The Synthesis and Thermochemistry
of
Organoboron and Phosphorus Compounds

A Thesis submitted by

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"To all those who wished me to reach this stage"

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ABSTRACT

The synthesis and standard heats of formation of some substituted arylboroxines are reported. Two new arylboroxines, p-tert-butylphenylboroxine and p-trifluoromethylphenylboroxine, have been prepared and characterized. The effect of substituting the phenyl ring of triphenylboroxine by, p-fluoro, p-chloro, p-bromo, p-methoxy, p-methyl and o-methyl groups was considered in terms of resonance stabilization of the boroxines and the strength of the (aryl) carbon to boron bond. While para-substitution increases the stability of the arylboroxines, ortho substitution decreases it by steric effects.

Three substituted aryldichloroboranes were synthesized and thermochemically studied. In ortho-tolyldichloroborane σ- overlap between the ortho-hydrogen and chlorine atoms of the dichloroboryl group is proposed to explain the enhanced stability of this compound. Steric effects in mesityldichloroborane appear to be dominant and destabilize this compound.

Several substituted aryldihydroxyboranes were prepared. Three of them, para-tolyl, ortho-tolyl and para-carboxyphenyldihydroxyboranes were studied thermochemically.

Solution reaction calorimetry and combustion calorimetry of some phosphorus compounds are reported and standard heats of formation of these compounds were determined.

Several simple aliphatic diols were combusted in a static bomb calorimeter and their standard heats of formation were derived.

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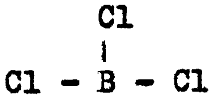
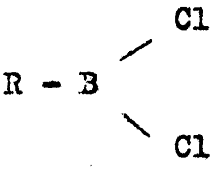
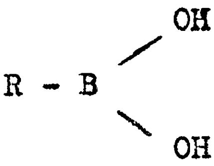
PART I

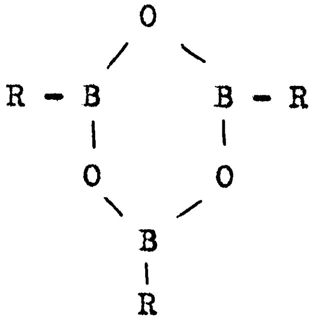
ORGANOBORON COMPOUNDS

SECTION I

NOMENCLATURE

The nomenclature of boron compounds has been in a state of flux.[1-7] Recently the American Chemical Society Council has approved a nomenclature for boron compounds[8] and this is as follows:

 $\mathrm{H-\overset{\overset{H}{\vert}}{B}-H}$	Borane
 $\mathrm{R-\overset{\overset{R}{\vert}}{B}-R}$	Tri-alkyl (or aryl) borane
 $\mathrm{RO-\overset{\overset{OR}{\vert}}{B}-OR}$	Tri-alkoxy (or phenoxy) borane
 $\mathrm{Cl-\overset{\overset{Cl}{\vert}}{B}-Cl}$	Boron trichloride
	Alkyl (or aryl) dichloroborane
	Alkyl (or aryl) dihydroxyborane



Tri-alkyl (or aryl) boroxine

INTRODUCTION

There has been rapid development of research in the field of boron chemistry with respect to industrial, technical and medicinal applications.

Within the last fifteen years the chemistry of boron compounds has been exhaustively reviewed, e.g. boron-hydrogen,[9,12,13,15,20] boron-carbon,[10,11,16,18,20,27] boron-halogen,[10,16,17,22,23] boron-phosphorus,[24] boron oxygen[10,16,24] and boron-nitrogen[14,21,25,26] compounds.

Many books[28-33] dealing with boron compounds are also available and cover most of the recent knowledge about boron and its compounds.

The most general procedure for the preparation of organoboron compounds is the condensation of a boron compound with an organic halide in the presence of an active metal as the condensing agent.[34]

$$BY_3 + 6M + 3RX \longrightarrow BR_3 + 3MY + 3MX$$

Y = halide, oxide or alkoxide

X = halide

M = Li, Na, Mg, Zn, Al, Hg or Sn.

