10⁻³</td>
<td>1.2 x 10⁻³</td>
<td>4.33</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>61.292</td>
<td>4.999 x 10⁻³</td>
<td>1.1 x 10⁻³</td>
<td>4.32</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>60.964</td>
<td>4.561 x 10⁻³</td>
<td>1.2 x 10⁻³</td>
<td>4.64</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>60.887</td>
<td>4.304 x 10⁻³</td>
<td>1.3 x 10⁻³</td>
<td>4.65</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>60.989</td>
<td>5.373 x 10⁻³</td>
<td>1.0 x 10⁻³</td>
<td>4.38</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>61.15 ± 0.32</td>
<td></td>
<td></td>
<td>4.44 ± 0.05</td>
<td></td>
</tr>
</tbody>
</table>

The error in ΔHhydrolysis includes the analysis uncertainty.

Using ΔHkel CH₃COOH in water -1.234 kJ mole⁻¹ (~0.295 kcal mole⁻¹) at these concentrations (Wagman, et al., 1965) ΔHhydrolysis for the reaction

\[(\text{CH}_3\text{COO})_2\text{O}(\text{L}) + \text{H}_2\text{O}(\text{L}) \rightarrow 2\text{CH}_3\text{COOH}(\text{L})\]

is obtained. This value, together
with the literature values for the same reaction are given in Table 6.4.

Table 6.4

<table>
<thead>
<tr>
<th>$\Delta H^\circ$ hydrolysis 25°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>kj mole$^{-1}$</td>
<td>kcal mole$^{-1}$</td>
</tr>
<tr>
<td>-58.68±0.32</td>
<td>-14.02±0.08</td>
</tr>
<tr>
<td>-58.26</td>
<td>-13.92</td>
</tr>
<tr>
<td>-58.38±0.38</td>
<td>-14.00±0.09</td>
</tr>
</tbody>
</table>

The value given in the Table for Conn et. al. has been corrected by Sadsö from 30.46°C to 25°C.

The hydrolysis of acetic anhydride has been studied quite extensively and the first order rate constant is known accurately, so it is interesting to see whether the value derived from this calorimetric work is comparable.

Besides the heat of hydrolysis there are two other major heating effects, one due to the heat of solution of acetic anhydride in water before it is hydrolysed, and the other due to the difference in heat of solution of acetic anhydride and acetic acid. The former is unimportant from the point of view of following the kinetics of the reaction as it takes place practically instantaneously in comparison to the hydrolysis reaction. The latter will vary slightly with changes in concentration of the aqueous solution, but if these small changes are considered negligible, then this heat effect will simply modify the observed heat from the heat of hydrolysis by a constant (small) amount. That is, the observed heat liberated will still be a linear measure of the extent of reaction.

Let the concentration of acetic anhydride at any time be $c$, then the rate of reaction $\frac{dc}{dt}$ will be proportional to the rate of heat evolved which is in turn proportional to the rate of change of temperature $\frac{dT}{dt}$ (assuming constant specific heats over the entire reaction period).
For first order reaction

\[ \frac{dc}{dt} = -Kc \]  

(1)

Now \[ \frac{dc}{dt} = -K \frac{dT}{dt} \]

(2)

\[ \int dc = -K \int T + \text{const} \]

\[ c = -K T + \text{const} \]

when \( c = 0 \) \( T = T_F \)

so \( c = K(T_F - T) \)  

(3)

Subst in (1) for \( \frac{dc}{dt} \) from (2) and for \( c \) from (3)

\[ -K \frac{dT}{dt} = -K(T_F - T) \]

\[ \frac{dT}{dt} = K(T_F - T) \]

\[ T_F = K^{-1} \frac{dT}{dt} + T \]

Integration of this equation gives

\[ KT = -\ln(T_F - T) \]

So a plot of \( t \) vs \( \ln(T_F - T) \) should be linear.

Now to a first approximation \( \Delta T \propto \Delta R \) for a thermistor so a plot of \( \log (R - R_F) \) vs \( t \) should be linear. No account has been taken in this argument of the increase in reaction rate with temperature, but the observed linearity of the graphs of \( \log (R - R_F) \) vs \( t \) are a justification of this approximation. The half lives of each hydrolysis reaction are given in Table 3.5 giving a mean value of 4.44 ± 0.05 mins. Now the rate constant \( K \) of a first order reaction is given by \( K = \frac{1}{t_{1/2}} \). The value so obtained is given in Table 6.5.
Table 6.5

<table>
<thead>
<tr>
<th>K (25^\circ\text{C}) (sec (-1))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.60 \pm 0.03 \times 10^{-3})</td>
<td>This work</td>
</tr>
<tr>
<td>(2.65 \times 10^{-3})</td>
<td>Gold, 1948</td>
</tr>
<tr>
<td>(2.67 \times 10^{-3}(25^\circ\text{C}))</td>
<td>Bunton et al., 1963</td>
</tr>
<tr>
<td>(2.61 \pm 0.02 \times 10^{-3})</td>
<td>Battler and Gold, 1961</td>
</tr>
<tr>
<td>(2.51 \pm 0.03 \times 10^{-3})</td>
<td>Becker &amp; Naxicke, 1967</td>
</tr>
</tbody>
</table>

The value of \(2.60 \pm 0.3 \times 10^{-3} \text{ sec}^{-1}\) must be regarded as an average value over the range of temperatures 25.00 to 25.25\(^\circ\text{C}\), but using Gold's (1948) value for the activation energy between 15 and 25\(^\circ\text{C}\), i.e. 10.51 kcal mole\(^{-1}\), then a temperature rise of 0.25\(^\circ\text{C}\) at 300K corresponds to an increase in the first order rate constant of 0.04 sec\(^{-1}\), which is of the order of the experimental error.

One further consequence of this work is that back extrapolation of the \(\log (R = R_p)\) vs t graphs to \(t = 0\) allows an estimation of the heat of solution of acetic anhydride in water before any hydrolysis has taken place. This procedure gives the following result: \(\Delta H_{\text{mol}} 298K\) acetic anhydride in water (H\(_2\)C(\text{AcO})\(_2\)) \(= 2.0\) to \(2.6 \times 10^{-3}\): \(\sim -2.74 \pm 0.35\) kJ mol\(^{-1}\) (\(-0.655 \pm 0.05)\) kcal mol\(^{-1}\)). This compares with the value for \(\Delta H_{\text{solution}}\) of acetic acid in water at twice the concentration of \(-1.234\) kJ mol\(^{-1}\) (\(-0.295\) kcal mol\(^{-1}\)).

3) Oxidation of Iodide by Peroxydisulphate

The per oxydisulphate ion \(S_2O_8^{2-}\) is one of the strongest oxidizing agents known. D.A. House has reviewed the chemistry of this substance in 1962.

Potassium per oxydisulphate is an easily handled crystalline solid which may be purified readily by recrystallization from water. Its reaction with iodide is quantitative according to \(S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2\) provided sufficient iodide is present (Kolthoff and Carr, 1953) the rate of reaction
depending on the ionic strength of the solution and the concentration of iodide.

Oxidation of potassium iodide by potassium peroxodisulphate in solution may be represented as

\[
(1) \quad \text{K}_2\text{S}_2\text{O}_8(\text{aq}) + 2\text{KI}(\text{aq}) \rightarrow 2\text{K}_2\text{SO}_4(\text{aq}) + \text{I}_2(\text{g}) \quad \text{H}_1
\]

\[
(2) \quad \text{I}_2(\text{g}) + \text{KI}(\text{aq}) \rightarrow \text{KI}_3(\text{aq}) \quad \text{H}_2
\]

Step (2) being quantitative within the order of 1% for the least concentrated potassium iodide solution used, i.e. 0.125M, as can be seen from a consideration of the equilibrium

\[
\text{I}^- + \text{I}_2 \rightleftharpoons \text{I}_3^-
\]

\[
K = \frac{[\text{I}_3^-]}{[\text{I}^-][\text{I}_2]} = \frac{\text{ff}_{\text{I}_3^-}}{\text{ff}_{\text{I}^-}}
\]

where \( K \) (25°C) = 768 ± 2 (Davies and Gwynne, 1952).

In practice there is always an excess of potassium iodide, but heat of solution data have been assumed equal to those in pure water.

Table 6.6 gives heat of reaction data for five such reactions at 25°C using 200 ml of KI solution.

Table 6.6

<table>
<thead>
<tr>
<th>No.</th>
<th>Heat of Reaction, ( \Delta H_{1+2} )</th>
<th>Moles ( \text{K}_2\text{S}_2\text{O}_8 )</th>
<th>Molarity of KI sol</th>
<th>Time of Reaction(mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-293.75 kcal mol(^{-1})</td>
<td>-70.207 kcal mol(^{-1})</td>
<td>7.0765 \times 10^{-3}</td>
<td>0.125</td>
</tr>
<tr>
<td>2</td>
<td>-293.69 kcal mol(^{-1})</td>
<td>-70.194 kcal mol(^{-1})</td>
<td>1.0476 \times 10^{-3}</td>
<td>0.29</td>
</tr>
<tr>
<td>3</td>
<td>-292.98 kcal mol(^{-1})</td>
<td>-70.025 kcal mol(^{-1})</td>
<td>6.4032 \times 10^{-4}</td>
<td>0.24</td>
</tr>
<tr>
<td>4</td>
<td>-293.65 kcal mol(^{-1})</td>
<td>-70.183 kcal mol(^{-1})</td>
<td>1.1056 \times 10^{-3}</td>
<td>0.36</td>
</tr>
<tr>
<td>5</td>
<td>-294.80 kcal mol(^{-1})</td>
<td>-70.458 kcal mol(^{-1})</td>
<td>1.0905 \times 10^{-3}</td>
<td>0.14</td>
</tr>
<tr>
<td>Mean</td>
<td>-293.77 kcal mol(^{-1})</td>
<td>-70.21 kcal mol(^{-1})</td>
<td>0.125</td>
<td>200</td>
</tr>
</tbody>
</table>

Assuming that within the concentration ranges used the heat of this reaction is constant to within the given error limits then
\[ \Delta H^\circ \left[ K_2S_2O_8, \text{cryst} \right]_{298 K} \] may be calculated using the following ancillary data.

\[ \Delta H^\circ \left[ H_1 \left( aq \right) \right] \left[ KI \right]_{1:1:1 = 1:50} = -307.105 \pm 0.125 \text{ kJ mole}^{-1} \]
\[ (-73.80 \pm 0.03 \text{ kcal mole}^{-1}) \quad \text{(Rossini et al., 1952)} \]

\[ \Delta H^\circ \left[ K_2SO_4(aq) \right] \left[ K_2SO_4 : H_2O \left( 1:1 \right) = 1:2000 \text{ to } 1:4000 \right] = -1409.23 \pm 0.04 \text{ kJ mole}^{-1} \]
\[ (-336.82 \pm 0.03 \text{ kcal mole}^{-1}) \quad \text{(Rossini et al., 1952)} \]

\[ \Delta H^\circ \left[ KI : H_2O \right] = 1:1430 \text{ to } 1:430 \] = 5.606 \pm 0.296 \text{ kJ mole}^{-1} \]
\[ (1.34 \pm 0.2 \text{ kcal mole}^{-1}) \quad \text{(Ne et al., 1963)} \]

Reactions (1) and (2) give the overall reaction in the calorimeter, i.e.,

\[ K_2S_2O_8(c) + 3KI(aq) \rightarrow 2K_2SO_4(aq) + KI_3(aq) \quad \Delta H_1 + \Delta H_2 \]

Now \[ \Delta H_1 + \Delta H_2 = -299.77 \text{ kJ mole}^{-1} \quad (70.21 \text{ kcal mole}^{-1}) \]
\[ \Delta H_2 = 5.606 \text{ kJ mole}^{-1} \quad (1.34 \text{ kcal mole}^{-1}) \]

\[ * * \Delta H_1 = -299.53 \text{ kJ mole}^{-1} \quad (71.75 \text{ kcal mole}^{-1}) \]

This gives \[ \Delta H^\circ \left[ K_2S_2O_8, \text{cryst} \right]_{298 K} = -1904.92 \pm 0.96 \text{ kJ mole}^{-1} (435.29 \pm 0.25 \text{ kcal mole}^{-1}) \]

Literature values for \[ \Delta H^\circ \left[ K_2S_2O_8, \text{cryst} \right]_{298 K} \] are given in Table 6.7.

<table>
<thead>
<tr>
<th>[ \Delta H^\circ \left[ K_2S_2O_8, \text{cryst} \right]_{298 K} ]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \text{kJ mole}^{-1} ]</td>
<td>[ \text{kcal mole}^{-1} ]</td>
</tr>
<tr>
<td>-1904.92 \pm 0.96</td>
<td>-455.29 \pm 0.23</td>
</tr>
<tr>
<td>-1902.21 \pm 1.67</td>
<td>-454.64 \pm 0.4</td>
</tr>
<tr>
<td>-1911.17 \pm 2.09</td>
<td>-456.75 \pm 0.5</td>
</tr>
<tr>
<td>-1911.53</td>
<td>-458.3</td>
</tr>
</tbody>
</table>

The value from G.W. Richards' thesis has been recalculated using ancillary data consistent with that given here. D.R. Stull's value is self-consistent in that any ancillary data not given in Circular 500 (Rossini et al., 1952) have been determined by him.

The circular 500 value is from very old data by Berthelot.
Lattice Energy of Potassium Peroxydisulphate

The subject of lattice energies has been reviewed by Sherman (1932) and Waddington (1959) and more recently by Ladd and Lee (1964, 1965).

Lattice energy may be defined as the increase in internal energy at absolute zero accompanying the separation of the constituent ions of the lattice to positions where they are infinitely removed from one another. The lattice energies of peroxysulphates have not previously been evaluated, so from the thermochemical data available at present an assessment of this quantity for the potassium salt will be made.

For the sake of completeness a brief review of some of the methods of assessing lattice energies will now be given.

From a consideration of the geometry of the crystal packing, the total attractive forces of the ions in the crystal lattice can be estimated from simple electrostatic theory leading to the value \( \frac{N_A e^2 z^+ z^-}{r} \) mole\(^{-1}\) where \( N_A \) is the Avogadro number, \( e \) the charge of the electron and \( r \) is the distance between the centres of adjacent positive and negative ions. \( \pm \) and \( \mp \) are the valencies of the positive and negative ions. \( \hbar \), the Madelung constant, is a number which is dependent purely on the lattice geometry and arises from the summation of all the attractive coefficients in the crystal.

The equilibrium positions of the ions in the lattice are as a result of the attractive forces and the repulsive non-coulombic forces. Many expressions have been used to take into account the repulsive forces, the simplest being that proposed by Born and Landé amounting to \( \frac{N_A B}{n} \) where \( B \) is a constant and \( n \), which may be derived from compressibility measurements, the 'Born exponent', usually lies between 3 and 10.

At the equilibrium distance \( r_0 \) when \( \frac{dr}{d\epsilon} = 0 \)

\[ U = \frac{N_A e^2 z^+ z^-}{r^2} \left(1 - \frac{1}{n}\right) \]

an expression known as the Born-Landé equation.
As a quantum mechanical development this simple expression was modified by Born and Mayer to take account of electron cloud overlap to

\[ U = \frac{\hbar^2 \alpha^2 z^2}{2r_0} \left( 1 - \frac{\rho}{r_0} \right) \]

where \( \rho \) is a constant with the dimensions of length. For most crystals \( \rho \) may be regarded as being practically constant with a value of 0.345 \( \AA \).

More sophisticated expressions which take into account dipole-induced dipole forces and zero point energies of the lattice have been developed. These will not be considered here.

If the Born-Mayer equation is modified to give

\[ U = \left( \frac{\hbar^2}{2}\frac{\alpha^2 z^2}{r_0^3} \right) \left( 1 - \frac{\rho}{r_0} \right) \]

where \( \alpha = \frac{\hbar}{\sqrt{\nu}} \), then it was found empirically by Kapustinskii (1935) that in passing from one lattice to another the change in \( \alpha \) was proportional to the change in interionic distance \( r_0 \). By taking the Goldschmidt ionic radius referring to co-ordination number \( 6 \), giving \( (r_+ + r_-) \) for \( r_0 \) and \( \alpha = 1.745 \) for rock-salt type lattices, then the same value is obtained for the lattice energy as that obtained by using \( \nu \) derived from X-ray measurements and a calculated value of \( \hbar \) for the given lattice.

Grouping all the constants together, then

\[ U = \frac{1201.6 \nu \alpha^2 z^2}{(r_+ + r_-)} \left[ 1 - \frac{0.345}{(r_+ + r_-)} \right] \text{ kJ mole}^{-1} \]

where \( \nu \) is the number of ions in the molecule.