R = alkyl or aryl group

In most cases the intermediate metal-organic halides are isolated and reacted with a suitable substrate resulting in the transference of organic group from metal to boron. The boron substrate may be chosen from a wide range of compounds. The most common are boron halides, trialkoxyboranes and trialkoxyboroxines.[64] Some of the reactions are shown in the following equations:

$$BX_3 + \left[\begin{array}{llll} Ar_2Hg & \xrightarrow{\hspace{2cm}} & ArBX_2 + ArHgX & \ldots (46,47) \\ SnR_4 & \xrightarrow{\hspace{2cm}} & RBX_2 + RSnX_3 & \ldots (48\text{-}50) \\ 3RMgX' & \xrightarrow{\hspace{2cm}} & R_3B + 3MgXX' & \ldots (54,55) \\ 4RMgX' & \xrightarrow{+H_2O} & (R_2B)_2O + 4MgXX' + 2HX & \ldots (53) \\ AlR_3 & \xrightarrow{\hspace{2cm}} & R_3B + AlX_3 & \ldots (56\text{-}58) \\ ZnPh_2 & \xrightarrow{\hspace{2cm}} & 2PhBX_2 + ZnX_2 & \ldots (61) \end{array}\right.$$

$$\begin{array}{lll}
B(OR)_3 + \left[\begin{array}{l} R'MgX \\ AlR'_3 \\ LiPh.NMe_2 \end{array}\right. & \begin{array}{l} \longrightarrow R'B(OR)_2 + MgXOR \\ \longrightarrow R'_3B + Al(OR)_3 \\ \longrightarrow pMe_2N.Ph.B(OR)_2{+}LiOR \end{array} & \begin{array}{l} \ldots\ (35\text{-}44) \\ \ldots\ (59) \\ \quad\ (63) \end{array} \\
(ROBO)_3 + R'MgX & \begin{array}{l} \longrightarrow R'_2B(OR) \\ \searrow\ (R'BO)_3 \text{ or } (R'_2B)_2O \end{array} & \begin{array}{l} \ldots\ (51) \\ \ldots\ (52) \end{array} \\
BAr_3 + LiAr & \longrightarrow LiB(Ar)_4 & \ldots\ (60)
\end{array}$$

The preparation of aryldihydroxyboranes by the action of a Grignard reagent on trimethoxyborane is conventional. Khotinsky and Melamed[35] used trimethoxyborane and obtained a 50% yield. Gilman and Vernon[36] claimed 86% yields by the same procedure. Bean and Johnson[39] reported that trimethoxyborane was not suitable for the preparation of aryldihydroxy boranes, and claimed an improved yield by using tri-n-butoxyborane at low temperature (-60°C).

Washburn et al.[43] reinvestigated the reaction of Grignard reagents with trimethoxyborane and finally developed an incremental method for the preparation of substituted aryldihydroxyboranes.[43] This method has been used for the preparation of aryldihydroxyboranes in this research.

An alternative synthesis of aryldihaloboranes has been the reaction of diarylmercury on boron halides at elevated temperature and pressure. Gilman and Moore[47] reinvestigated the reaction and reported that the reaction of diarylmercury and boron trichloride occurs very readily at room temperature and atmospheric pressure but it is not instantaneous and needs stirring for thirty minutes. Moreover, 100% excess of boron trichloride was necessary for the completion of reaction. They prepared aryldihydroxyboranes by the hydrolysis of these aryldihaloboranes and claimed 70% yield of the recrystallized dihydroxyborane. These authors also reported that the substituent in the aryl radical attached to the organomercury compound has a distinct effect upon the reaction. The hydroxy and amino groups, which aid electrophilic substitution reactions, not only seem to aid the displacement of mercury by boron but also the displacement of boron by a proton. Thus in these cases the required aryldihaloboranes could not be obtained. The carboxy group on the other hand decreases the reactivity of the aryl radical so that the mercury is not displaced by boron even at elevated temperature.

Gerrard et al.[65] improved the reaction of arylmercury compounds with boron halides. They prepared a number of substituted arylhaloboranes by the reaction of boron trichloride and tribromide with substituted arylmercury halides in refluxing benzene. In this method 100% excess of borontrichloride is not required, the reaction is quantitative. However a slight excess of boron halide is helpful to ensure complete reaction. This method is better than the other available methods[67-69] and shows little isomerization.[66]

A brief discussion of isomerization, observed in orthotolyldihaloboranes, is relevant in view of the unsuccessful synthesis of 2,6,dimethylphenyldihaloborane. Eggers and Kettle[66] investigated the isomerization of o-tolyldihaloboranes and o-xylyldihaloboranes and concluded that this isomerization is due to the migratory aptitude of the o-methyl due to steric crowding. They also proposed that this rearrangement of methyl groups occurs only in the transition state involving the aromatic system and boron halides.