Usually the Kapustinskii equation gives values for the lattice energy which are low, and Yatsimirskii (1961) has recommended the inclusion of an additional term, giving

\[ U = \frac{1201.6 \nu \alpha^2 z^2}{(r_+ + r_-)} \left[ 1 - \frac{0.345}{(r_+ + r_-)} \right] + 10.46 \nu \alpha^2 \text{ kJ mole}^{-1} \]

Often values of \( r_- \) are unknown and a real difficulty is experienced here when the anion is not spherical. This may be overcome by means of a method suggested by Yatsimirskii (1947).
Consider a salt MX, then from the following cycle

\[ \begin{align*}
N(s) + X(s) & \quad \xrightarrow{\Delta H^0_{NM} + \Delta H^0_{FX}} \quad N^+(g) + X^-(g) \\
N_2(g) + 2e^- & \quad \xrightarrow{U + 2RT} \quad M(s) + X(s)
\end{align*} \]

where \( N(s) \) and \( X(s) \) are elements in their standard states

\[ U + 2RT = \Delta H^0_{NM} + \Delta H^0_{FX} = \Delta H^0_{MN} \]

then

\[ U_{(M}) + 2RT = \Delta H^0_{N_2} + \Delta H^0_{X} = \Delta H^0_{N_2M} \]

So for two salts \( NaX \) and \( H_2X \)

\[ U_{(NaX}) + 2RT = \Delta H^0_{Na^+} + \Delta H^0_{X} = \Delta H^0_{NaX} \]

and

\[ U_{(H_2X}) + 2RT = \Delta H^0_{H_2^+} + \Delta H^0_{X} = \Delta H^0_{H_2X} \]

Subtracting these

\[ U_{(NaX}) - U_{(H_2X}) = \Delta H^0_{Na^+} - \Delta H^0_{H_2^+} = \Delta H^0_{NaX} - \Delta H^0_{H_2X} \]

And also by subtracting the Kapustinski equations for the lattice energies of both salts

\[ U_{(NaX}) - U_{(H_2X}) = \Delta \left[ \frac{1}{r_{Na^+} + r_{X^-}} - \frac{1}{r_{H_2^+} + r_{X^-}} \right] \]

So by equating these two expressions for the difference in lattice energies of the two salts, and if values for

\[ \Delta H^0_{Na} = \Delta H^0_{Na^+} \]

and

\[ \Delta H^0_{H_2} = \Delta H^0_{H_2X} \]

and also \( r_{Na^+} \) and \( r_{H_2^+} \) are all known then a value for \( r_X^- \) may be calculated which when fed into the Kapustinski equation will give a value for the lattice energy of the salt.
The value for $r_\text{X}^-$ so obtained is called the thermochemical ionic radius.

Now consider how this applies to peroxysulphate salts.

In the case of $\text{Na}_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{S}_2\text{O}_8$

$\text{Na}^+ = 0.98 \text{ Å}$

$\text{K}^+ = 1.33 \text{ Å}$

$\Delta H^{0f} \text{Na}^+(g) = 610.926 \text{ kJ mole}^{-1} (146.015 \text{ kcal mole}^{-1})$

$\Delta H^{0f} \text{K}^+(g) = 514.92 \text{ kJ mole}^{-1} (123.07 \text{ kcal mole}^{-1})$

(values taken from N.B.S. Circ. 500)

A value for $\Delta H^{0f} \text{K}_2\text{S}_2\text{O}_8(c) - \Delta H^{0f} \text{Na}_2\text{S}_2\text{O}_8(c)$ is required.

Now $\Delta H^{0f} \text{K}_2\text{S}_2\text{O}_7(c) = \Delta H^{0f} \text{Na}_2\text{S}_2\text{O}_7(c) = -53.93 \text{ kJ mole}^{-1}$

$\Delta H^{0f} \text{K}_2\text{S}_2\text{O}_7(c) = \Delta H^{0f} \text{Na}_2\text{S}_2\text{O}_7(c) = -70.71 \text{ kJ mole}^{-1}$

Assuming that the same sort of differences must apply between the sodium and potassium sulphates and peroxysulphates by virtue of similar charge density and size of ions

$\Delta H^{0f} \text{K}_2\text{S}_2\text{O}_7(c) = \Delta H^{0f} \text{Na}_2\text{S}_2\text{O}_7(c) = -69 \text{ kJ mole}^{-1}$

(All values for $\Delta H^{0f}$ taken from N.B.S. Circ. 500 except for $\Delta H^{0f}[\text{Na}_2\text{S}_2\text{O}_7(c)$

which is from Shidlovskii and Valkina, 1961)

In the case of $K_2\text{S}_2\text{O}_8$ and $\text{Na}_2\text{S}_2\text{O}_8$, the expression for the thermochemical ionic radius of $S_\text{O}_3^{2-}$ simplifies to

$\frac{\Delta U}{A} K^2N^2 = N(K+P) + K^2(N+\rho)$

$+ \left[ \frac{2\Delta U}{A} NK(K+N) + N(N+2K+2\rho) + K(K+2N+2\rho) \right] s$

$+ \left[ \frac{\Delta U}{A} (K^2+4KN+N^2) - (2K+N+\rho) + (2K+N+\rho) \right] s^2$

$+ \frac{2\Delta U}{A} (K+N)s^3$

$+ \frac{\Delta U}{A} s^4 = 0$
where \[ \Delta U = \Delta U^0 \text{K}_2\text{S}_2\text{O}_8(c) - \Delta U^0 \text{Na}_2\text{S}_2\text{O}_8(c) \]

A is a composite term from the Kapustinskii equation

such that \[ \frac{\Delta U}{\Delta} = 0.074052 \text{ kJ mole}^{-1} \]
\[ = 0.545 \text{ kJ from the Born Mayer equation} \]

K = Goldschmidt ionic radius \( K^+ = 1.33 \text{Å} \)
N = Goldschmidt ionic radius \( \text{Na}^+ = 0.98 \text{Å} \)
S = thermochemical ionic radius \( \text{S}_2\text{O}_8^{2-} \)

Solution of this equation for \( s \) gives
\[ s = \text{S}_2\text{O}_8^{2-} = 2.90 \text{ Å} \]

Substitution of this value in the Kapustinskii equation with the

Yatsimirskii correction gives
\[ \Delta U = 1624 \text{ kJ mole}^{-1} \] (388 kcal mole\(^{-1}\))
\[ \Delta U = 1751 \text{ kJ mole}^{-1} \] (419 kcal mole\(^{-1}\))

Consider now the following thermochemical cycles

\[ 2 \Delta H^f \text{K}^+(aq) + \Delta H^f \text{S}_2\text{O}_8^{2-}(aq) \rightarrow 2 \text{K}^+(aq) + \text{S}_2\text{O}_8^{2-}(aq) \]

\[ \Delta H^f \text{K}_2\text{S}_2\text{O}_8(s) - \Delta H^f \text{Na}_2\text{S}_2\text{O}_8(s) \]

\[ = 0.074052 \text{ kJ mole}^{-1} \]
\[ = 0.545 \text{ kJ from the Born Mayer equation} \]

\[ K = \text{Goldschmidt ionic radius } K^+ = 1.33 \text{Å} \]
\[ N = \text{Goldschmidt ionic radius } \text{Na}^+ = 0.98 \text{Å} \]
\[ S = \text{thermochemical ionic radius } \text{S}_2\text{O}_8^{2-} \]

\[ s = \text{S}_2\text{O}_8^{2-} = 2.90 \text{ Å} \]

Substitution of this value in the Kapustinskii equation with the

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\[ \Delta U = 1624 \text{ kJ mole}^{-1} \] (388 kcal mole\(^{-1}\))
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Consider now the following thermochemical cycles

\[ 2 \Delta H^f \text{K}^+(aq) + \Delta H^f \text{S}_2\text{O}_8^{2-}(aq) \rightarrow 2 \text{K}^+(aq) + \text{S}_2\text{O}_8^{2-}(aq) \]

\[ \Delta H^f \text{K}_2\text{S}_2\text{O}_8(s) - \Delta H^f \text{Na}_2\text{S}_2\text{O}_8(s) \]

\[ = 0.074052 \text{ kJ mole}^{-1} \]
\[ = 0.545 \text{ kJ from the Born Mayer equation} \]

\[ K = \text{Goldschmidt ionic radius } K^+ = 1.33 \text{Å} \]
\[ N = \text{Goldschmidt ionic radius } \text{Na}^+ = 0.98 \text{Å} \]
\[ S = \text{thermochemical ionic radius } \text{S}_2\text{O}_8^{2-} \]

\[ s = \text{S}_2\text{O}_8^{2-} = 2.90 \text{ Å} \]

Substitution of this value in the Kapustinskii equation with the

Yatsimirskii correction gives
\[ \Delta U = 1624 \text{ kJ mole}^{-1} \] (388 kcal mole\(^{-1}\))
\[ \Delta U = 1751 \text{ kJ mole}^{-1} \] (419 kcal mole\(^{-1}\))

Consider now the following thermochemical cycles

\[ 2 \Delta H^f \text{K}^+(aq) + \Delta H^f \text{S}_2\text{O}_8^{2-}(aq) \rightarrow 2 \text{K}^+(aq) + \text{S}_2\text{O}_8^{2-}(aq) \]

\[ \Delta H^f \text{K}_2\text{S}_2\text{O}_8(s) - \Delta H^f \text{Na}_2\text{S}_2\text{O}_8(s) \]

\[ = 0.074052 \text{ kJ mole}^{-1} \]
\[ = 0.545 \text{ kJ from the Born Mayer equation} \]

\[ K = \text{Goldschmidt ionic radius } K^+ = 1.33 \text{Å} \]
\[ N = \text{Goldschmidt ionic radius } \text{Na}^+ = 0.98 \text{Å} \]
\[ S = \text{thermochemical ionic radius } \text{S}_2\text{O}_8^{2-} \]

\[ s = \text{S}_2\text{O}_8^{2-} = 2.90 \text{ Å} \]
Using the following values given in Table 6.3

Table 6.3

<table>
<thead>
<tr>
<th>Quantity</th>
<th>kJ mole(^{-1})</th>
<th>kcal mole(^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta H^\circ_{f}(\text{K}_2\text{S}_2\text{O}_8, \text{cryst}))</td>
<td>-1903.0</td>
<td>-455.3</td>
<td>Mean of Stull, Richards and this work</td>
</tr>
<tr>
<td>(\Delta H^\circ_{f} K^+_8)</td>
<td>514.92</td>
<td>123.07</td>
<td>Rossini et al., 1952</td>
</tr>
<tr>
<td>(\Delta \text{mol} \text{K}_2\text{S}_2\text{O}_8 \text{ in H}_2\text{O})</td>
<td>67.53</td>
<td>16.14</td>
<td>H1 and Hepler, 1962</td>
</tr>
<tr>
<td>(\Delta H^\circ_{f} K^+_8)</td>
<td>-343.8</td>
<td>-83.35</td>
<td>Noyes, 1962</td>
</tr>
</tbody>
</table>

the following thermodynamic quantities of \(\text{S}_2\text{O}_8^{2-}\) are calculated to be

\[\Delta H^\circ_{f} \text{S}_2\text{O}_8^{2-} (g) = -1303 \text{ kJ mole}^{-1} \quad (\text{-311 kcal mole}^{-1})\]

\[\Delta H^\circ_{f} \text{S}_2\text{O}_8^{2-} (aq) = -2165 \text{ kJ mole}^{-1} \quad (\text{-518 kcal mole}^{-1})\]

\[\text{S}_2\text{O}_8^{2-} (g) \rightarrow \text{S}_2\text{O}_8^{2-} (aq) \quad \Delta H = -865 \text{ kJ mole}^{-1} \quad (\text{-207 kcal mole}^{-1})\]
Discussion

From the point of view of considering a slow reaction to be suitable as a test reaction in solution calorimetry it is worthwhile to see what extra conditions must be imposed upon the reaction over and above those conditions suggested by Gunn (1965) for a rapid test reaction.

1) The speed of reaction should preferably be controllable, ideally from under one minute to several hours.

2) If the reaction speed is not sufficiently controllable, then the heat of reaction must be assessable by means of a cyclic route involving rapid reactions so that the reaction heat can be estimated by using calorimeters of proven accuracy.

3) The question of evolved gas is not so important in a slow reaction as a quick one as sufficient time may be allowed for the evolving gases to equilibrate with the calorimeter, thus the latent heat of evaporation of the calorimeter liquid, which is the major factor, may be readily estimated. Of course the evolving gas must not be sufficient to alter significantly the heat capacity of the system.

4) The dissolution of the test substance should preferably be rapid so that a homogeneous system is rapidly established thus preventing undue physical interactions with particle or relative 'hot spots' in the calorimeter.

The possibility of using the magnesium, hydrochloric acid reaction as a standard has been briefly considered by Gunn (1965). A knowledge of the standard enthalpy of formation of the final state is, however, dependent on determinations of this same reaction and as such suffers a major disadvantage because to speed up the reaction sufficiently to allow an accurate determination leads to rapid evolution of hydrogen. Sheats and Saffman (1945) investigated this reaction in order to determine $\Delta H^\circ$ of magnesium
chloride and its hydrate using 1M HCl, but no recent determinations of this reaction have been made in an attempt to increase the accuracy of these data. The evolution of gas does not appear to be a significant disadvantage in this slow reaction, unless work of the highest accuracy is being undertaken, but the trouble experienced with the particles of magnesium in this work does indicate a disadvantage - which might be overcome by modifying the apparatus so as to prevent a physical interaction of the particles with the parts of the calorimeter taking place.

Hydrolysis of acetic anhydride with water is base catalysed so an evaluation of the magnitude of the heat of this reaction can be made independently by using fast reactions only, as was done by Conn et al., (1942) and Nased (1962). The instability of this compound in air is a serious disadvantage in any consideration of acetic anhydride as a test substance, but this could be overcome by taking precautions during handling. Lack of a convenient but precise method of estimating its purity must be regarded unfavourably as well, tending to indicate that the usefulness of using acetic anhydride as a test substance is at present doubtful. Another point which must always be considered for a first order reaction is that the time taken for any further change to be observable by the particular apparatus is dependent solely on the half life and initial concentration of the reactant. Thus for acetic anhydride with a half life of 4.44 mins at 25°C 99.9% reaction is complete after 44.4 mins and 99.99% after 53.8 mins so this particular reaction will serve as a test reaction operating over a quite limited time range.

Studies of the kinetics of peroxydisulphate oxidations reveal quite complicated mechanisms, the details of which have not been completely determined. One disadvantage of using potassium peroxydisulphate as a
standard is that it is slowly thermally decomposed in aqueous media. Work by Kolthoff and Miller (1951) has shown that the thermal decomposition of peroxide ions follows the rate law

\[ -\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = k_1[\text{S}_2\text{O}_8^{2-}] + k_2[R^+] [\text{S}_2\text{O}_8^{2-}] \]

demonstrating that hydrogen ion catalysed and uncatalysed decompositions take place which have been suggested to be

\[ \text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O}_4^- + \text{H}_2\text{O} \]

for the uncatalysed decomposition

and

\[ \text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} + R^+ \rightarrow \text{H}_3\text{O}_4^- + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \]

for the hydrogen ion catalysed decomposition.

In neutral solution the hydrogen ion concentration is too low for the latter decomposition to be significant and so the rate law may be expressed as

\[ -\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = k_1[\text{S}_2\text{O}_8^{2-}] \]

Kolthoff determined \( k_1 \) at ten degree intervals over the range 50 to 90° C, giving an activation energy of 140.164 kJ mole\(^{-1}\) (33.5 kcal mole\(^{-1}\)). Correction of Kolthoff's values to 25°C gives \( k_1 = 1.15 \times 10^{-6} \text{ min}^{-1} \) at pH 7 giving a half life \( t_\frac{1}{2} = 6 \times 10^5 \text{ mins} \). Using these values the times taken for various percentage thermal decompositions have been calculated and are given in Table 6.8.