Muettertles[68] investigated this isomerization via the preparation of these compounds by reaction of boron halides and hydrocarbons in the presence of Al. He emphasised the presence of hydrogen halide to form a couple, $HCl-AlCl_3$, which acts reversibly with the hydrocarbons. He mentioned also that the aryl-dihaloboranes are stable up to 150°C, undergoing only a slight decomposition at this and higher temperatures.

He also reported that the p-xylenes rearrange at 150°C to meta-xylenes and this can react with boron-trichloride in the presence of $HCl-AlCl_3$ to give a stable meta-xylyldichloroborane. The isomerization of alkylbenzenes[70] has also been reported earlier and the protonation of aromatic hydrocarbons was suggested in the transition state complex, which rearranges to a stable form. Recently Brouwer[71] studied the protonation in alkylbenzenes and halobenzenes by proton magnetic resonance spectroscopy. He observed that 2-chlorotoluenium and 2-bromotoluenium ions rearrange to stable 3-halo-toluenium ions in the presence of $HF-SbF_5$. The presence of hydrogen halide with the Lewis acid seems, therefore, to be necessary for rearrangement.

Eggers and Kettle[66] suggested that the isomerization of o-tolyldihaloborane, prepared by the reaction of o-tolylboroxine and boron trichloride, does not seem to have any relation to the presence of hydrogen halide. It appears that the boroxine was slightly hydrated and decomposed on heating. The possibility of decomposition of o-tolylboroxine by heat is logical according to our thermochemical results. The B-C bond in o-tolylboroxine has been found to be weaker than that of the p-tolylboroxine.

The steric effect in the transition state of o-arylmercuric chloride and boron trichloride has also been observed in the case of 2,6 dimethylphenyldichloroborane preparation. We could not isolate any aryl dihaloborane and it seems that the presence of two vicinal methyl groups (i.e. 2,6 dimethyl groups) prevents the formation of above aryldihaloborane.

The thermochemistry of organometallic compounds has always been a difficult problem.[76] Combustion calorimetry, although applied to various organometallic compounds,[72-75] is being developed gradually. A complete oxidation of the organometallic compounds is not always attained and some metal residue may be left after the combustion, in a partially oxidized state, as a mixture of metal oxides, carbonate and carbide. The development of rotating bomb calorimetry and fluorine-bomb calorimetry appears to be a major advance in solving this problem.[76-78]

The thermochemistry of organoboron compounds is still faced with the above difficulties[79] and it has been mainly due to Skinner et al.[75] who considered other methods and developed reaction calorimetry to obtain an appreciable volume of thermodynamic data on boron compounds. They discovered that several typical reactions of organoboron compounds were quite suitable for measuring heats of formation. Thus hydrolysis hydroboronation, aqueous oxidation and reduction reactions of a number of organo-boron compounds have been studied.

The above work was mainly concerned with aliphatic boron compounds. They determined the heat of formation of many alkoxyboranes, alkylaminoboranes and alkylhaloboranes[81] and calculated from them B-C, B-N and B-O bond energies in these compounds.[82] These values need some correction due to a new heat of formation of boron in the gaseous state (134.5 kcal.mole^{-1}).[81]

The thermochemistry of arylboron compounds has been given a little attention.. Finch and Gardner[83] exploited thermochemically an "oxidative hydrolysis" reaction in a basic medium and determined the heat of formation of phenyldihydroxyborane, diphenylhydroxyborane, triphenylboroxine and diphenylborinic anhydride. These compounds are the "key" compounds in arylboron chemistry and the method seems to be a promising one. The heat of formation of diphenylhydroxyborane has been improved subsequently.[85] Recently hydrolysis of triphenylborane and some phenylhaloboranes have been thermochemically studied by the same group of workers[84] who discussed these structures on the basis of strength of the phenyl-boron bonds and the π-electronic contribution to the bond. This was a major step towards the thermochemical study of arylboron compounds and produced some important data for future work in this field. An exhaustive review on the thermochemistry of boron compounds has been published by A. Finch and P.J. Gardner.[79]

The thermochemistry of substituted arylboron compounds received little attention and this is the principal reason that these compounds are the subject of this thesis.

The substituent effect in arylboron compounds has been studied earlier, but in relation to other fields. Branch et al.[41] reported pK_a measurements on substituted aryldihydroxyboranes and correlated the strength of these acids on the basis of resonance and the electronegativity of the substituent groups. In general electron attracting groups increased, and the electron donating groupsdecreased, the acidic strength of these compounds. The pK values of these compounds has been compared with those of substituted benzoic acids and structural effects were discussed.[86]

Kuivila et al.[42] studied the kinetics of various reactions of substituted aryldihydroxyboranes. They reported on bromodeboronation, oxidative deboronation and protodeboronation and observed that in general these reactions obeyed the Hammett equation.

Beachell and Beistel[87] investigated the proton and "B magnetic resonance spectra of a series of para-substituted aryldihydroxyboranes. They noted a linear correlation between the "B chemical shift (relative to phenyldihydroxyborane) and the corresponding Hammett constants for the substituents.

In a recent investigation,[88] the substituted dihaloboranes have been studied by several physical methods and the results of dipole moment measurements, ^{1}H, ^{19}F, ^{11} B n.m.r. and infrared spectroscopy are discussed in relation to structural parameters in these compounds.

The infrared spectra of substituted aryldihydroxyboranes have been discussed by several authors.[89] Sarafanowa and Makoza[90] reported the largest collection of infrared data on substituted aryldihydroxyboranes and discussed it on the basis of hydrogen bonding present in these compounds. Gerrard et al.[91] reported the infrared spectra of some substituted aryldihaloboranes and made assignments for the B-halogen stretching and deformation frequencies. Eggers[88] also discussed infrared studies of some substituted aryldihaloboranes in relation to the strength of B-aryl bond.

The arylboroxines have been least studied. Ultraviolet spectra of triphenylboroxine and some related compounds have been reported.[92] Armstrong and Perkins[93] quantitatively evaluated the electronic densities and bond orders in these compounds. Surprisingly they mention that the substitution in the benzene ring in aryldihydroxyboranes has no effect on the B-C bond order. Also, the charge distribution in the boroxine rings show that six electrons are more localized than in borazine.

Triphenylboroxine has been thermochemically studied and has been discussed in terms of strain energy in the ring.[83] This thesis reports the first thermochemical studies on the substituted triarylboroxines and the data will be interpreted in terms of various physical quantities, for example, resonance energies, B-C bond order, electronegativity of the substituted groups etc.

Since boron-carbon bond energies are discussed in this thesis it is, therefore, necessary to clarify the idea of "bond energy". In principle bond energies can be classified into two groups,[94]

(a) Standard bond dissociation energies DE^{o} or DH^{o}

(b) Mean bond dissociation energies $\bar{DE}^{o}$ or $\bar{DH}^{o}$.

The standard bond dissociation energy is the energy liberated from a dissociation reaction, carried out in an ideal gas state at $0^{o}K$, where the products are in their "ground states". This can be represented as follows,

$$AB_{(g)} \xrightarrow{\hspace{3cm}} A_{(g)} + B_{(g)}, \ DE^{o}$$

Dissociation energies which have been calculated from spectral data refer to this temperature but those derived from other sources refer to room or higher temperatures. However the difference is usually small.

Thus bond dissociation energies measure in a quantitative way the force holding together the atoms of a molecule. The nature of these forces is quite complicated and is clarified in Fig. 1. If the potential energy of interaction of a neutral species A - B (held together by a chemical bond between A and B) is plotted as a function of bond distance r_{AB}, the minimum in the curve corresponds to the distance r_0, which is the equilibrium separation of A and B in the stable molecule. The potential energy of A and B at this point is $-V_0$ measured with respect to zero potential energy at infinite separation. The actual work required to "completely" separate A and B from each other is actually slightly less than V_0 by an amount which is due to the fact that in A - B molecule, A and B are not at rest relative to each other, but possess vibrational energy (the zero-point energy).