**Table 6.8**

<table>
<thead>
<tr>
<th>% Decomposition of ( \text{S}_2\text{O}_8^{2-} ) (aq)</th>
<th>Time taken for this decomposition (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>145</td>
</tr>
<tr>
<td>0.1</td>
<td>145</td>
</tr>
<tr>
<td>0.01</td>
<td>142</td>
</tr>
<tr>
<td>0.001</td>
<td>132</td>
</tr>
</tbody>
</table>

In fact, during the course of a reaction between potassium peroxysulphate
and potassium iodide the percentage thermal decomposition of peroxodisulphate is less than that indicated in Table because the peroxodisulphate is continually being used up in reaction with the iodide. The reaction between peroxodisulphate and iodide

\[ \text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{SO}_4^{2-} \]

is principally bimolecular (Moose, 1962), the rate of reaction being expressed by

\[ -\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = k_2[\text{S}_2\text{O}_8^{2-}][\text{I}^-] \]

With a large excess of iodide present, however, as in the calorimeter, the reaction is pseudo first order with respect to the peroxodisulphate concentration, the iodide concentration remaining approximately constant. Consider the following scheme

\[ \begin{align*}
\text{S}_2\text{O}_8^{2-} & \xrightarrow{k_x} \text{I}^- \\
\text{I}^- & \xrightarrow{k_y} \text{K}_1
\end{align*} \]

where the overall reaction of peroxodisulphate is by two paths, 1) by reaction with iodide at concentration \([\text{I}^-]\) and bimolecular rate constant \(k_2\) giving a pseudo unimolecular rate constant \([\text{I}^-]k_2\) and 2) by first order thermal decomposition with unimolecular rate constant \(k_1\)

\[ \text{Then } \frac{dx}{dt} = [\text{I}^-]k_2 x \]

\[ \frac{dz}{dt} = k_1 x \]

\[ \frac{dx}{dt} = \frac{dz}{dt} = \frac{k_1}{[\text{I}^-]k_2} \]
\[
\int_0^2 z \, dz = \int_0^1 \frac{K_1}{(1-z)K_2} \, dy \\
2 = \frac{K_1}{(1-z)K_2} \\
\text{so } \frac{z}{y} = \frac{K_1}{(1-z)K_2}
\]

Now \( K_2 \) is not strictly constant and decreases over the course of the reaction due to the increasing presence of \( I_2^- \) ions, and varying between 0.099 and 0.12 mole\(^{-1}\) litres min\(^{-1}\) (Jeffe and King, 1929). Taking a value for \([I^-]\) of 0.1 – which is less than the lowest used in this work, and using \( K_2 = 0.1 \) mole\(^{-1}\) litres min\(^{-1}\) and \( K_3 = 10^{-6} \) min\(^{-1}\) then

\[
\frac{z}{y} = \frac{10^{-6}}{10^{-2}} = 10^{-4}
\]

Thus the amount of \( S_2O_3^{2-} \) which decomposes thermally under the conditions in the calorimeter is of the order of 0.01% or less.

Extensive work on the dissolution of KCl in water (recommended as a solution calorimeter standard by Kishchenko and Kaganovich, 1949) by Gunn, 1965 and Sumner and Wade, 1959, and others, has shown its unsuitability as a test reaction significant variation being obtained in different laboratories for the heat of solution. At least part of this variability has been attributed to lattice defects, strain energy or surface effects of the ionic crystals. Similar variable effects may be present in the ionic potassium peroxysulphate crystals, but as the weight of potassium peroxysulphate required is less than a quarter of the weight of potassium chloride to give the same heat change, these crystal effects must be reduced by a similar amount.

The effect of varying reactant concentrations on the heat of reaction may be seen from the following reasoning.
If as before

(1) $K_2S_2O_8(s) + 2KI(aq) \rightarrow 2K_2S_2O_4(aq) + I_2(s) \quad \Delta H_1$

(2) $KI(aq) + I_2(s) \rightarrow KI_3(aq) \quad \Delta H_2$

The heat change observed in the calorimeter is given by $\Delta H_1 + \Delta H_2$.

Let us assume that a change of temperature is required to lie within the range $0.1^\circ C < T < 1^\circ C$ and assume the water contains 75% of the heat capacity of the calorimeter. This total heat capacity of calorimeter is $\frac{3}{4}x$ where $x$ is the number of ml of solution. These conditions require amounts of potassium peroxysulphate ranging from $0.18 \times 10^{-5}$ to $1.8 \times 10^{-5}$ mole corresponding to $0.36$ to $3.6 \times 10^{-5}$ moles of potassium sulphate formed. So the ratio $K_2SO_4:H_2O$ varies from $1:1.5 \times 10^3$ to $1:1.5 \times 10^4$ and $\Delta H^0K_2SO_4(aq)$ in this region is $-1409.17 \pm 0.21 \text{ kJ mole}^{-1} (-536.30 \pm 0.09 \text{ kcal mole}^{-1})$ where the error is the range.

If the strength of the potassium iodide solution is allowed to lie within 0 to 0.55 molar then $\Delta H^0KI(aq) = -307.15 \pm 0.25 \text{ kJ mole}^{-1} (-73.41 \pm 0.06 \text{ kcal mole}^{-1})$ where again the error is the range.

Thus

$$\Delta H_1 + \Delta H_2 = -\Delta H^0[K_2S_2O_8(c)] + 2\Delta H^0[KI(aq)] + 2\Delta H^0[K_2SO_4(aq)] + \Delta H_2$$

$$= -\Delta H^0[K_2S_2O_8(c)] -2204.95 \pm 0.92 \text{ kJ mole}^{-1} (-829.78 \pm 0.22 \text{ kcal mole}^{-1})$$

$$+ \Delta H_2$$

Now $\Delta H_2$ varies with concentration is not known, but the total variation is unlikely to be more than $1.46 \text{ kJ mole}^{-1} (0.35 \text{ kcal mole}^{-1})$

$$\left\{\frac{\Delta H_2[KI:H_2O]}{1:240 \text{ to } 1:480} = 5.605 \text{ kJ mole}^{-1}(1.34 \text{ kcal mole}^{-1}) \right\}$$

(Wu et al., 1963)

corresponding to a possible 0.5% variation in the observed heat of reaction with changes in initial concentrations.

Work will also be required to determine the temperature coefficient of the heat of this reaction as this is completely unknown at present.
Should the volatility of the iodine solution be found to be unacceptable, then the oxidation of thiosulphate with peroxysulphate, which proceeds according to

\[ \text{S}_2\text{O}_3^{2-} + 2\text{Na}_2\text{S}_2\text{O}_3(aq) \rightarrow \text{Na}_2\text{S}_4\text{O}_6(aq) + 2\text{H}_2\text{O}(aq) \]

can be more acceptable. Unfortunately, the standard heats of formation of the aquated thiosulphate and dithionate salts are not known accurately at present, but the approximate values given in N.B.W. Circ. 500 indicate that the heat of reaction should be about \(-359.8\) kJ mole\(^{-1}\) (\(-86\) kcal mole\(^{-1}\)).
Chapter Five References

Gold, W., J. C.C., 1946, 64, 926.
1965, 2, 373, Pergamon Press.
Richards, S. E., Thesis 1969, University of Bath.
Rossini, F. J., Wagner, J. D., Evans, C. L., Levine, S. and Jeffe, E.,


CHAPTER SEVEN

Experimental

Synthesis of the Heterocyclic compounds

All these preparations were of the same type, involving the elimination of water between the diol or two molecules of ethanol and either phenyl or n-butyl boronic anhydride, and may be expressed by the following equations:

\[ \text{HO(CH}_2\text{)}_n\text{OH} + 3\text{H}(\text{OBR})_3 \rightarrow \text{O(CH}_2\text{)}_n\text{OBR} + \text{H}_2\text{O} \]

\[ 2\text{C}_2\text{H}_5\text{OH} + 3\text{H}(\text{OBR})_3 \rightarrow (\text{C}_2\text{H}_5\text{O})_2\text{BR} + \text{H}_2\text{O} \]

In the case of the diols, anisotropic removal of the water using either benzene or toluene in a Dean and Stark apparatus was used, but this method could not be employed in the case of ethanol as the ethanol/benzene or ethanol/toluene anisotropy would distill off first.

2-n-Butyl-1,3,2-Dioxaboralan

To a refluxing mixture of ethane diol (3.2 mls, 3.5g, 0.057 mole) in benzene (50 mls), n-butyl boronic anhydride was slowly added (4.8g, 0.057 moles corresponding to 90g-C\textsubscript{4}H\textsubscript{10}). Water was immediately anisotropically removed and the reaction was completed in under 2 hrs. The amount of water removed (1.0 mls) corresponded to 90 to 100% theoretical.

The benzene was removed by distillation and the product distilled 56-60\textdegree C/34-37mmHg. Yield 6.4g(88%).

Redistilled:- The product came over at 30-52\textdegree C/38mmHg with much foaming.

Redistilled:- After the initial foaming was removed, no foaming was observed. The fraction collected boiled very sharply at 61\textdegree C/23mmHg.

This substance appeared to be fairly stable in air over a period of several hours.

Analysis for C\textsubscript{6}H\textsubscript{13}O\textsubscript{2}B

<table>
<thead>
<tr>
<th>% W</th>
<th>% C</th>
<th>% H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>8.45</td>
<td>56.32</td>
</tr>
<tr>
<td>Found</td>
<td>8.53</td>
<td>57.08</td>
</tr>
</tbody>
</table>
2-n-Butyl-1,3,2-Monaboreane

The propane-1,3-diol was previously distilled, bpt 211°C. Propene-1,3-diol (3.34 g, 0.0505 moles) and n-butyl boronic anhydride (4.24 g, 0.0505 moles corresponding to OH-n-C₄H₉) were mixed with benzene (sodium dried, 60 ml) and refluxed under nitrogen with stirring. Within 1 hour the theoretical amount of water had been removed (0.9 mls) and the benzene was then distilled off.

The product was distilled at 67-70°C/19mmHg. Yield 3.4 g (75%).

Redistilled:- Fraction boiled very sharply at 65°C/19mmHg.

Analysis for C₂H₅O₂H % B % C % H
Calculated 7.62 59.20 10.65
Found 7.67 60.34 10.67

2-n-Butyl-1,3,2-Monaboreane

The butane-1,4-diol was fractionated through a short column before use, the fraction used collected at 226°C.

Butane-1,4-diol (4.71 mls, 4.72 g, 0.0531 moles) and n-butyl boronic anhydride (4.46 g, 0.0531 moles corresponding to OH-n-C₄H₉) were mixed with benzene (sodium dried, 35 mls) and refluxed under nitrogen with stirring. Within 1 hour 95% of the theoretical amount of water had been removed (0.9 mls) and the benzene was then distilled off.

The product was distilled at 63-6°C/0.06mmHg. Yield 4.3 g (58%).

Redistilled:- Fraction collected boiled at 72°C/0.02mmHg. It was a very viscous colourless liquid.

Analysis for C₆H₁₇O₂H % B % C % H
Calculated 6.93 61.53 10.98
Found 6.97 59.06 11.12

Diethoxy n-Butyl boronate

The preparation of this compound was analogous to the preparation of diethoxy phenyl boronate (Gerrard et al., 1955).
Dried ethanol (12.4 mls, 2.0g, 0.213 moles) in two fold excess was refluxed for 12 hours with n-butyl boronic anhydride (4.5g, 0.0537 moles corresponding to \(\text{OBO}_2\)).

On distillation a first fraction came over at 64-66°C corresponding to the benzene/ethanol/water ternary azeotrope (lit bpt 64.6°C). After the ethanol/benzene azeotrope (bpt 77.8) and some benzene had been distilled off, the pressure was lowered and the remaining benzene removed.

The product distilled over at 95-96°C/93mmHg. Yield 6g (70%).

Redistilled: Fraction collected boiled at 56°C/40mmHg. It was a colourless mobile liquid.

Analysis for \(\text{C}_{7\text{H}}\text{_9O}_2\text{H}\) % B % C % H

Calculated 6.84 59.79 12.12

Found 6.83 61.55 12.19

2-Phenyl-1,1,2-Bis(boronic anhydride)

Freshly distilled butane-1,4-diol (3.0 mls, 3.0g, 0.033 moles) and phenylboronic anhydride (3.5g, 0.034 moles corresponding to \(\text{OBO}_2\)) were refluxed in toluene (sodium dried, 100 mls), for 1 hour with stirring under nitrogen.

The theoretical amount of water (0.6-0.7 mls) was evolved and the toluene distilled off.

The product distilled at 128-132°C/0.2mmHg.

Redistilled: Boiling point 129-130°C/0.2mmHg. Final yield 3.4g (57%).

Diethoxy Phenylboronate

This compound was prepared by the method of Gerrard et.al. (1955).

Dried ethanol (25 mls, 20g, 0.45 moles) and phenylboronic anhydride (7.83g, 0.0753 moles corresponding to \(\text{OBO}_2\)) were refluxed for 15 hours with toluene (sodium dried, 55 mls). On distillation, over a period of 12 hrs, the temperature of the distillate passed through three points
corresponding to the toluene/ethanol/water ternary azeotrope (bpt 74.4°C), the toluene/ethanol azeotrope (bpt 76.7°C) and toluene (bpt 110.6°C).

Distillation at reduced pressure caused much frothing, a clear liquid finally coming over at 55 to 62°C/0.6 to 0.7mmHg. Yield 6.6 g (50%).

Redistilled-: Fraction collected boiled at 65°C/0.3mmHg, (lit 50°C/0.4mmHg).

The 2-phenyl-1,3,2-dioxaborolan, 2-phenyl-2,4-dioxo-3-borabicyclo[3.2.2]nonane which were used had previously been prepared by Dr. P. McLaughlin, and had only to be (in some cases) purified and analysed. The analytical data are given in Table 7.1.

Table 7.1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analysis Figures</th>
<th>Bpt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>(Calc)</td>
<td>65°C/0.1mmHg</td>
</tr>
<tr>
<td>(\text{O(C}_2\text{H}_5\text{)}_2\text{OHC}_6\text{H}_5)</td>
<td>7.31</td>
<td>64.43</td>
</tr>
<tr>
<td></td>
<td>(Found)</td>
<td>7.22</td>
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<tr>
<td>(\text{O(C}_2\text{H}_3\text{)}_3\text{OHC}_6\text{H}_5)</td>
<td>6.63</td>
<td>66.22</td>
</tr>
<tr>
<td></td>
<td>(Calc)</td>
<td>6.63</td>
</tr>
<tr>
<td></td>
<td>(Found)</td>
<td>6.63</td>
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<tr>
<td>(\text{O(C}_2\text{H}_4\text{)}_4\text{OHC}_6\text{H}_5)</td>
<td>6.15</td>
<td>68.23</td>
</tr>
<tr>
<td></td>
<td>(Calc)</td>
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</tr>
<tr>
<td></td>
<td>(Found)</td>
<td>6.17</td>
</tr>
<tr>
<td>(\text{C}(\text{H}_2\text{CH}_2\text{)}_2\text{CHOK}_6\text{H}_5)</td>
<td>5.35</td>
<td>72.33</td>
</tr>
<tr>
<td></td>
<td>(Calc)</td>
<td>5.41</td>
</tr>
</tbody>
</table>

**Drying of Ethanol**

The ethanol used in the preparations of the diethoxy phenyl and α-butyloborates was dried by the following standard procedure (Vogel, 1957).

Magnesium turnings (0.5g) and iodine crystals (0.05g) were added to ethanol (20 ml) and refluxed until the solution was colourless. A further portion of ethanol (90 ml) was then added and the mixture refluxed for 30 minutes.

Dry ethanol was then distilled off after discarding the first 5 ml of forerun.
Dehydration of n-Butylboronic Acid to n-Butylboronic Anhydride

The n-butylboronic acid was prepared by Mr. K.S. Hassein by the method of Snyder et al. (1938).

Heating under vacuum was found to be ineffective because the acid appeared as aseotropic with the water, recondensing on the cold parts of the apparatus.

An attempt at ase troposing the water with benzene only caused the acid to darken in colour.

Dehydration using Thionyl Chloride

Thionyl chloride was distilled (bpt 75.5°C/759.8 mmHg 1lit 78.3°C/746 mmHg) and added to the butylboronic acid in excess. Immediate effervescence occurred and the mixture was refluxed under oxygen-free nitrogen for 1½ hrs whence it was a dark coloured liquid.

The excess thionyl chloride was then distilled off and the n-butylboronic anhydride distilled at 83-84°C/0.8 mmHg. In a repeated prep the anhydride distilled 77-79°C/0.6 mmHg.

The liquid was analysed for boron, found 13.0% B calc for (C5H9)3BO 14.6% B.
Vapour Pressure Measurements

Two methods were employed, one a dynamic distillation technique and the other by means of an isoteniscope.

1) Dynamic Distillation

A small glass apparatus was built which would allow the boiling point of less than 2 mls of a liquid to be determined at various pressures. Control of pressure was by means of a Cartesian Manostat.

The apparatus was checked by the use of ethylene glycol, the vapour pressure of which is given by

\[ \log_{10} P(\text{mmHg}) = 9.2037 - \frac{2975.6}{T} \] (Gallaugher and Hibbert, 1937)

Table 7.2 gives the results obtained.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Temp. T (K)</th>
<th>Pressure (mmHg)</th>
<th>log10P</th>
<th>( \log_{10} P \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>129</td>
<td>402</td>
<td>70.5</td>
<td>1.848</td>
<td>2.488</td>
</tr>
<tr>
<td>136</td>
<td>409</td>
<td>92.5</td>
<td>1.966</td>
<td>2.445</td>
</tr>
<tr>
<td>145</td>
<td>418</td>
<td>126.5</td>
<td>2.102</td>
<td>2.392</td>
</tr>
<tr>
<td>152</td>
<td>425</td>
<td>166.5</td>
<td>2.221</td>
<td>2.353</td>
</tr>
<tr>
<td>160</td>
<td>433</td>
<td>220.5</td>
<td>2.343</td>
<td>2.309</td>
</tr>
<tr>
<td>168</td>
<td>441</td>
<td>299.5</td>
<td>2.476</td>
<td>2.268</td>
</tr>
<tr>
<td>180</td>
<td>453</td>
<td>442.5</td>
<td>2.646</td>
<td>2.208</td>
</tr>
</tbody>
</table>

From a plot of \( \log_{10} P \) vs \( \frac{1}{T} \), \( \log_{10} P = 9.203 - \frac{2975.6}{T} \)

Now \( \Delta H_{\text{vap}} = -2.303 \times \frac{\log_{10}P}{d \frac{1}{T}} \)

so \( \Delta H_{\text{vap}} = 57.0 \text{ kJ mole}^{-1} (13.62 \text{ kcal mole}^{-1}) \)

This compares with the value of \( \Delta H_{\text{vap}} \) obtained from the literature of 57.01 kJ mole\(^{-1}\) (13.62 kcal mole\(^{-1}\)).