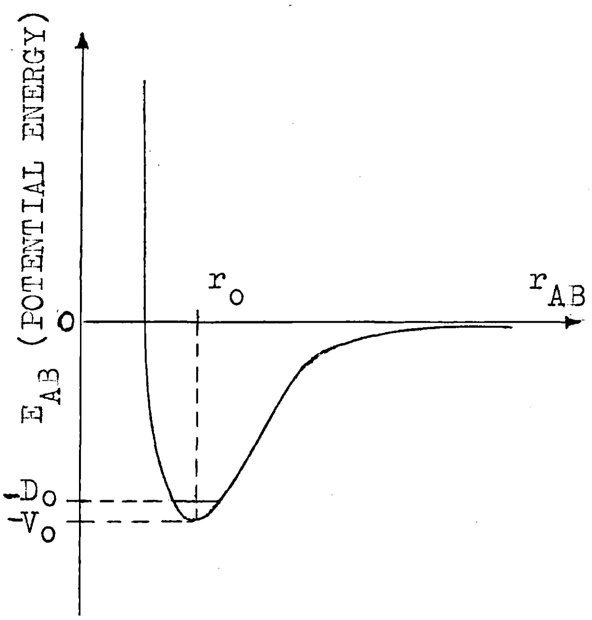


Fig. 1. Potential Energy Diagram for a Diatomic Molecule

For simple diatomic molecules the zero-point energy is equal to $\frac{1}{2}h\nu_o$, where ν_o is the fundamental vibration frequency and h is the Planck's constant.

In general $DH^o(A-B)$ differs from both D_o and V_o. The quantity D_o (A-B) (or DE^o) corresponds to the bond dissociation energy at 0°K all species considered to be ideal gases. The two quantities $DH^o(A-B)$ and $D_o(A-B)$ differ by the net enthalpy change in raising the system from 0°K to the standard temperature of 25°C, which is usually negligible.

The standard bond dissociation energy can, therefore, be defined as the enthalpy change in the chemical process in which one mole of a specified bond is broken, reactant and products being in the hypothetical ideal gas state, at one atmosphere pressure and at 25°C. Thus if A-B represents a molecule with fragments A and B, then $DH^o(A-B) = \Delta H_r$ for the process,

$$AB(g) = A(g) + B(g)$$

In other words, it is the heat of atomization (ΔH^a) of the species in ideal gas state.

It is possible to calculate ΔH_f^a (enthalpy of formation from the atoms) from the equation

$$\Delta H_f^a = \Delta H_f^o \text{ (compound, gas)} - \Sigma \Delta H_f^o \text{ (atoms)}$$

where ΔH_f^a = Heat of formation from the atoms in gaseous state.

ΔH_f^o(compound, g) = Standard heat of formation of the gaseous compound.

$\Sigma \Delta H_f^o$ = Sum of the heats of formation of the gaseous atoms in their ground state.

Thus if the dissociation energy of a bond A - B and the heat of formation of the atoms A and B are known in gaseous state, then the heat of formation of the compound (in gaseous state) can be calculated as,

$$\Delta H_f^o \, AB = \Delta H_f^o \, A + \Delta H_f^o \, B - DH^o(A - B)$$

Conversely, this equation can be applied to determine bond dissociation energies.

In a polyatomic molecule like AB_n, A is attached to n similar atoms B and the process of atomization occurs as follows:

$$AB_n \longrightarrow AB_{n-1} + B, D_1$$

$$AB_{n-1} \longrightarrow AB_{n-2} + B, D_2$$

$$AB_{n-2} \longrightarrow AB_{n-3} + B, D_3$$

and so on.

Thus every step will show a different dissociation energy and the total energy liberated will be given by,

$$D_1 + D_2 + D_3 \ldots + D_n = D$$

and will always be the same.