Table 7.3 compares vapour pressures obtained in this work with derived values from Gallaugher and Hibbert's work.
Table 7.3

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Pressure (mm Hg)</th>
<th>This work</th>
<th>Gallaugher and Hibbert</th>
</tr>
</thead>
<tbody>
<tr>
<td>402</td>
<td>70.5</td>
<td>65.6</td>
<td></td>
</tr>
<tr>
<td>409</td>
<td>92.5</td>
<td>85.3</td>
<td></td>
</tr>
<tr>
<td>418</td>
<td>126.5</td>
<td>122.4</td>
<td></td>
</tr>
<tr>
<td>425</td>
<td>166.5</td>
<td>160.3</td>
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</tr>
<tr>
<td>433</td>
<td>220.5</td>
<td>215.9</td>
<td></td>
</tr>
<tr>
<td>441</td>
<td>299.5</td>
<td>237.7</td>
<td></td>
</tr>
<tr>
<td>453</td>
<td>442.5</td>
<td>434.3</td>
<td></td>
</tr>
</tbody>
</table>

The thermometer accuracy was tested by boiling deionised water in the apparatus. Observed at $101^\circ$C

bpt at 766.0 mm Hg 100.2 C

This section presents the experimental data obtained from the dynamic distillation work.

In the case of the phenylboronates, some of the work was done by Dr. P. McNamara using an apparatus standardized against propanoic acid over a range 30$^\circ$-140$^\circ$C, showing a mean deviation of 2% from the literature. The results of this work are also presented here, for the sake of completeness, as they were used in the estimation of $\Delta H_{\text{vap}}$. 
1) Vapour Pressure Measurements of 2-n-Butyl-1,3,2-Dioxaborolan.

\[
\text{O(CH}_2\text{)}_2\text{OBn-C}_2\text{H}_4
\]

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure, p (mm Hg)</th>
<th>Temp. (°K)</th>
<th>(\frac{10^3}{T})</th>
<th>(\log_{10} p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.0</td>
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<td>3.342</td>
<td>0.613</td>
</tr>
<tr>
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<td>8.5</td>
<td>304.7</td>
<td>3.282</td>
<td>0.929</td>
</tr>
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<td>12.5</td>
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<td>3.152</td>
<td>1.097</td>
</tr>
<tr>
<td>50.0</td>
<td>17.0</td>
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<td>3.094</td>
<td>1.230</td>
</tr>
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<td>27.0</td>
<td>333.4</td>
<td>2.997</td>
<td>1.431</td>
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<td>1.628</td>
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<td>2.780</td>
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<td>57.5</td>
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<td>2.851</td>
<td>1.760</td>
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<td>2.922</td>
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</tr>
<tr>
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<td>74.0</td>
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<tr>
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<td>8.5</td>
<td>306.2</td>
<td>3.266</td>
<td>0.929</td>
</tr>
</tbody>
</table>

Giving \(\log_{10} p = 7.719 - \frac{2103}{T}\)
2) Vapour pressure Measurements of 2-n-Butyl-1,3,2-Dioxaborinan.

\[ \text{Table 7.5} \]

<table>
<thead>
<tr>
<th>Temp. (^{\circ}\text{C})</th>
<th>Pressure, (p) (mm Hg)</th>
<th>Temp. (T) (K)</th>
<th>(\frac{T}{10^3})</th>
<th>(\log_{10})</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3.138</td>
<td>0.903</td>
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<td>311.8</td>
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<td>0.813</td>
</tr>
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<td>10.5</td>
<td>329.7</td>
<td>3.033</td>
<td>1.021</td>
</tr>
<tr>
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<td>15.0</td>
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<td>2.957</td>
<td>1.176</td>
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<td>2.897</td>
<td>1.301</td>
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<td>2.701</td>
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<td>1.495</td>
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<td>3.019</td>
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<td>0.929</td>
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<td>5.5</td>
<td>305.2</td>
<td>3.276</td>
<td>0.740</td>
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</tbody>
</table>

\(\text{Giving } \log_{10} = 7.335 = \frac{2250}{2}\)
3) Vapour Pressure Measurements of 2-n-Butyl-1,3,2-Dioxaborolane, $\text{O(C}_2\text{H}_5)_2\text{OB}-\text{C}_3\text{H}_9$

Table 7.6

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure, p (mm Hg)</th>
<th>Temp. T (K)</th>
<th>$\frac{\log^2}{T}$</th>
<th>log10P</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.0</td>
<td>0.05</td>
<td>337.2</td>
<td>2.966</td>
<td>-1.301</td>
</tr>
<tr>
<td>60.0</td>
<td>0.05</td>
<td>335.2</td>
<td>3.001</td>
<td>-1.301</td>
</tr>
<tr>
<td>70.0</td>
<td>0.11</td>
<td>343.2</td>
<td>2.914</td>
<td>-0.959</td>
</tr>
<tr>
<td>79.0</td>
<td>0.55</td>
<td>352.2</td>
<td>2.539</td>
<td>-0.260</td>
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<tr>
<td>90.0</td>
<td>1.25</td>
<td>363.2</td>
<td>2.753</td>
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</tr>
<tr>
<td>94.0</td>
<td>1.5</td>
<td>367.2</td>
<td>2.723</td>
<td>0.176</td>
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<td>106.0</td>
<td>3.6</td>
<td>379.2</td>
<td>2.637</td>
<td>0.556</td>
</tr>
</tbody>
</table>

Giving \( \log_{10} p = 11.08 - \frac{4000}{T} \)

Difficulty was experienced with this substance because of its viscous nature. Satisfactory readings above the temperatures given here could not be obtained because the viscous nature of the liquid induced a considerable hold up, thus causing all the material to be driven out of the heated flask at high temperatures.
### Table 7.7

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure, p (mm Hg)</th>
<th>Temp. T (K)</th>
<th>$\frac{10^5}{T}$</th>
<th>log$_{10}^p$</th>
</tr>
</thead>
<tbody>
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<td>9.0</td>
<td>312.2</td>
<td>3.203</td>
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</tr>
<tr>
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<td>323.2</td>
<td>3.095</td>
<td>1.171</td>
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<td>28.5</td>
<td>340.7</td>
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<td>1.455</td>
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<tr>
<td>76.0</td>
<td>40.0</td>
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<td>2.864</td>
<td>1.602</td>
</tr>
<tr>
<td>84.0</td>
<td>55.5</td>
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<td>2.897</td>
<td>1.434</td>
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<td>2.966</td>
<td>1.380</td>
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<td>3.038</td>
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<td>0.924</td>
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<td>6.0</td>
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<td>3.360</td>
<td>0.778</td>
</tr>
</tbody>
</table>

Giving $\log_{10}^p = 8.155 - \frac{2286}{T}$
5) Vapour Pressure Measurements of 2-Phenyl-1,3,2-dioxaborolan,
\[ \text{O(\text{CH}_2)\text{OBC}_2\text{H}_5} \]

All these measurements were taken by Dr. P. McHargara.

<table>
<thead>
<tr>
<th>Temp. (^{\circ}\text{C})</th>
<th>Pressure, (p) (mm Hg)</th>
<th>Temp. (T) (K)</th>
<th>(10^3)</th>
<th>(\log_{10} P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>124</td>
<td>43</td>
<td>397</td>
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<td>100</td>
<td>426</td>
<td>2.336</td>
<td>2.000</td>
</tr>
<tr>
<td>161</td>
<td>125</td>
<td>434</td>
<td>2.304</td>
<td>2.097</td>
</tr>
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<td>185</td>
<td>267</td>
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<td>2.183</td>
<td>2.427</td>
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<tr>
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<td>197</td>
<td>447</td>
<td>2.237</td>
<td>2.295</td>
</tr>
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<td>2.421</td>
<td>1.806</td>
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<td>136</td>
<td>55</td>
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<td>2.444</td>
<td>1.740</td>
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<td>122</td>
<td>32</td>
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<td>1.505</td>
</tr>
</tbody>
</table>

**Giving** \(\log_{10} P = 7.750 - \frac{2472}{T}\)
Two series of measurements by Dr. F. McNamara were obtained.

### Table 7.9

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure, p (mm Hg)</th>
<th>Temp. T (K)</th>
<th>$\frac{10^3}{T}$</th>
<th>log$_{10}P$</th>
</tr>
</thead>
<tbody>
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<td>137</td>
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<td>2.152</td>
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<td>167</td>
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<td>2.150</td>
<td>2.223</td>
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<td>2.192</td>
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</table>

Giving $\log_{10}P = 8.650 - \frac{2000}{T}$
7) Vapour Pressure Measurements of 2-Phenyl-1,3,2-Dioxaborolan,

\[ \text{O(CH}_2\text{)}_2\text{OB} = \text{H}_3 \]

The first two series of measurements were obtained by Dr. P. H. Askara.
The third series was obtained by the author, to extend the temperature range.

Table 7.10

<table>
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<tr>
<th>Temp. (°C)</th>
<th>Pressure, p (mm Hg)</th>
<th>Temp. T (K)</th>
<th>[\frac{10^3}{T}]</th>
<th>[\log_{10} p]</th>
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<tbody>
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<tr>
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</tr>
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<td>2.096</td>
<td>2.195</td>
</tr>
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<td>471</td>
<td>2.123</td>
<td>2.093</td>
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<td>461</td>
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<td>431</td>
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<td>1.519</td>
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Table 7.11

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<tr>
<th>Temp. (°C)</th>
<th>Pressure, p (mm Hg)</th>
<th>Temp. T (K)</th>
<th>$\frac{10^3}{T}$</th>
<th>log$_{10}p$</th>
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<td>0.000</td>
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<td>377</td>
<td>2.633</td>
<td>0.393</td>
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<td>0.699</td>
</tr>
<tr>
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<td>2.457</td>
<td>1.041</td>
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<td>1.441</td>
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Giving $\log_{10} p = 3.974 - \frac{3057}{T}$
8) Vapour Pressure Measurements of 3-phenyl-2,4-dioxo-3,5-cyclohexadiene-1,2,2-trimethanol

The first series of measurements were obtained by Dr. P. McNamara.

The second series by the author.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure, p (mm Hg)</th>
<th>Temp. T (K)</th>
<th>$\frac{10^3}{T}$</th>
<th>$\log_{10} p$</th>
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<td>496</td>
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<td>496</td>
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<td>1.792</td>
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<td>491</td>
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<td>466</td>
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<td>1.612</td>
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<td>333</td>
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<td>-0.824</td>
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<tr>
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<td>373-5</td>
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<tr>
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<td>397</td>
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<tr>
<td>135</td>
<td>3.0</td>
<td>406</td>
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<td>0.477</td>
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<td>-0.301</td>
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<tr>
<td>106</td>
<td>0.8-0.9</td>
<td>379</td>
<td>2.639</td>
<td>-0.097 to -0.046</td>
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</table>

Giving $\log_{10} p = 9.245 - \frac{3569}{T}$
9) Vapour Pressure Measurements of Diethoxy-Phenylboronate,
\[(\text{C}_2\text{H}_5\text{O})_2\text{BCl}_3\]

Table 7.13

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure, p (mm Hg)</th>
<th>Temp. T (K)</th>
<th>(\frac{T^2}{P})</th>
<th>(\log_{10}p)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3.276</td>
<td>-0.824</td>
</tr>
<tr>
<td>40.0</td>
<td>0.35</td>
<td>313.2</td>
<td>3.193</td>
<td>-0.456</td>
</tr>
<tr>
<td>49.0</td>
<td>0.65</td>
<td>322.2</td>
<td>3.104</td>
<td>-0.187</td>
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<tr>
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<td>0.75</td>
<td>324.7</td>
<td>3.080</td>
<td>-0.125</td>
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<tr>
<td>55.5</td>
<td>1.30</td>
<td>329.7</td>
<td>3.033</td>
<td>0.114</td>
</tr>
<tr>
<td>69.0</td>
<td>3.0</td>
<td>342.2</td>
<td>2.922</td>
<td>0.477</td>
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<tr>
<td>74.0</td>
<td>4.0</td>
<td>347.2</td>
<td>2.880</td>
<td>0.602</td>
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<td>77.0</td>
<td>5.0</td>
<td>350.2</td>
<td>2.855</td>
<td>0.699</td>
</tr>
<tr>
<td>91.0</td>
<td>11.0</td>
<td>364.2</td>
<td>2.746</td>
<td>1.041</td>
</tr>
<tr>
<td>74.0</td>
<td>4.5</td>
<td>347.2</td>
<td>2.880</td>
<td>0.693</td>
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</table>

Giving \(\log_{10}p = 10.767 - \frac{3526}{T}\)
2) Isoteniscope Measurements

The isoteniscope consisted of a 'U' tube approximately 5 inches long and 
\( \frac{3}{4} \) inch bore, partly filled with mercury. The sample (ca. 0.5 ml or
less) was contained in a side arm and the whole apparatus degassed by
repeated pumping, with the sample frozen in liquid nitrogen, to a pressure
of ca. 0.01 mm Hg, and thawing. After the system was judged to be completely
degassed it was sealed off and submerged in a water bath, the temperature of
which was maintained constant to within \( \pm 0.02^\circ C \). The temperature of the
bath was determined by means of an N.P.L. calibrated mercury in glass
thermometer accurate to \( \pm 0.01^\circ C \). Pressure measurements were made by
determining the relative heights of the mercury in the vertical arms of the
'U' tube by means of a travelling telescope which enabled a precision of
\( \pm 0.05 \text{mm Hg} \) to be attained.

Readings were normally taken at hourly intervals after altering the
bath temperature to allow for thermal equilibration.

The precision of this system was checked by determining the vapour
pressure of deionised water from 0 to 55\(^\circ\)C, the vapour pressure of which was
determined accurately by Keyes (1947) who expressed his results in the form

\[
\log_{10} p (\text{mm Hg}) = A + \frac{B}{T} + C \log T + D T + E T^2 + F T^3 + G T^4
\]

By plotting these values at 10 degree intervals over the range 0 to
55\(^\circ\)C on a \( \log_{10} p (\text{mm}) \times \frac{1}{T} \) plot the expression

\[
\log_{10} p = 3.977 - \frac{2267}{T} 
\]

was obtained.

Table 7.14 gives the results obtained.
Table 7.14

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure, p (atm)</th>
<th>Temp. T (K)</th>
<th>$\frac{10^3}{T}$</th>
<th>$\log_{10}p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>5.00</td>
<td>273.5</td>
<td>3.656</td>
<td>0.699</td>
</tr>
<tr>
<td>5.25</td>
<td>7.17</td>
<td>273.4</td>
<td>3.592</td>
<td>0.856</td>
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<tr>
<td>10.6</td>
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<td>284.0</td>
<td>3.521</td>
<td>1.003</td>
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<td>15.9</td>
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<td>299.1</td>
<td>3.459</td>
<td>1.146</td>
</tr>
<tr>
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<td>63.92</td>
<td>317.6</td>
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<td>1.838</td>
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</table>

From a plot of $\log_{10}p$ vs $\frac{1}{T}$, $\log_{10}p = 9.050 - \frac{226}{T}$

This corresponds to $\Delta H_{\text{vap}} = 43.77$ kJ mole$^{-1}$ (10.45 kcal mole$^{-1}$) which compares to $\Delta H_{\text{vap}} = 43.41$ kJ mole$^{-1}$ (10.37 kcal mole$^{-1}$) from Keyes data over the same temperature range.

Table 7.15 gives interpolated pressure measurements at 10 degree intervals to compare with those values given by Keyes.

Table 7.15

<table>
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<th>Temp. (°C)</th>
<th>Pressure (atm)</th>
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</thead>
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<td>4.74</td>
</tr>
<tr>
<td>10</td>
<td>9.33</td>
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<tr>
<td>20</td>
<td>17.70</td>
</tr>
<tr>
<td>30</td>
<td>32.02</td>
</tr>
<tr>
<td>40</td>
<td>55.73</td>
</tr>
</tbody>
</table>

The slightly, but persistently, high readings of pressure observed were due, presumably, to incomplete degassing of the water sample.
The experimental data obtained by means of the isoteniscope is presented here.