We can represent this reaction as,

$$AB_{n(g)} \longrightarrow A_{(g)} + nB_{(g)}, \ \Delta H_r^o = n\bar{D}(A-B)$$

In case of a simple molecule CH_4, this corresponds to the chemical process of atomization.

$$CH_{4(g)} \longrightarrow C_{(g)} + 4H_{(g)}, \ 4\bar{D}(C-H)$$

and so

$$\bar{D}H^o = \frac{1}{4}\Delta H_r^o = \frac{1}{4}[4\Delta H_f^o H(g) + \Delta H_f^o C(g) - \Delta H_f^o CH_4(g)]$$

This is called the "mean bond dissociation energy" and is the "bond energy" used in thermochemical estimations and can be illustrated by the following cycle:

$$\begin{tikzcd}
AB_n(g) \arrow[rr, "\Delta H_a^o = -\Delta H_f^a"] & & A_{(g)} + B_{(g)} \\
& \text{elements } A + nB \text{ (standard states)} \arrow[ul, "{\Delta H_f^o[AB_n , g]}"] \arrow[ur, "\Sigma\Delta H_f^o(\text{atoms})"'] &
\end{tikzcd}$$

Since reliable values are available for the heat of formation of the gaseous atoms for most of the common elements,[95] only the standard heat of formation of the compounds in the gaseous state is needed to evaluate the bond energies.

Szwarc[96] has reviewed various methods for the determination of bond energies, while Benson[94] and Kerr[97] reviewed the bond dissociation energies in various organic and inorganic compounds.

In polyatomic molecules, with several different types of bonds (e.g. $Y - \underset{\substack{| \\ Z}}{\overset{\substack{W \\ |}}{M}} - X$), it is usually considered that each bond of a given type has a constant characteristic energy value transferable from one molecule to another. In other words, as a first approximation, bond energies are additive.

Skinner and Pilcher[95] have discussed the failure of exact addivity for these bond energies in hydrocarbons.

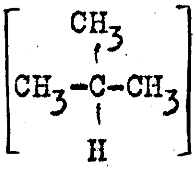
A number of empirical bond energy schemes are available which are limited to the aliphatic and aromatic hydrocarbons only. Benson et al.[99] applied their "Rules of Addivity of Group Properties" to a great number of organic, and inorganic molecules. Recently the same author extended these "Addivity Rules", with some refinement in their nomenclature, to organometallic compounds.[100] It is, therefore advantageous to describe how the above rules relate to some simple molecules.

A large molecule can conveniently be divided into groups, in such a way that any molecular property (e.g. ΔH_f^o) can be obtained with good precision by simply adding up the values for it assigned to each group. A group can be defined as any polyligated atom plus its near neighbour atoms. Thus all of the non-cyclic parrafin hydrocarbons can be composed from four groups, symbolized as,

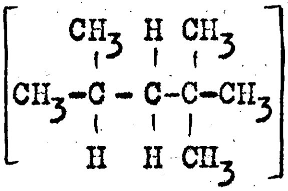
1. C — $C(H)_3$ (-10.08)
2. C — $(C)_2H_2$ (-4.95)
3. C — $(C)_3H$ (-1.48)
4. C — $(C)_4$ (+1.95)

where in brackets are the assigned partial molal enthalpies (in kcal.mole^{-1}) for each group. Thus for the calculation of heat of formation of gaseous ethane, isobutane and 2,4,4 trimethylpentane we use the above values as follows:-

$$\Delta H_f^o[CH_3-CH_3] = 2[C-C(H)_3] = -21.16 \text{ kcal.mole}^{-1}$$
(exp. -20.2 kcal.mole^{-1})

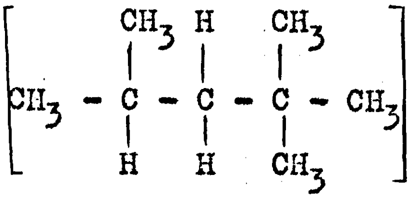


$$\Delta H_f^o\left[CH_3-\overset{CH_3}{\underset{H}{C}}-CH_3\right] = 3[C-C(H)_3] + 1[C-(C)_3H] = -31.72 \text{ kcal.mole}^{-1}$$
(exp. -32.2 kcal.mole^{-1})



$$\Delta H_f^o\left[CH_3-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3\right] = 5[C-C(H)_3] + 1[C-(C)_2H_2] + 1[C-(C)_3H] + 1[C-(C)_4] = -54.88 \text{ kcal.mole}^{-1}$$

In highly branched molecules (as above) small corrections (ca. 0.7 kcal.mole) are generally applied for the repulsion of non-nearest neighbours, so



$$\Delta H_f^o\left[CH_3-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3\right] = (-54.88 + 0.7) = -54.18\ \text{kcal.mole}^{-1}$$

(exp. -53.6 kcal.mole^{-1})

The thermodynamic conventions employed in this thesis are as follows:

(a) All reactions were carried out at 1 atmosphere pressure.