1) Vapour Pressure Measurements of 2-n-Butyl-1,3,2-Dioxaborolan

\[ \text{O} \left( \text{CH}_2 \right)_2 \text{C} = \text{O} \left( \text{CH}_2 \right) \text{CH}_3 \]

Table 7.16

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure, ( p ) (mm Hg)</th>
<th>Temp. T (K)</th>
<th>( \frac{10^3}{T} )</th>
<th>( \log_{10} p )</th>
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<td>12.33</td>
<td>306.4</td>
<td>3.264</td>
<td>1.108</td>
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</table>
2) Vapour Pressure Measurements of 2-n-Butyl-1,3,2-Dioxaborinan

\[
\text{O} = \text{CH}_2 \rightleftharpoons \text{CBr} = \text{C}_4 \text{H}_2
\]

**Table 7.17**

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure, ( p ) (mm Hg)</th>
<th>Temp. ( T ) (K)</th>
<th>( \frac{10^3}{T} )</th>
<th>( \log_{10} p )</th>
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<td>3.527</td>
<td>0.594</td>
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<td>1.187</td>
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<td>17.66</td>
<td>318.1</td>
<td>3.143</td>
<td>1.247</td>
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### Table 7.18

<table>
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<th>Pressure, p (mm Hg)</th>
<th>Temp. T (K)</th>
<th>( \frac{10^3}{T} )</th>
<th>( \log_{10} p )</th>
</tr>
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</tr>
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<td>3.522</td>
<td>-0.301</td>
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<td>0.63</td>
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<td>3.410</td>
<td>-0.168</td>
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<td>238.1</td>
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<td>-0.444</td>
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</table>
4) Vapour Pressure Measurements of Diethoxy-n-butylbenzene
\((\text{C}_2\text{H}_5\text{O})_2\text{Hn-C}_9\text{H}_3\)

**Table 7.19**

<table>
<thead>
<tr>
<th>Temp. (^\circ\text{C})</th>
<th>Pressure, (p) (mm Hg)</th>
<th>(\text{Temp. } T) (K)</th>
<th>(\frac{10^3}{T})</th>
<th>(\log_{10} P)</th>
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</thead>
<tbody>
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<td>3.531</td>
<td>0.630</td>
</tr>
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<td>7.17</td>
<td>292.9</td>
<td>3.434</td>
<td>0.835</td>
</tr>
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<td>55.55</td>
<td>5.75</td>
<td>338.7</td>
<td>3.464</td>
<td>0.760</td>
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</table>
5) Vapour Pressure Measurements of 2-Pheny1-1,3,2-Dioxaborolan

\[ \text{O(CH}_2\text{)}_2\text{CB}_2\text{H}_5 \]

Table 7.20

<table>
<thead>
<tr>
<th>Temp. (^{\circ}\text{C})</th>
<th>Pressure, (p) ((\text{mm Hg}))</th>
<th>Temp. (T) ((\text{K}))</th>
<th>(\frac{10^3}{T})</th>
<th>(\log_{10}P)</th>
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</thead>
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<td>3.15</td>
<td>290.2</td>
<td>3.470</td>
<td>0.533</td>
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<tr>
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<td>4.00</td>
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<td>0.979</td>
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<td>15.97</td>
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<td>0.996</td>
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</table>

Table 7.21

<table>
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<th>Temp. (^{\circ}\text{C})</th>
<th>Pressure, (p) ((\text{mm Hg}))</th>
<th>Temp. (T) ((\text{K}))</th>
<th>(\frac{10^3}{T})</th>
<th>(\log_{10}P)</th>
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</thead>
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<td>3.598</td>
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<td>283.0</td>
<td>3.533</td>
<td>0.243</td>
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<tr>
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<td>2.12</td>
<td>288.0</td>
<td>3.471</td>
<td>0.326</td>
</tr>
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<td>293.2</td>
<td>3.410</td>
<td>0.400</td>
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<td>3.242</td>
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<td>0.597</td>
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<td>295.0</td>
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<td>0.408</td>
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</table>

6) Vapour Pressure Measurements of 2-Pheny1-1,3,2-Dioxaborolan

\[ \text{O(CH}_2\text{)}_2\text{CB}_2\text{H}_5 \]
7) Vapour Pressure Measurements of 3-Phenyl-2,4-Dioxo-3-Horabicyclo[3.2.2]Nonane

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure, P (mm Hg)</th>
<th>Temp. (K)</th>
<th>( \frac{L^2}{P} )</th>
<th>( \log_{10} P )</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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<td>0.29</td>
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</tr>
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<td>2.999</td>
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<td>-0.108</td>
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</table>
8) Vapour Pressure Measurements of Dimethoxy-Phenylboronate

\((C_2H_5O)_2B(OH)_2\)

Two series of measurements were obtained for this compound.

Table 7.23

<table>
<thead>
<tr>
<th>Temp. ( ^\circ \text{C} )</th>
<th>Pressure, ( \text{mm Hg} )</th>
<th>Temp. ( T ) (K)</th>
<th>( \frac{10^3}{T} )</th>
<th>( \log_{10} p )</th>
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<td>0.732</td>
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<td>5.15</td>
<td>282.2</td>
<td>3.544</td>
<td>0.911</td>
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<tr>
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<td>5.445</td>
<td>1.074</td>
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<td>13.90</td>
<td>295.5</td>
<td>5.407</td>
<td>1.143</td>
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<td>5.343</td>
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</tr>
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<td>5.231</td>
<td>1.407</td>
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<td>5.097</td>
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<td>5.286</td>
<td>1.015</td>
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<td>7.02</td>
<td>293.6</td>
<td>5.406</td>
<td>0.846</td>
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</table>
Despite the excellent results obtained for the vapour pressure measurements of water by means of the isotoniscope, the results obtained for the dioxaboron compounds by this method were singularly unsatisfactory, the plots of log $p$ vs $\frac{1}{T}$ being in all cases slightly curved (convex with respect to the abscissa) and furthermore being - in the case of diethoxyphenylboronate for which a duplicate series of measurements was obtained - non-reproducible. When plotted on the same scale as the readings obtained by means of the dynamic distillation method, for which excellent straight line log $p$ vs $\frac{1}{T}$ plots were obtained, the negative gradients were generally observed to be less, and in all cases the curves were substantially displaced either up or down on the log $p$ axis with respect to the dynamic distillation measurements.

Non-linear log $p$ vs $\frac{1}{T}$ plots over a limited temperature range are usually taken to be indicative of the presence of more than one component. It is difficult to understand how any decomposition of these compounds could have taken place under the experimental conditions, and if this possibility is rejected it only leaves the possibility of the presence of an inert gas due to incomplete degassing of the sample, thermal non-equilibration being excluded by observing the same pressure over a period of time. While it is entirely likely that absolute degassing was not achieved it would seem most probable that the presence of a soluble gas would be to lead to anomalously high pressures at high temperatures due to the decreased solubility of a gas in a liquid at higher temperatures. This was observed, for instance, in the isotoniscope measurements of pure water, where the observed pressure was slightly higher than the literature values and was correspondingly higher at higher temperatures. This type of behaviour was not observed with the dioxaboron compounds, the observed pressure being invariably lower at a higher temperature. Such behaviour would, therefore, appear to indicate increasing solubility of the inert gas with increasing temperature. In the case of the bicycle compound, which is a solid melting at about 90°C, a
maximum in the logp vs $\frac{1}{T}$ curve was obtained at approximately 80°C indicating that the solubility of the inert gas was increasing to such an extent with temperature as to cause a reduction in the total pressure above this temperature. Such an observation is not too surprising in the region of the melting point, as the gas would be expected to be much more soluble in the liquified bicycle compound than in the solid. This behaviour could be rationalized in terms of a glass-like liquid phase which slowly loses its 'crystal' properties with increasing temperature.

Figure 7.1

For the n-butyl dioxaboron rings the deviations of the logp vs $\frac{1}{T}$ plots from linearity increase steadily with increasing viscosity of these compounds, the seven membered heterocyclic being very viscous at room temperature. This implies that degassing was less effective for the more viscous compounds, and that further deviations from ideal solubility are greater for the more viscous compounds.
The change in viscosity with molecular weight of the phenyl diazaboron compounds is less marked, but the seven membered ring is a solid at room temperature. Its behaviour is similar to that of the solid bicycle compound.

Because of the unsatisfactory state of these isoteniscope readings, they were not considered in estimations of $\Delta H_{vap}$; the results of the dynamic distillation method being preferred.
Heat of solution of Butane-1,4-Diol in eab

Butane-1,4-diol was fractionated up a 50 cm heated column packed with glass helicities, the middle fraction being taken and shown to be 99.9% pure by G.L.C. Three calorimeter runs were made and the results given in Table 7.24.

Table 7.24

<table>
<thead>
<tr>
<th>Amount butane-1,4-diol (mole x 10^2)</th>
<th>N(H_2O:dial)</th>
<th>△Hobs (joules)</th>
<th>△H solution 25°C kj mole^{-1} kcal mole^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.469</td>
<td>756</td>
<td>-157.46</td>
<td>-10.719 -2.562</td>
</tr>
<tr>
<td>1.434</td>
<td>764</td>
<td>-147.46</td>
<td>-10.142 -2.424</td>
</tr>
<tr>
<td>1.352</td>
<td>821</td>
<td>-140.39</td>
<td>-10.394 -2.482</td>
</tr>
</tbody>
</table>

Mean -10.42 ± 0.25 kj mole^{-1} (-2.49 ± 0.06 kcal mole^{-1})

Heat of solution of Cyclohexane-1,4-Diol in eab

The cyclohexane-1,4-diol was purified by sublimation under reduced pressure using a water pump.

The results of two calorimetric runs are given in Table 7.25.

Table 7.25

<table>
<thead>
<tr>
<th>Amount of dial (mole x 10^{-3})</th>
<th>N(H_2O:dial)</th>
<th>△Hobs (joules)</th>
<th>△H solution 25°C kj mole^{-1} kcal mole^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.52</td>
<td>4409</td>
<td>3.034</td>
<td>1.204 0.288</td>
</tr>
<tr>
<td>2.27</td>
<td>4393</td>
<td>2.752</td>
<td>1.217 0.291</td>
</tr>
</tbody>
</table>

Mean 1.209 ± 0.008 kj mole^{-1} (0.289 ± 0.002) where error is spread.
Heat of solution of 3-Phenyl-2,4-Dioxo-5-Borabicyclo5,2,2-hexane in 1,4-Dioxan

The purification of the bicycle-compound has been described already. The 1,4-dioxan was purified by distilling from sodium in oxygen free apparatus. The results of three calorimetric runs are given in Table 7.26.

Table 7.26

<table>
<thead>
<tr>
<th>Amount of bicycle compound (molex10^2)</th>
<th>N(dioxan: bicycle compound)</th>
<th>ΔHobs (joules)</th>
<th>ΔH solution 25°C (kj mole^-1)</th>
<th>ΔH solution 25°C (kcal mole^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.160</td>
<td>769</td>
<td>15.559</td>
<td>4.924</td>
<td>20.532</td>
</tr>
<tr>
<td>2.278</td>
<td>1067</td>
<td>11.273</td>
<td>4.939</td>
<td>20.704</td>
</tr>
<tr>
<td>1.561</td>
<td>1557</td>
<td>7.709</td>
<td>4.939</td>
<td>20.664</td>
</tr>
</tbody>
</table>

Mean 20.67 ± 0.04 kj mole^-1 (4.94 ± 0.01 kcal mole^-1)

Heat of solution of 2-Phenyl-1,1,2-Dioxaboropan in Benene

The purification of the heterocyclic compound has been described already. The benzeene used was sodium dried, oxygen free, Analytical reagent. The results of three calorimetric runs are given in Table 7.27.

Table 7.27

<table>
<thead>
<tr>
<th>Amount of heterocyclic (molex10^2)</th>
<th>N(Benzen: heterocyclic)</th>
<th>ΔHobs (joules)</th>
<th>ΔH solution 25°C (kj mole^-1)</th>
<th>ΔH solution 25°C (kcal mole^-1)</th>
</tr>
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<tr>
<td>1.764</td>
<td>1276</td>
<td>37.360</td>
<td>21.463</td>
<td>5.129</td>
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<td>21.382</td>
<td>5.229</td>
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<tr>
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<td>1737</td>
<td>27.578</td>
<td>21.295</td>
<td>5.089</td>
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</table>

Mean 21.55 ± 0.29 kj mole^-1 (5.15 ± 0.07 kcal mole^-1)
Reaction of Boric Acid and Propionic Anhydride

Boric acid (5g, 0.081 moles) was heated with propionic anhydride (40g, 0.29 moles) under dry nitrogen. A vigorous reaction occurred and the solid dissolved. On cooling white needle-like crystals formed which, after decanting the supernatant liquid, were washed with sodium dried ether. After filtering and pumping off the surplus ether a melting point was taken. The melting point was not sharp, one part appearing to melt at 70-80°C and a second part at ca. 105°C.

Reaction of Boric Acid and Butyric anhydride

Using the same procedure as for propionic anhydride, boric acid (2.5g, 0.04 moles) and butyric anhydride (23g, 0.145 moles) were heated under dry N₂. A sudden reaction took place and some of the liquid was distilled off coming over at 163-165°C (bp butyric acid 163.5°C). On cooling the whole not solid but proved to be soluble in dry ether. Several recrystallizations from dry ether at low temperatures were carried out, the final product melted partly at 60°C, the bulk of the material melting at 77-80°C.

Reaction of Boric Acid and Propionyl Chloride

Boric acid (11.1g, 0.180 moles) and propionyl chloride (50 mls, 53g, 0.573 moles) were refluxed with dry toluene (100 mls). Provision was made for the hydrogen chloride gas evolved to be dissolved in water and constantly titrated with sodium hydroxide solution so that the extent of the reaction could be followed. On cooling, after the reaction had finished, a white mass was formed. Most of the toluene was removed and a pump and dry ether used to wash the product. Benzene proved to be a suitable solvent and recrystallization from this was carried out. Yield 22.4g mp 112-115°C.

Further recrystallization from toluene (which allowed a lower temperature to be used) afforded white feathery crystals.

Mpt. Started softening ca. 75°C and partly melted at 90°C. The remainder melted at 115°C. (Sample A)
A portion of this sample (denoted now by B) was pumped until no further loss of weight was observed.

Npt of B in a sealed tube under nitrogen.  B started to shrink at 50°C to form a glassy solid which melted noticeably at 60°C and by 80°C all had melted.

Npt of B in an evacuated tube.  B first started to change at 60°C forming a transparent solid.  At 110°C marked shrinkage occurred and it melted 116°C-122°C.

Analysis.  Ratio boron:propionate
A  1:2.02
B  1:1.88

Reaction of Boric Acid and Propionyl Chloride

Using a 3:1 molar ratio of propionyl chloride to boric acid in benzene the mixture was refluxed.  After the reaction was complete the benzene was removed by distillation and the remaining liquid portion collected in a cold trap under vacuum (0.5 mmHg).  The contents of the cold trap were fractionated the first fraction coming over at 30°C/760mmHg and the second 146-150°C/760mmHg this corresponding most closely to propionic acid (bpt 141°C, bpt anhydride 163°C, chloride 80°C) $\frac{25}{D} 1.396 (\frac{20}{D} \text{ propionic acid} 1.3874, \text{anhydride} 1.0110$).

Reaction of Boric Acid and Butyryl Chloride

Boric acid (3g, 0.146 moles) and butyryl chloride (48 ml, 49.4g, 0.464 moles) were refluxed in dry benzene (100 ml) until evolution of hydrogen chloride had ceased (after ca. 5 hrs).  After stripping off the benzene at a pump the product was repeatedly recrystallized from dry ether - which proved to be a good solvent at 25°C but in which the product was highly insoluble at -76°C.  After a slow recrystallization white feathery needles were produced.  Final traces of ether were removed by blowing a stream of dry nitrogen over the crystals.  Yield 23g

Npt in an evacuated tube 83-89°C.
Analysis. \textit{Boric acid:butyric acid} = 1:1.99

Calculated for \( \left[ \text{C}_3\text{H}_7\text{CO}_2 \right]_2\text{B} \cdot \text{O} \)  
- C 49.78\%  H 7.32\%  O 37.30\%  B 5.60\%
- Found  C 47.64\%  H 7.20\%  O 37.39\%  B 5.99\%

\[ \text{M wt calc.} \quad 336.018 \]
- Found (cryoscopically in benzene) \( 364 \pm 19 \)

\textbf{Reaction of Boric Acid and Valeryl Chloride}

Boric acid (118g, 0.19 moles) and valeryl chloride (70g, 0.53 moles) were refluxed with dry benzene (150 ml). After the reaction was completed, the benzene was pumped off and collected in a cold trap - it was slightly yellow but on standing at room temperature overnight it turned red. On application of a cold spot to the product, long needles crystallized out and the remaining liquid was decanted off. This liquid was fractionated, main fraction coming over 58-60\(^\circ\)C/0.5-0.6mmHg. The IR spectrum and refractive index of this sample were different from valeric acid and compared closely to valeric anhydride.

The crystalline product was recrystallized several times from dry ether.

\textbf{Analysis. Ratio: boric acid:valeric acid} = 1:2.02

Calculated for \( \left[ \text{C}_6\text{H}_{12}\text{O}_2 \right]_2\text{B} \cdot \text{O} \)  
- C 54.33\%  H 8.21\%  O 32.57\%  B 4.90\%
- Found  C 53.00\%  H 8.43\%  O 32.43\%  B 4.99\%

\textbf{Reaction of Boric Acid and n-Hexoyl Chloride}

Boric acid (9.3g, 0.15 moles) and n-hexoyl chloride (59g, 0.44 moles) were refluxed with dry benzene (150 ml). The benzene was stripped off and the remaining solution cooled to 0\(^\circ\)C whence it slowly crystallized until completely solid. This was filtered at 0\(^\circ\)C and recrystallized from dry ether several times. The product still appeared to be moist so it was
pumped overnight using a mercury diffusion pump while being warmed gently. The final substance was a waxy, white solid with a low (45-50°C) melting point.

**Analysis.** Boric acid: hexol acid = 1:1.52 i.e. 2:3

Because this compound was extremely hygroscopic it proved very difficult to handle. Cryoscopic M.t in benzene gave M.t 581, but this value must be low because of partial hydrolysis.

Calculated for \((\text{C}_9\text{H}_6\text{O}_4)\cdot\text{H}_2\cdot\text{O}\) 498.229

Found, C 55.96% H 9.13% B 9.54%

**Reaction between Boric Acid and n-Heptanoyl Chloride**

Using exactly the same procedure as for the previous acid chlorides, after removing the solvent benzene, the white solid solid upon cooling.

Attempts at filtering this material were unsuccessful, incomplete separation occurring, and on warming to room temperature the solid redissolved. Because of the large proportion of heptanoyl anhydride present recrystallization from ether proved ineffective at purifying the acyloxyborane.

**Attempted Preparation of Macetoxyphenylborane**

Using the method of Gerrard et al. (1958) who reported the reaction

\[
\text{C}_6\text{H}_5\text{B(OCONH}_2\text{)}_2 + 2\text{CH}_3\text{COOH} \rightarrow \text{C}_6\text{H}_5\text{B(OOCCH}_3\text{)}_2 + 2\text{HCl}
\]

to phenylboronic dichloride (28g, 0.173 moles) in dry n-pentane (40 mls) a stoichiometric amount of acetic acid (21g, 0.356 moles) was added slowly with vigorous stirring. Immediate reaction occurred, and by the time all the acid was added, the whole had set as a white solid. Pure, dry, oxygen-free methyl ethyl ketone was found to be a good solvent and was used for two recrystallizations. M.p 208-210°C and analysis 8.46% B indicated that disproportionation

\[
\text{C}_6\text{H}_5\text{B(OOCCH}_3\text{)}_2 \rightarrow \text{H}_2\text{C}_6\text{H}_5\text{BO} + (\text{CH}_3\text{CO})_2\text{O}
\]

had taken place. M.p phenylboronic anhydride 209-214°C; 8.45% B
Repeat Preparation

Using phenylborondichloride (30g, 0.189 moles) and acetic acid (22.7g, 0.378 moles) in an identical procedure as before, a product was obtained at 120-130°C. Using oxygen free 'AR' acetic anhydride as a solvent after two recrystallizations very pale yellow needles were obtained.

Mpt: began to darken 163°C melting 172°-173°C
Lit mpt for diacetoxyphenyloborane 172-174°C Gerrard et al., 1958

Analysis. Acetate:boron = 1.02:1
69.1% B

Reaction between Benzoyl Chloride and Boric Acid

Boric acid (6.2g, 0.1 mole) and benzoyl chloride (42g, 0.3 moles) were refluxed in dry benzene (150 mL) for 22 hrs. The amount of hydrogen chloride liberated indicated that ca. 50% of the benzoyl chloride had reacted. After decanting the liquid and removing the benzene by distillation, the solution was cooled to 0°C. No product came out of solution.

Reaction between Borontrichloride and Benzoic Acid

To borontrichloride (9.2g, 0.031 moles) in benzene (30 mL), benzoic acid (29.6g, 0.243 moles) in dry benzene (250 mL) (in which it nearly all dissolved) was added slowly. The reaction mixture was cooled in an ice bath. After all the benzoic acid solution had been added most of the benzene was distilled off. A solid (white but slowly turning yellow) was produced and the remaining benzene was pumped off. The solid was washed several times with dry benzene and pumped dry. Mpt 203-205°C.

Analysis. Benzoic acid:boric acid = 2.05:1
3.9% B, 39.4% C₆H₆CO₂
Carboxylic Acid Chlorides

The propionyl chloride, butyryl chloride and benzoyl chloride were S.D.H. chemicals which were distilled up a short, glass helix packed column before use. Sometimes it was necessary to prepare propionyl chloride by the reaction of equimolar quantities of propionic acid with phosphorus pentachloride. After distilling up a short column (bpt 80-84°C/760mmHg, lit 80°C) a yield of 84% was obtained.

The higher acid chlorides were prepared by the standard method (Vogel, 1957) by the reaction of the carboxylic acid with a 100% excess of freshly distilled thionyl chloride.

Valeryl Chloride After distilling twice up a short column packed with glass helicies, fraction collected bpt 125-129°C (lit 127°C) Yield 64%.

Hexoyl Chloride After distilling twice up a short column, fraction collected bpt 151-152°C (lit 153°C) Yield 70%.

Heptanoyl Chloride After distilling twice up a short column, fraction collected bpt 172-173.5°C Yield 85%.

Preparation of Phenylboron Dichloride

To tetraphenyl tin (45g, 0.105 moles) boron trichloride (50g, 0.427 moles) was added (cooled to -78°C) according to the method of Burch et.al. (1960). On warming to room temperature the boron trichloride was prevented from escaping (bpt -12°C) by means of a CO₂/acetone cold finger. After reaction was complete the mixture was fractioned twice up a short column packed with glass helicies. Fraction collected 170-174°C/760mmHg (lit, Burch et.al. 1960, 79°C/15mmHg; Finch et.al. 1967, 170-174°C/760mmHg). Final yield based on \((\text{C}_6\text{H}_5)_4\text{Sn} + 4\text{BCl}_3 \rightarrow 4\text{C}_6\text{H}_5\text{BCL}_2 + 4\text{SnCl}_4\) was 45%.
Attempted Syntheses of Boron Sulphide

(1) Because of the experimental difficulties involved in using the method recommended by Jerumanis et Lalancette (1964), involving the heating of elementary boron with sulphur in a sealed tube at 650°C, it was decided to attempt the reaction at lower temperatures.

Amorphous boron (analysed 87% pure) was mixed with sulphur and refluxed. No reaction appeared to take place even after prolonged heating time. Amorphous boron and sulphur were heated together in a sealed glass tube at ca. 440°C for several hours. No reaction appeared to take place.

Analysis of the amorphous boron

Amorphous boron (ca. 0.25g) was dissolved by refluxing with fuming nitric acid (25 ml) for several hours. An aliquot was titrated with 0.1M NaOH to the HNO₃/NaOH equivalence point and then to the H₂SO₃/NaOH equivalence point in the presence of mannitol. Two determinations gave 87.4% and 86.6% B.

(2) By Reaction of Boron with Hydrogen Sulphide (Brauner, 1963)

Hydrogen sulphide from a cylinder was passed via silica gel and P₂O₅ drying tubes over amorphous boron heated to a dull red in a pyrex tube. A small amount of vitreous white solid was formed which was very difficult to remove from the tube. Sublimation (0.03 to 0.05mmHg/100°C) produced a small amount of white feathery crystals.

The sample was analysed for sulphur by the following method. A sealed ampoule containing the sulphide was broken under a dilute iodine solution in a stoppered flask. After the liberated H₂S was dissolved, the excess iodine was titrated using 0.1 M Na₂S₂O₃. Boron analysis by titrating with 0.1 M NaOH in the presence of mannitol was also carried out.

% S found 33.69; calc. for B₂S₃ 31.64
% B found 15.12; calc. for B₂S₃ 18.76

The high percentage of hydrolysable sulphur found can be explained by assuming the presence of 20 to 30% B₂S₅.
(3) By Reaction of Hexamethyldisilthiane with Boron Trichloride

Abel et al. (1965) reported the reaction

$$2\text{Me}_3\text{SiCl} + \text{Na}_2\text{S} \rightarrow (\text{Me}_3\text{Si})_2\text{S} + 2\text{NaCl}$$

by the addition of hexamethyldisilthiane to boron trichloride at -78°C.

Hexamethyldisilthiane (16.2g, 0.14 moles) was added slowly with stirring to boron trichloride (14g, 0.12 moles) at -78°C. Immediately a white solid began to form and by the time all the silthiane had been added the mixture was a solid mass. On warming to room temperature the solid dissolved to form a clear solution. The liquid was removed by vacuum distillation but the solid did not sublime at 130°C/0.5mmHg. Analysis of hydrolysable sulphur and boron at this stage gave 55.9% S; 25.9% B.

(Theoretical for $\text{H}_2\text{S}$ 31.6% S; 13.4% B.) After washing with dry ether a hydrolysed sample gave a positive test for Cl⁻ with $\text{AgNO}_3$; after all sulphide had been boiled off as $\text{H}_2\text{S}$.

Reanalysis for B, S and Cl gave 14.9% B, 45.4% S, 25.3% Cl giving

$$\text{B:Si:Cl} = 2:2:1.$$  
Test for Si was negative so remaining elements must be C and H.

Found C 5.74%, H 1.56%. These analyses figures correspond most closely to

$\text{CH}_2\text{Si}\text{SiH}_2\text{Cl}$. The product did not melt below 300°C.

Preparation of Hexamethyldisilthiane

The method reported by Abel (1961) from the reaction

$$2\text{Me}_3\text{SiCl} + \text{Na}_2\text{S} \rightarrow (\text{Me}_3\text{Si})_2\text{S} + 2\text{NaCl}$$

carried out by heating the reactants in a sealed tube at 240°C for 20 hrs was unsuccessful because of the repeated explosions of the sealed tubes.

The following method (private communication from Dr. E.W. Abel) of reacting $\text{H}_2\text{S}$ with $\text{Me}_3\text{SiCl}$ in the presence of pyridine in dry ether was found to be satisfactory; the final mixture being fractionated, the disilthiane coming over at 161°-163°C in 25% yield (lit bpt 165°C).
Reaction of \( \text{m-Amylthioborane} \) with \textit{Valeric Acid}

\( \text{m-Amylthioborane} \) was prepared by Dr. C.B. Watts by the method of Mikhailov and Dubnov (1962) by condensing pentane thiol (3 ml) with boron trichloride (1 ml) in ether and abstracting the liberated hydrogen chloride with triethylamine. This material was redistilled, bpt 136-146\(^\circ\)C/0.1mmHg, lit bpt 168-173\(^\circ\)C/0.2mmHg (Petterson et al., 1961), \( n_\text{D}^{20} \) 1.5149, lit \( n_\text{D}^{20} \) 1.5145 (Petterson et al., 1961).

\( \text{m-Amylthioborane} \) (31.8g, 0.099 moles) was refluxed with \textit{valeric acid} (bpt 183-4\(^\circ\)C, lit 186-7\(^\circ\)C; 65.7g, 0.644 moles) under dry nitrogen. A white precipitate quickly formed. After 2 hrs the thiol which was produced was stripped off under vacuum leaving a moist, slightly yellow solid.

\textbf{Analysis.} Titration with and without mannitol gave boron:valerate = 1:1.7 and 1:1.9.
Handling

The acyloxyboranes were all extremely moisture sensitive and at all stages were handled in dry nitrogen, either in a glove bag or, in the case of recrystallizing procedures, in an apparatus designed to allow only dry nitrogen to come into contact with the compounds.

Solvents were rigorously dried before use, and in the case of compounds containing a B-C bond it was found necessary to flush the solvent with dry nitrogen to remove dissolved oxygen.

The dioxaboron compounds varied in stability with respect to the presence of oxygen and water, but they were all handled in an atmosphere of dry nitrogen in a glove bag.

Chemical Analysis

Elemental carbon and hydrogen analyses were carried out by Alfred Bernhardt, Microanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany.

Boron analysis for compounds containing a B-C bond, which did not hydrolyse directly to boric acid, was carried out by using a modification of Thomas' method (1946) as follows:-

The sample of boron compound was refluxed with 'AR' sulphuric acid (20 mls) for 10 minutes until the substance was charred black. After cooling, 100 volume hydrogen peroxide (10 mls) was added and again the mixture refluxed until colourless (10-15 minutes).

On cooling, methanol (150 mls) was added and the mixture distilled into water, this causing the methyl borate/methanol azeotrope (the first 50 mls of which contained practically all the boron present) to hydrolyse to boric acid and methanol. Care was taken to ensure that the distillate was collected under water so preventing the escape of the volatile azeotrope.

The aqueous solution was then titrated with 0.1 N sodium hydroxide solution potentiometrically, first to neutralise any sulphuric acid present,
and then with addition of sufficient mannitol to the second end point corresponding to the neutralization of the monobasic boric acid, mannitol complex.

It was found expedient to plot derivative curves, i.e. $\frac{\Delta \text{vol}}{\Delta \text{vol}}$ vs vol to obtain accurate equivalence points, the boric acid acting as a monobasic acid equivalent to the difference between the two end points.

The use of borosilicate glassware during this analysis procedure necessitated that a blank was carried out as small but significant amounts of boric were leached from the glass.

In the case of the acyloxyboron compounds, where a boric acid/carboxylic acid analysis was required, the following procedure was used.

Hydrolysis of these compounds in water was rapid and quantitative and the resultant mixture of boric acid and carboxylic acid solutions was titrated potentiometrically using 0.1 M sodium hydroxide, first to the carboxylic acid end point, and then, after addition of mannitol, to the boric acid end point. A derivative plot was again used to estimate the equivalence points.

In the initial stages, acid base indicators were tried but the colour change at the end points was, in all cases, very imprecise.

The samples of compounds analysed were all loaded into sealed ampoules under an inert atmosphere before the analysis to prevent decomposition in the atmosphere.
Cryoscopic Measurements for Molecular Weight Determinations

The apparatus used in this work is described in detail elsewhere (Finch et al., 1965) and consists essentially of a double-walled glass cell, into which is placed dry, cryoscopically pure benzene (10 ml). A thermistor enters the benzene from above and a reciprocating annular glass stirrer serves to agitate the liquid. Small weighed quantities of the solid whose molecular weight is to be determined are added to the benzene via a side insert and the freezing point of the solution determined after each addition by cooling the cell in a salt/ice freezing mixture and measuring the thermistor resistance via a simple Wheatstone bridge when the readings become steady.

The freezing point depression for a dilute ideal solution is given by
\[ \Delta T_F = \frac{m}{M} m_c, \]
where \( m_p \) is the cryoscopic constant and \( m_c \) is the molality of the solution. For a small temperature range \( \Delta R \propto \Delta H \) the change in thermistor resistance, thus \( -\Delta R \propto \frac{m}{M} \) where \( m \) is amount of solute and \( M \) is its molecular weight.

Thus \( -\Delta R = \frac{m}{M} \)

For two substances of molecular weights \( M_1 \) and \( M_2 \) giving rise to \( \Delta R_1 \) and \( \Delta R_2 \) for a given weight in
\[ -\Delta R_1 = \frac{k_m}{M_1} \]
\[ -\Delta R_2 = \frac{k_m}{M_2} \]
\[ \frac{\Delta R_1}{\Delta R_2} = \frac{M_2}{M_1} \]

In practice a plot of \( \Delta R vs \) wt of solute added to 10g benzene for the unknown substance and naphthalene was obtained, the ratio of their gradients being inversely proportional to their molecular weights. So by using naphthalene as a standard the molecular weight was obtained by comparison to it.
The solid was compressed between two pieces of precision ground glass rod inside a precision bore glass tube and weighted. It was then ejected into the cryometer via the side inlet (under an atmosphere of dry nitrogen if moisture sensitive) and the tube and rod reweighed.

The results for butyryloxyborane and naphthalene are given in Table 7.28.

<table>
<thead>
<tr>
<th>Butyryloxyborane</th>
<th>Resistance (ohms)</th>
<th>Weight (g)</th>
<th>Resistance (ohms)</th>
<th>Weight (g)</th>
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Cryoscopic readings in 10 ml dry cryoscopic benzene

Butyryloxyborane. Gradient = 215 ± 5 ohms g⁻¹
Naphthalene. Gradient = 610 ± 15 ohms g⁻¹

M at naphthalene 128
M at butyryloxyborane = \( \frac{610 \pm 15}{215 \pm 5} \times 128 = 364 \pm 19 \)

The results for hexyryloxyborane and naphthalene are given in Table 7.29.