(b) The standard states for the reactants and products were their most stable forms at 25°C and one atmosphere pressure and their heat of formation is, therefore, denoted by ΔH_f^o.

(c) The heat of formation (ΔH_f^o) of the elements in their standard state are zero.

(d) When the reaction is exothermic the enthalpy change is given a negative sign and vice versa.

(e) All heat quantities are quoted in terms of the thermochemical calorie which is defined as,

1 calorie = 4.1840 abs. Joule

(f) When the reactions are carried out in solution the values for the heat of solution of various reactants and products are added to the standard heat of formation of those compounds.

(g) The reactions are carried out at dilutions for which further heat of dilution is assumed to be negligible.

(h) In general, the heat of mixing of the products was assumed to be zero.

For example the reaction of an aryl-dihydroxyborane with hydrogen peroxide in excess aqueous base is represented as follows:

$$PhB(OH)_2(\text{cryst.}) + [H_2O_2]_{aeb.} \longrightarrow [PhOH]_{aeb.} + [B(OH)_3]_{aeb.}, \Delta H_{obs.}$$

or

$$\Delta H_f^o[PhB(OH)_2, \text{cryst.}] = \Delta H_f^o[PhOH]_{aeb.} + \Delta H_f^o[B(OH)_3]_{aeb.} - \Delta H_f^o[H_2O_2]_{aeb} - \Delta H_{obs.}$$

The errors were evaluated as follows:

For four observations or less, the uncertainty interval was expressed as the range. For five observations or more, the uncertainty interval was expressed as twice the standard deviation of the mean.

SECTION 2

EXPERIMENTAL

(A) GENERAL TECHNIQUES.

(i) HANDLING and STORAGE.

Organoboron compounds are generally moisture and oxygen sensitive, so they were treated with maximum precautions and care. The compounds which were stable to moisture (like aryldihydroxyboranes) were crystallized from boiled (oxygen-free) distilled water and were stored in an atmosphere of (oxygen-free) nitrogen. The compounds stable to dry oxygen but affected by moisture (like triarylboroxine) were stored over anhydrous $CaCl_2$ and P_2O_5 and treated in an atmosphere of dry (oxygen-free) nitrogen to avoid any hydrolysis, dehydration or change in weight.

(ii) PURIFICATION OF REAGENTS AND SOLVENTS.

All of the liquid reagents (aryldihalides, trimethoxyborane, solvents etc.) were distilled before their use. The solid compounds (aryldihydroxyboranes, etc.) were crystallized, several times, from appropriate solvents and dried before their use. The purification of the solvents was affected as follows:

ETHER, was first dried (over $CaCl_2$ and sodium wire) then distilled from sodium and stored over sodium wire. It was used after filtration.

BENZENE(ANALAR) was distilled and stored over sodium.

TETRAHYDROFURAN[101], was distilled from sodium, and then from a little lithium aluminium hydride, and stored over sodium.

DIOXAN[102] was first distilled from solid sodium hydroxide and then from sodium. It was redistilled, from sodium before use.

ETHANOL and METHANOL[102], were first distilled, then refluxed over magnesium and a trace of iodine for twelve hours and distilled before use.

n-HEXANE[102] was fractionally distilled, through a 36 cm. long column, packed with helices and insulated with asbestos, over sodium and the fraction at 65-68°C was collected and used.

(iii) ELEMENTAL ANALYSIS.

Carbon, hydrogen and halogens were determined by A. Bernardt, Max Planck Institute, Mulheim, Germany.

Analysis of boron and easily-hydrolysable halogen was performed as follows:[105]

CHLORINE: Two methods were used.

Volhard Method.- The compounds (dihaloboranes, 0.2-0.4 g) were taken in an ampoule, which was broken under $\frac{N}{10}$ sodium hydroxide solution (50 ml.) and boiled. After acidification (conc. HNO_3), the solution was treated with a known excess standard silver nitrate solution. The white precipitate was filtered off and washed with acidified (HNO_3) distilled water and the filtrate (and washings) were titrated with ($\frac{N}{10}$) standard ammonium thiocyanate, using ferric ammonium alum as the indicator. The volume back-titrated was the excess silver nitrate solution added.