<table>
<thead>
<tr>
<th>Hexyryloxyborane</th>
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<th>Weight (g)</th>
<th>Resistance (ohms)</th>
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<td>0.2002</td>
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</table>

Cryoscopic readings in 10 ml dry cryoscopic benzene

Gradient of hexyryloxyborane 32 ohms g⁻¹

Gradient of naphthalene 145 ohms g⁻¹

M at naphthalene 128
M at hexyryloxyborane \( \frac{145}{32} \times 128 = 581 \)
No errors have been assigned to these results because, despite efforts to the contrary, substantial hydrolysis took place owing to the extremely hydroscopic nature of this substance. The effect of this would be to reduce the molecular weight as boric acid and boric acid are formed from hydrolysis of this material.

**Calorimetry**

Because the operation of the adiabatic solution calorimeter described in Chapter Five is not straightforward, a detailed account of the procedure which has been found most suitable to employ is now given.

It must be remarked that in the case of a calorimeter fluid which is chemically unstable in air, this procedure must be modified slightly.

**Loading the Calorimeter**

1) The ampoule holder, with ampoule in position, and the stirrer are inserted into the lid of the calorimeter and then the lid is sealed onto the calorimeter, a film of grease serving to render the joint air tight.

2) Calorimeter fluid (200 ml) is then pipetted into the calorimeter via one of the inlets in the lid.

3) After clamping in position inside the adiabatic Dewar, the three thermistors and the heater are inserted in position. Flushing with an inert gas may be carried out before the final insertions are completed.

The P.T.F.E. sleeves on which these inserts are seated serve to maintain the probes in fixed positions, i.e. no rotation - which may take place with greased joints - can take place.

4) The height of the ampoule is adjusted until the level of the calorimeter fluid is slightly above the level of the side bulb of the ampoule.

5) The stirrer motor is attached and the height of the stirrer blades is adjusted so that the blades are about 1 cm above the bottom of the calorimeter.
Operation

1) With both the calorimeter stirrer and the external stirrers functioning, the temperature of the calorimeter is brought to just under 29°C (i.e. about 20 ohms above the internal thermistor reading) either by means of the heater or by the addition of cold water to the adiabatic Dewar.

2) With the adiabatic control unit switched on, the temperature difference between the inside and outside of the calorimeter is adjusted, by means of the coarse and fine adiabatic controls, so that the temperature increase of the calorimeter due to heat of stirring is quite small (less than, say, 0.05 ohms \( \text{min}^{-1} \)). The heat loss through the walls of the calorimeter now being very similar to the heat of stirring, this ensures that the temperature of all parts inside the calorimeter is practically the same (a particularly important point with regard to the substance inside the ampoule, the temperature of which may lag behind the temperature of the calorimeter, (laid by a substantial amount in the case of large heat of stirring).

It also ensures that the rate of temperature change during a long afterperiod is conveniently small.

3) The flow of water through the external cooling coil is adjusted so that the monitor heater in switching on and off at approximately its maximum rate, the boost heater should remain off. To effect this the stirring inside the adiabatic Dewar must be quite vigorous.

4) At this stage the whole apparatus must be left for at least one hour to thermally equilibrate, during which time the temperature is manually adjusted by means of the heater, to such a value as to be at 29.0 ± 0.1°C at the beginning of the run.

5) During the run resistance readings of the thermistor are taken every minute, indicating the internal temperature of the calorimeter, and also a note of the galvanometer indicating the temperature difference between inside and outside the calorimeter is made at the same time, this galvanometer having previously been adjusted to read some suitable arbitrary value.
Eleven readings were generally found to be sufficient during the forerun, the ampoule being shattered on the eleventh minute by lowering the lower bulb into the stirrer blades and tapping lightly the side bulb against the side of the calorimeter. After breaking the ampoule should be returned and clamped in the original position.

It is convenient to describe the next stage of operations under three headings, 1) Fast reactions, 2) Slower reactions and 3) Slow reactions, which are defined in terms of the ability of the adiabatic unit to follow the reaction using only the monitor heater, intermittent use of the boost heater, or continuous use of the boost heater.

1) Fast Reactions

The sudden temperature change induced by a fast reaction results in a substantial deflection of the temperature difference galvanometer whose equilibrium position must be restored as quickly as possible by judicious control of the power output of the boost heater via the Variac transformer (see Figure 5.1) and possibly by altering the rate of flow of the cooling water through the adiabatic Dewar.

For a fast reaction such as the heat of solution of \( 'THAM' \) in 0.1M \( HCl \) it was found convenient to set the Variac on 230V and return it to about 70V as the galvanometer spot returned to its equilibrium position.

Because of the changes inside the calorimeter, affecting heat of stirring and also a possible change in the rate of flow of cooling water, the equilibrium position of the temperature difference galvanometer may be, at this stage, slightly different to its equilibrium position during the forerun. This new position must now be maintained during the remainder of the after-period by adjustment of the adiabatic unit fine control.

A suitable temperature rise for a fast reaction was found to be about 30°, corresponding to a heat of reaction of about 250 to 300 joules (60 to 70 calories). Significantly larger changes were found to throw the system too far out of equilibrium, giving rise to anomalous results.
2) Slower Reactions

By this is meant that during reaction, the rate of temperature increase is too great to be followed by the monitor heater alone, resulting in the intermittent switching of the boost heater.

While the rate of heating is too great for the monitor heater, the heat output of the boost heater can be continuously adjusted by means of the Variac control so that the temperature difference galvanometer maintains practically the same value. As the reaction proceeds the rate of temperature increase decreases, requiring the heat output of the boost heater to be less and less until control by the monitor heater alone is attained. Because the boost heater is operated by a larger temperature difference than the monitor heater, if the same temperature difference is to be maintained during this period, frequent adjustments of the adiabatic fine control are required. If this procedure is carried out, the temperature difference during the fore-period is much less than during the after-period. A more satisfactory technique is to maintain a constant temperature difference throughout the entire run by manipulation of the adiabatic fine control at the start of the reaction. This is not easy to accomplish at first, but after several runs have been made the 'feel' of the reaction is readily obtained.

3) Slow Reactions

This heading serves to denote reactions during which the rate of increase of temperature of the calorimeter is always able to be followed by the adiabatic unit operating on the monitor heater alone.

As such the method of operation is essentially the same as during the latter part of the 'Slower Reactions'.

The essential point is, therefore, that the temperature difference between inside and outside the calorimeter must be maintained constant during the entire reaction and after-period. Because of this the rate of heat
absorbed or evolved by the calorimeter through the walls during reaction and after-period is constant and it is this which is an important point in the justification of extrapolating the after-period resistance vs time plot back through the reaction period to the time of the start of the reaction.

To enable this extrapolation to be done accurately, it was found that the amount of readings needed during the after-period was about that of the time of reaction. Thus for a reaction taking 60 minutes, about sixty readings, at minute intervals, during the after-period would be required. During the after-period the calorimeter is in a state of equilibrium and may be left unattended for substantial periods, thus preventing the need for continuous readings. It is very difficult to tell when a slow reaction has completely finished, the only time indication being a constant rate of change of temperature which, because of near cancellation of heat of stirring with heat losses through the walls of the calorimeter, makes $\frac{dT}{dt}$ small and hence from Appendix Two $\frac{dR}{dt}$ is practically constant (for constant $\frac{dR}{dt}$ over a temperature range of 0.1°C $\frac{dR}{dt}$ varies by less than 0.1%). In practice the temperature range during the after-period is much less than this.)

**Calibration**

After the reaction is completed and all after-period readings have been taken, the apparatus must be cooled down to 25°C as before the start of the reaction and left to thermally equilibrate.

The procedure for calibration is exactly the same as for a slow reaction, care being taken to ensure that the initial and final resistance readings correspond to those of the reaction.

After the calibration readings are completed the time of calibration is noted and then the heater switched on and the four potential readings taken (see Figure 5.5). Because of the constancy of these readings with time it is considered unnecessary to take them actually during the calibration heating period, thus leaving the operator free to maintain a check on the adiabatic control.
The resistance readings for reaction and calibration are plotted on a resistance vs time graph, the pre-period and latter part of the after-period being linear indicating that the rate of enthalpy change inside the calorimeter due to heat of stirring, and heat flow through the calorimeter walls, is constant. The reaction pre-period is extrapolated to the time of breaking of the ampoule to obtain the resistance reading at the start of reaction and the calibration pre-period extrapolated to the start of the heating period. It is assumed that the heat of stirring and the rate of heat flow during the reaction period and reaction after-period is constant, an assumption which is justified by maintaining the temperature difference across the walls of the calorimeter constant during this period, and by regarding any changes in viscosity of the calorimeter fluid - which would affect the heat of stirring - to be negligible. The linear after-period is then back extrapolated to the time of ampoule breaking to obtain the resistance reading at the end of reaction. A similar back extrapolation for the calibration after-period, to the start of the heating period, is also carried out.

Thus four resistance readings $R_1$ and $R_2$ corresponding to the thermistor resistances before and after reaction, and $R_3$ and $R_4$ corresponding to the thermistor resistances before and after calibration, are obtained. These, together with the four potential readings from the heater circuit, and the time of heating are sufficient to determine the heat of reaction.

A Typical Run

The purpose of this section is to describe an actual calorimetric run involving the reaction between potassium peroxydisulphate crystals and aqueous potassium iodide at 25°C.

The calorimetric fluid consisted of a solution of 9.763g potassium iodide made up to 200 ml with water (0.29 M).

Amount of potassium peroxydisulphate in ampoule 0.2332g (1.0476x10^{-3} moles).
Readings taken at minute intervals are of the temperature recording thermistor resistance (ohms) (25.00°C 2 4609 ohms and on change of 1°C being equivalent to ca. 160 ohms) and of the temperature differential galvanometer, a more positive reading indicating an increase in temperature of the calorimeter with respect to the outside. One division on this galvanometer represents a temperature change of ca. 5 x 10^-3°C. In the following Tables the readings of this galvanometer are recorded under the column marked T.D.G. (temperature differential galvanometer).

After setting up the calorimeter as described in Chapter Five, the following reaction readings were taken and, after cooling and resetting, the calibration readings taken.
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**Reaction Readings cont'd.**

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### Calibration Readings

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</table>

**Time of heating**: 261.35 secs

**Potentiometer readings (volts)**

\[
V_1 = 0.4246 \quad P_1 = 0.0138 \\
V_2 = 0.2913 \quad P_2 = 0.4090
\]

**New potential across heater**

\[
V = 10V_1 + P_2 - P_1 = 4.6 + 12 \text{ volts}
\]

**Current through heater**

\[
I = \frac{V}{R_s} \quad \text{where} \quad R_s = 0.9932 \text{ in this circuit}
\]

\[
I = 0.24937 \text{ amps.}
\]
Giving heat of calibration 18.574 joules

= 303.083 joules (72.840 cals)

and the heater resistance \( R = \frac{V}{I} = 18.574 \text{ ohms} \)

From the graph of resistance vs time by extrapolating the reaction fore-period to 11 mins \( (R_1) \) and the linear part of the reaction after-period, i.e. from 94 mins to 149 mins back to 11 mins \( (R_2) \) and similarly for the calibration readings giving \( R_3 \) and \( R_4 \)

\[
\begin{align*}
R_1 &= 4605.9 \text{ ohms} \\
R_2 &= 4548.5 \text{ ohms} \\
R_3 &= 4610.0 \text{ ohms} \\
R_4 &= 4553.4 \text{ ohms}
\end{align*}
\]

\[
\frac{R_1}{R_2} = 1.0128195 \\
\frac{R_3}{R_4} = 1.0128302
\]

Giving \( \log \left( \frac{R_1}{R_2} \right) = 1.01513 \)

Thus heat of reaction = 303.083 x 1.01513 joules

= 307.674 joules (73.536 cals)

and hence \( \Delta H_{\text{reaction}} = 293.69 \text{ kJ mole}^{-1} (70.195 \text{ kcal mole}^{-1}) \)
**Purification and Analysis of Potassium Peroxysulphate**

B.D.H. 'AR' potassium peroxysulphate was recrystallized from water three times, powdered, and dried for three days in a vacuum desiccator over concentrated sulphuric acid at 30°C. This sample was then analysed by the method of Kolthoff and Carr (1953) utilizing the reaction

\[ \text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2 \]

the iodine being titrated with sodium thiosulphate.

The 0.1 M sodium thiosulphate was first standardized by titrating against the iodine liberated by ca. 0.1g KI (‘AR’ previously dried for 1½ hrs at 120°C) with ca. 1g HI (‘AR’) in the presence of 5-10 ml 2M H_2SO_4.

Four such determinations gave the concentration of the thiosulphate solution as 0.10025 M, 0.10020 M, 0.10019 M, 0.10017 M, giving a mean value of 0.100220 M Na_2S_2O_3.

Using two quantities of the potassium peroxysulphate (1.6069 x 10^{-3} and 1.6069 x 10^{-3} mole) in ca. 30 ml water to which potassium iodide (4g) was added. After acidifying with 1 to 2 ml of 6N acetic acid the liberated iodine was titrated with the standardized thiosulphate solution. The reaction was found to take approximately 1 hour for completion.

In each case the volume of thiosulphate solution used was 32.07 ml corresponding to 1.6067 x 10^{-3} mole K_2S_2O_3.

Thus the potassium peroxysulphate was 100.000 ± 0.013% pure.
Chapter Seven References


Errors

For four or more observations the uncertainty interval is taken as twice the standard deviation of the mean, i.e. \( \pm \sqrt{\frac{s_i^2}{n(n-1)}} \) (as recommended by Rossini and Deming, 1939) where \( s_i \) is the deviation of the \( i \) th observation from the arithmetic mean, and \( n \) is the number of observations. The probability that the measured quantity lies within this range is 67\%.

For two of three observations the uncertainty interval is taken as the range.

Combination of errors

For the sum of a series of values \( \sum_{i=1}^{n} (x_i \pm s_{x_i}) \) where \( s_{x_i} \) is obtained as above, the total error is taken to be

\[ \pm \sqrt{\sum_{i=1}^{n} (s_{x_i})^2} \] giving a total value \( \pm \sqrt{\sum_{i=1}^{n} (s_{x_i})^2} \)
APPENDIX I

To determine whether a molecule such as 1,3,5-trioxan can exist without angle strain.

The problem may be phrased as follows:

Given a six-membered ring with internal angles $\alpha$ and $\beta$ which alternate around the ring, the sides are of constant length. What conditions are imposed upon the values of $\alpha$ and $\beta$?

Let us assume in the first instance that such restrictions are compatible with a chair form.

Then if the sides are represented by unit vectors $\mathbf{a}_1$ to $\mathbf{a}_6$ as shown such an assumption is equivalent to $\mathbf{a}_1 \cdot \mathbf{a}_4 = \mathbf{a}_2 \cdot \mathbf{a}_5 = \mathbf{a}_3 \cdot \mathbf{a}_6 = -1$

From the dig $\mathbf{a}_1 \cdot \mathbf{a}_2 = \cos(\pi - \alpha) = -\cos \alpha$ etc.

Thus so far we have

\[
\begin{align*}
\mathbf{a}_1 \cdot \mathbf{a}_2 &= -\cos \alpha \\
\mathbf{a}_2 \cdot \mathbf{a}_3 &= -\cos \beta \\
\mathbf{a}_3 \cdot \mathbf{a}_4 &= -\cos \alpha \\
\mathbf{a}_4 \cdot \mathbf{a}_5 &= -\cos \beta \\
\mathbf{a}_5 \cdot \mathbf{a}_6 &= -\cos \alpha \\
\mathbf{a}_6 \cdot \mathbf{a}_1 &= -\cos \beta \\
\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3 + \mathbf{a}_4 + \mathbf{a}_5 + \mathbf{a}_6 &= 0
\end{align*}
\]

(cyclic structure)

Now introduce a set of cartesian axes in unit directions $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$

Then

\[
\mathbf{e}_r = l_x \mathbf{i} + m_x \mathbf{j} + n_x \mathbf{k}
\]

where $l_x$, $m_x$, $n_x$ are the direction cosines of the vector $\mathbf{e}_r$

And let the axes be orientated and with the origin in such a way that

\[
\begin{align*}
\mathbf{e}_1 &= \mathbf{i} \\
\mathbf{e}_2 &= l_2 \mathbf{i} + m_2 \mathbf{j} \\
\mathbf{e}_3 &= l_3 \mathbf{i} + m_3 \mathbf{j} + n_3 \mathbf{k}
\end{align*}
\]

Then

\[
\begin{align*}
\mathbf{e}_4 &= -\mathbf{i} \\
\mathbf{e}_5 &= -l_2 \mathbf{i} - m_2 \mathbf{j} \\
\mathbf{e}_6 &= l_3 \mathbf{i} - m_3 \mathbf{j} - n_3 \mathbf{k}
\end{align*}
\]
Thus $s_1 - s_2 = -\cos \alpha \Rightarrow l_2 = -\cos \alpha$

$s_2^2 = 1 \Rightarrow l_2^2 + m_2^2 = 1$

so $m_2 = (1 - \cos^2 \alpha)^{\frac{1}{2}}$

$s_3 - s_4 = -\cos \alpha \Rightarrow l_3 = \cos \alpha$

$s_2 - s_3 = -\cos \beta \Rightarrow l_2 l_3 + m_2 m_3 = -\cos \beta$

\[ m_3 = \frac{-\cos \beta + \cos^2 \alpha}{(1 - \cos^2 \alpha)^{\frac{1}{2}}} \]

$s_2^2 = 1 \Rightarrow l_3^2 + m_3^2 + n_3^2 = 1$

giving $n_3^2 = 1 - \cos^2 \alpha - \frac{(-\cos \beta + \cos^2 \alpha)^2}{(1 - \cos^2 \alpha)}$

\[ n_3 = \frac{(1 - \cos^2 \alpha - \cos^2 \beta + 2\cos \alpha \cos \beta)}{(1 - \cos^2 \alpha)^{\frac{1}{2}}} \]

For physical reality the direction cosines must be real so in the case of $n_3$

\[ 1 - 2\cos^2 \alpha - \cos^2 \beta + 2\cos \alpha \cos \beta \cos^2 \alpha \geq 0 \quad \text{because} \quad 1 - \cos^2 \alpha \geq 0 \quad \text{all} \ \alpha \]

\[ (1 - \cos^2 \beta) - 2\cos^2 \alpha (1 - \cos^2 \alpha) \geq 0 \]

\[ (1 - \cos^2 \beta) = 2\cos^2 \alpha \geq 0 \]

\[ \cos \beta \geq 2\cos^2 \alpha - 1 \]

\[ \cos \beta \geq \cos 2\alpha \]

But $\cos \beta = \cos (2\pi - \beta)$

$\cos \beta \geq \cos 2\alpha$ and $\cos (2\pi - \beta) \geq \cos 2\alpha$

For $0 \leq \beta \leq \pi$

$\cos \beta$ is monotonic decreasing and with increasing $\beta$, $2\alpha$ increases

so $\beta \leq 2\alpha$

$\cos (2\pi - \beta)$ is monotonic decreasing but with increasing $\beta$, $2\alpha$ decreases

so $2\pi - \beta \geq 2\alpha$

Thus $\pi = \frac{\beta}{2} > \alpha > \frac{\beta}{4}$

This result can be expressed diagrammatically, see Figure 1.
The shaded portion represents the range of values of $\alpha$ which can be taken for a particular $\rho$.

So in the case of $1,3,5$-trioxan, if the $< 100^\circ$ angle is taken to be about $110^\circ$, then the $< 100^\circ$ angle can range from $180^\circ$ to $55^\circ$ i.e. $125^\circ$ to $55^\circ$ and the system still remains in an undistorted chair conformation. This range of values easily encompasses the actual value.

It is interesting to note that if $\alpha = \beta$,

then $\pi - \frac{\alpha}{2} \geq \alpha \geq \frac{\alpha}{2}$

i.e. $\alpha$ ranges from $0^\circ$ to $\frac{2\pi}{3}^\circ$ ($0^\circ$ to $120^\circ$); from six coincident lines through every possible bond angle to a planar regular hexagon.
Appendix Two

Expansion of the thermistor relationship \( R = A \exp \left( \frac{B}{T} \right) \) as a power series

Let \( T = K + \Theta \)

so \( R = A \exp \left( \frac{B}{K + \Theta} \right) \)

Now \( \frac{1}{K + \Theta} = \frac{1}{K} \left( 1 + \frac{\Theta}{K} \right)^{-1} \)

\[ = \frac{1}{K} \left( 1 - \frac{\Theta}{K} + \left( \frac{\Theta}{K} \right)^2 - \left( \frac{\Theta}{K} \right)^3 + \ldots \right) \left( \frac{\Theta}{K} - 1 \right) \]

so \( R = A \exp \frac{B}{K} \left\{ 1 - \frac{\Theta}{K} + \left( \frac{\Theta}{K} \right)^2 + \ldots \right\} \)

\[ = A \exp \frac{B}{K} \exp \left( -\frac{B \Theta}{K^2} \right) \exp \left( -\frac{B^2 \Theta^2}{2K^3} \right) \exp \left( -\frac{B^3 \Theta^3}{6K^4} \right) \ldots \]

\[ = A \exp \frac{B}{K} \left[ 1 - \frac{B \Theta}{K^2} + \frac{B^2 \Theta^2}{2K^3} - \frac{B^3 \Theta^3}{6K^4} + \frac{B^4 \Theta^4}{24K^5} \ldots \right] \]

\[ \times \left[ 1 + \frac{B^2 \Theta^2}{K^3} + \frac{B^4 \Theta^4}{24K^5} + \ldots \right] \]

\[ \times \left[ 1 + \frac{B^4 \Theta^4}{K^5} + \ldots \right] \]

Multiplying this out as far as fourth order terms of \( \Theta \)

\[ R = A \exp \frac{B}{K} \left[ 1 - \frac{B \Theta}{K^2} + \frac{B^2}{K^3} (\frac{B}{2K} + 1) \Theta^2 - \frac{B^3}{K^4} (\frac{B^2}{6K^2} + \frac{B}{K} + 1) \Theta^3 \right. \]

\[ + \frac{B^4}{K^5} (\frac{B^3}{24K^3} + \frac{B^2}{2K^2} + \frac{B}{K} + 1) \Theta^4 \ldots \]

Now when \( \Theta = 0 \), \( R = A \exp \frac{B}{K} = R_K \)

Also take a typical value of \( B \) as \( 3000 \) \( K \)

and \( K = 300 \)

so \( R = R_K \left[ 1 - 0.03333 \Theta + 0.00067 \Theta^2 - 0.00010 \Theta^3 \right] \)
Appendix Three

To justify that 

\[
\frac{\text{Heat of reaction}}{\text{Heat of calibration}} = \log \frac{R_1}{R_2} \left/ \frac{\log R_2}{\log R_0}\right.
\]

are the initial and final resistances of the thermistor during reaction, and 

\(R_3\) and \(R_4\) apply to the calibration. It is assumed the reaction is exothermic.

If the heat capacity of the calorimeter is assumed to remain constant 
during reaction and calibration period,

then \[
\frac{\text{Heat of reaction}}{\text{Heat of calibration}} = \frac{T_2 - T_1}{T_4 - T_3}
\]

where \(T_1\) and \(T_2\) are initial and final temperatures during reaction \(T_3\) and \(T_4\) 
are initial and final temperatures during calibration.

Now for a thermistor \( R = \text{Aexp} \frac{B}{T} \)

where \(R\) is resistance

\(T\) is absolute temperature

\(A\) and \(B\) are constants

Let \(T_1\) correspond to \(R_1\); \(T_2\) to \(R_2\); \(T_3\) to \(R_3\); \(T_4\) to \(R_4\)

then 

\[
\frac{T_2 - T_1}{T_4 - T_3} = \frac{\frac{1}{R_2}}{\frac{1}{R_3}} = \frac{\ln \frac{R_2}{R_3}}{\ln \frac{R_1}{R_0}} = \frac{\ln \frac{R_2}{R_3}}{\ln \frac{R_1}{R_0}}
\]

\[
= \left(\frac{\ln \frac{R_2}{R_3}}{\ln \frac{R_1}{R_0}}\right) \left(\frac{\ln R_1 - \ln A}{\ln R_2 - \ln A}\right) \left(\frac{\ln R_3 - \ln A}{\ln R_4 - \ln A}\right)
\]

Now consider \[
\frac{\ln R_3 - \ln A}{\ln R_1 - \ln A}
\]

If the initial reaction temperature corresponding to \(R_1\) is close to 
the initial calibration temperature, corresponding to \(R_3\)

Then \(R_3 = R_1 + r_1\), where \(r_1\) is small

Thus 

\[
\frac{\ln R_3 - \ln A}{\ln R_1 - \ln A} = \frac{\ln R_1 - \ln A + \ln(1 + \frac{r_1}{R_1})}{\ln R_1 - \ln A}
\]

Because \(r_1\) is small \(\frac{r_1}{R_1}\) is very small and so \(\ln(1 + \frac{r_1}{R_1})\) may be approximated 
to \(\frac{r_1}{R_1}\) by Taylor expansion.
\[
\ln R_1 - \ln A \approx 1 + \frac{R_1}{2 \ln R_1}
\]

Typically \( R_1 = 5000 \text{ ohms} \)

\( A = 0.05 \text{ ohms for an } 753 \text{ thermistor} \)

Thus \( \frac{R_1}{2 \ln R_1} \ll \frac{R_1}{50,000} \)

Therefore for this to exceed 0.1% \( R_1 < 30 \text{ ohms} \).

So the approximation is valid to within 0.1% if the initial and final resistances during calibration are both within 40 ohms of the initial and final reaction resistances, a condition which is very easy to realize in practice.
Appendix Four. Part I

To determine the effect of particles present in the calorimeter on the heat of stirring assuming

1) that the rate of reaction of the particles is first order with respect to their surface area

2) that the heat of stirring due to the presence of particles is proportional only to their mass at any given time.

Referring to Figure 6.1 page

Let heat of stirring due only to particles, \( \frac{dW}{dt} \), be \( W_0 \)

Let heat of stirring when no particles are present be \( W_1 \)

Heat of stirring due to particles at any other time except \( t_A \) is \( W \)

Let mass of particles at initial time \( t_A \) be \( M_0 \)

Thus at any time \( W = aM \) where \( M \) is mass of particles at that time, and \( a \) is a constant.

In particular at time \( t_A \); \( a = \frac{M_0}{W_0} \)

Now for any solid at fixed shape (Volume)\( ^{1/3} \) \( \propto \) (Surface Area)\( ^{2/3} \)

But volume \( \propto \) mass

So assuming that during reaction the shape of the particles does not alter, but only their size

\[ M^{\frac{1}{3}} \propto A^{\frac{2}{3}} \quad (A \text{ is surface area}) \]

\[ M^{\frac{1}{3}} = C A^{\frac{2}{3}} \quad (C \text{ is a constant}) \]

\[ A = \frac{1}{C} M^{\frac{2}{3}} \]

Now for a first order reaction rate w.r.t. surface area

\[ \frac{dM}{dt} = -bA \quad (b \text{ is a constant}) \]

Substituting for \( A \)

\[ \frac{dM}{dt} = -b \cdot \frac{1}{C} M^{\frac{2}{3}} \]

\[ M = \frac{b^3}{27c^2} (t - t_e)^3 \quad \text{where} \quad t = t_e \quad \text{when} \quad M = 0 \]
Now when $t = t_1$, $m = M_0$

So $M_0 = \frac{b^3}{27\rho^3} (t_2-t_1)^3$

Substituting this value for $\frac{b^3}{27\rho^3}$ in the above expression for $M$

$$M = \frac{M_0}{(t_2-t_1)^3} (t_2-t)^3$$

Now $a = \frac{W_0}{M_0} = \frac{W}{M}$

or

$$\frac{M}{M_0} = \frac{W}{W_0}$$

Thus

$$W = \frac{M_0W}{(t_2-t_1)^3} (t_2-t)^3$$

So the total heat of stirring at any time

$$\frac{dT}{dt} = W_1 + W$$

$$= W_1 + \frac{M_0W}{(t_2-t_1)^3} (t_2-t)^3$$

$$T = T_2 + W_1 (t_2-t) - \frac{M_0W}{4(t_2-t_1)^3} (t_2-t)^4$$

Thus when $t = t_1$ and $T = T_2$

$$\frac{T_2 - T_1}{t_2-t_1} = W_1 + \frac{1}{4} \frac{M_0W}{t_2-t_1}$$

Part II

Assuming the kinetics in Part I, to determine the temperature increase

in terms of time of reaction

From Part I

$$M = \frac{M_0}{(t_2-t_1)^3} (t_2-t)^3$$

Now rate of increase in temperature in proportional to rate of
depletion of the particles

i.e. $\frac{dT}{dt} = - \frac{dm}{dt} \quad (p \text{ is a constant)}$
Thus \( \frac{dx}{dt} = \frac{3p \rho_0}{(t_2-t_1)^3} \), \( (t_2-t)^2 \)

\[ T = \frac{-p \rho_0}{(t_2-t_1)^3} \frac{(t_2-t)^3}{(t_2-t_1)} + \text{constant} \]

which gives \( T - T_1 = p \rho_0 \left( 1 - \frac{(t_2-t)^3}{(t_2-t_1)^3} \right) \)

i.e. \( T - T_1 \propto (t_2-t)^3 \)
Appendix Five

The calorimeter described in Chapter Five may be considered to be a reaction vessel containing a thermally homogeneous fluid which changes its temperature over certain periods due to changes taking place within it (either chemical reaction or electrical calibration and heat of stirring). Temperature gradients exist between the fluid and the other parts of the calorimeter and the whole system is immersed in an enclosure whose temperature will be considered to be maintained precisely at the same temperature as the calorimetric fluid. Heat exchange, therefore, takes place between the calorimeter fluid and the calorimeter and also between the calorimeter and the surrounding enclosure. The question which arises is 'does the total heat exchange involved when the calorimeter fluid changes temperature from $T_1$ to $T_2$ depend on the temperature time profile?' An analytic approach to this question will now be presented.

Let the temperature of the calorimeter fluid and the outside temperature be $\Theta$.

Let us suppose that there is an 'average temperature' of the calorimeter $\phi$ such that heat transfer from $\Theta$ to $\phi$ is in accordance to a first order rate law. This assumption will presumably become more and more realistic as any temperature differences in the calorimeter tend to zero.

Let the rate of heat of stirring be $w$

Let the rate of heating due either to a reaction or calibration be expressed as a function of time $f(t)$

For simplicity only an exothermic reaction will be considered, i.e. $f(t) \leq 0$ and $\Theta > \phi$

Then $\frac{d\Theta}{dt} = f(t) - a(\Theta - \phi) + w$ \hspace{1cm} (a > 0) \hspace{1cm} (1)

and $\frac{d\phi}{dt} = b_1(\Theta - \phi) + b_2(\Theta - \phi)$ \hspace{1cm} ($b_1, b_2 > 0$)

where $b_1(\Theta - \phi)$ represents heat transfer from the calorimeter fluid to the cold parts of the calorimeter, and $b_2(\Theta - \phi)$ represents heat transfer from outside.
Hence \( \frac{d^2\theta}{dt^2} = b(\theta - \beta) \) where \( b = b_1 + b_2 \) \( \ldots \ldots \) (2)

From (1) and (2) we obtain

\[
\frac{d^2\theta}{dt^2} + (a+b) \frac{d\theta}{dt} = \frac{d\beta(t)}{dt} + b\theta
\]  

\( \ldots \ldots \) (3)

and

\[
\frac{d^2\phi}{dt^2} + (a+b) \frac{d\phi}{dt} = b\phi(t) + bw
\]  

\( \ldots \ldots \) (4)

Solving for \( \theta \) and \( \phi \)

\[
\theta = \exp(-(a+b)t) \int f(t) \exp(a+b)t \, dt + b\exp(-(a+b)t) \int \exp(a+b)t \, f(t) \, dt \, dt \]

\( \ldots \ldots \) (5)

\[
\phi = b\exp(-(a+b)t) \int \exp(a+b)t \, f(t) \, dt + \frac{bw}{(a+b)} t = \frac{bw}{(a+b)} t
\]

\( \ldots \ldots \) (6)

From these equations we can obtain \( H, K, G, J \) the arbitrary constants in terms of \( \theta, \phi \) and \( \int f(t) \, dt \) when \( t = 0 \)

i.e. \( \theta_0, \phi_0 \int f(t) \, dt \)

During the fore-period, when in equilibrium

\[
\phi_0 = \theta_0 = \frac{w}{(a+b)}
\]

showing the temperature effect of the heat of stirring.

Assuming that the heat of stirring does not alter during reaction period and after-period and the reaction takes from \( t = 0 \) to \( t = \tau \) and \( \theta_F \) and \( \phi_F \) are taken to be the temperatures of the after-period extrapolated back through the reaction period to \( t = 0 \)

\[
\theta_F = \frac{b}{(a+b)} \int_0^\tau f(t) \, dt + \theta_0
\]

\[
\phi_F = \frac{b}{(a+b)} \int_0^\tau f(t) \, dt + \theta_0 = \frac{w}{(a+b)}
\]

The final temperatures \( \theta_F \) and \( \phi_F \) are thus not dependent on \( f(t) \) but only on \( \int f(t) \, dt \), i.e. the total temperature rise \( \theta_F - \theta_0 = \phi_F - \phi_0 = \frac{w}{(a+b)} \int_0^\tau f(t) \, dt \)

is therefore proportional to the area under the \( f(t) \) vs \( t \) profile, which represents the heat of reaction, and not on the shape of the reaction profile.