Mohr's Method.- The compounds (dihaloboranes, 0.2-0.4 g.) were hydrolysed with $\frac{N}{10}$ sodium hydroxide solution (50 ml.) and boiled for fifteen minutes. The solution, after cooling, was neutralized with dil. HNO_3 and titrated against standard ($\frac{N}{10}$) silver nitrate solution using potassium chromate as the indicator.

BORON: Two methods were used.

(a) The compounds (0.2-0.4 g.) were refluxed with sodium hydroxide solution ($\frac{N}{10}$, 100 ml) and hydrogen peroxide

(2.0 ml 30%), for twenty minutes, then neutralized with dilute hydrochloric acid (to a methyl red end point) and titrated with standard ($\frac{N}{10}$) sodium hydroxide solution, after addition of excess mannitol, using phenolphthalein as the indicator.

(b)[106] The organoboron compounds (0.2-0.4 g.) were digested with conc. H_2SO_4 (10 ml) and heated to complete charring of the substance. Then hydrogen peroxide (30% solution, 2-5 ml.) was added drop by drop, with heating, till the solution became clear. The solution was allowed to cool, methanol (100 ml.) was added (cautiously) and the trimethoxyborane (formed) was distilled in a conical flask (250 ml. capacity) containing distilled water (100 ml.). The trimethoxyborane, distilled, is hydrolysed with water to give boric acid, which after neutralization of the solution (methyl red) and addition of mannitol, was titrated with standard sodium hydroxide ($\frac{N}{10}$ solution).

(iv) SPECIAL TESTS:

The presence of mercury and bromine in aryldihaloboranes was checked before their use.

Mercury was tested for by hydrolysing the compound in sodium hydroxide solution, acidifying with conc. HCl and then passing H_2S gas. The test was always negative.

Bromine in the presence of chlorine was tested for as follows:[105]

The compound (ca. 1 ml.) was dissolved in sodium hydroxide solution ($\frac{N}{10}$, ca. 20 ml.), acidified with HNO_3 (conc.), and followed by the addition of carbon tetrachloride (ca. 2 ml.). Then $KMnO_4$ solution (saturated) was added dropwise to liberate the halogen. A yellow or orange colour in the CCl_4 layer would indicate the presence of bromine. The test was negative in all cases.

(v) Spectroscopy.

Infrared spectra of the compounds were recorded on a Perkin-Elmer 337 grating infrared spectrometer, using KBr optics. The infrared spectra of solids were taken in Nujol (mull) and those of liquids as films between two KBr plates.

Proton magnetic resonance spectra of the compounds were obtained with a Varian model HA60-IL spectrometer with tetramethylsilane as external reference.

(vi) POTENTIOMETRY.

All pH measurements were performed on a Universal Precision Potentiometer, model 79 pH meter, W.G. Pye and Co., Cambridge, England.

(vii) CALORIMETRY. The solution-reaction calorimetry was performed in a constant-temperature-environment calorimeter, designed in the laboratory. A full description of the method and the apparatus is given in Part II, page 164. The combustion calorimetry was carried out in a static bomb calorimeter, described on pages 176 ff.

(B) MOLECULAR WEIGHT DETERMINATIONS.

Two methods were used:

(i) the cryoscopic method and

(ii) the differential vapour pressure method.

(i) The cryoscopic method:

The cryoscope was constructed in the laboratory[108] and is a modification of Zemany's design.[109] The cryoscopic cell was of all glass construction [Fig. 2]. Agitation was automatic and effected by means of a chrome-plated stirrer actuated by an external solenoid. The intermittent pulse to the solenoid was supplied by a slowly rotating cam operating a microswitch [Fig. 3]. The temperature sensitive element was a thermistor [F-2311/300, Standard Telephone and Cables Ltd.] incorporated in a Wheatstone bridge connected to a sensitive galvanometer (Scalamp Galvanometer, 110 ohms, W.G. Pye and Co., Cambridge, England).

The cryoscope was first calibrated using a specially purified sample of naphthalene to determine the calibration

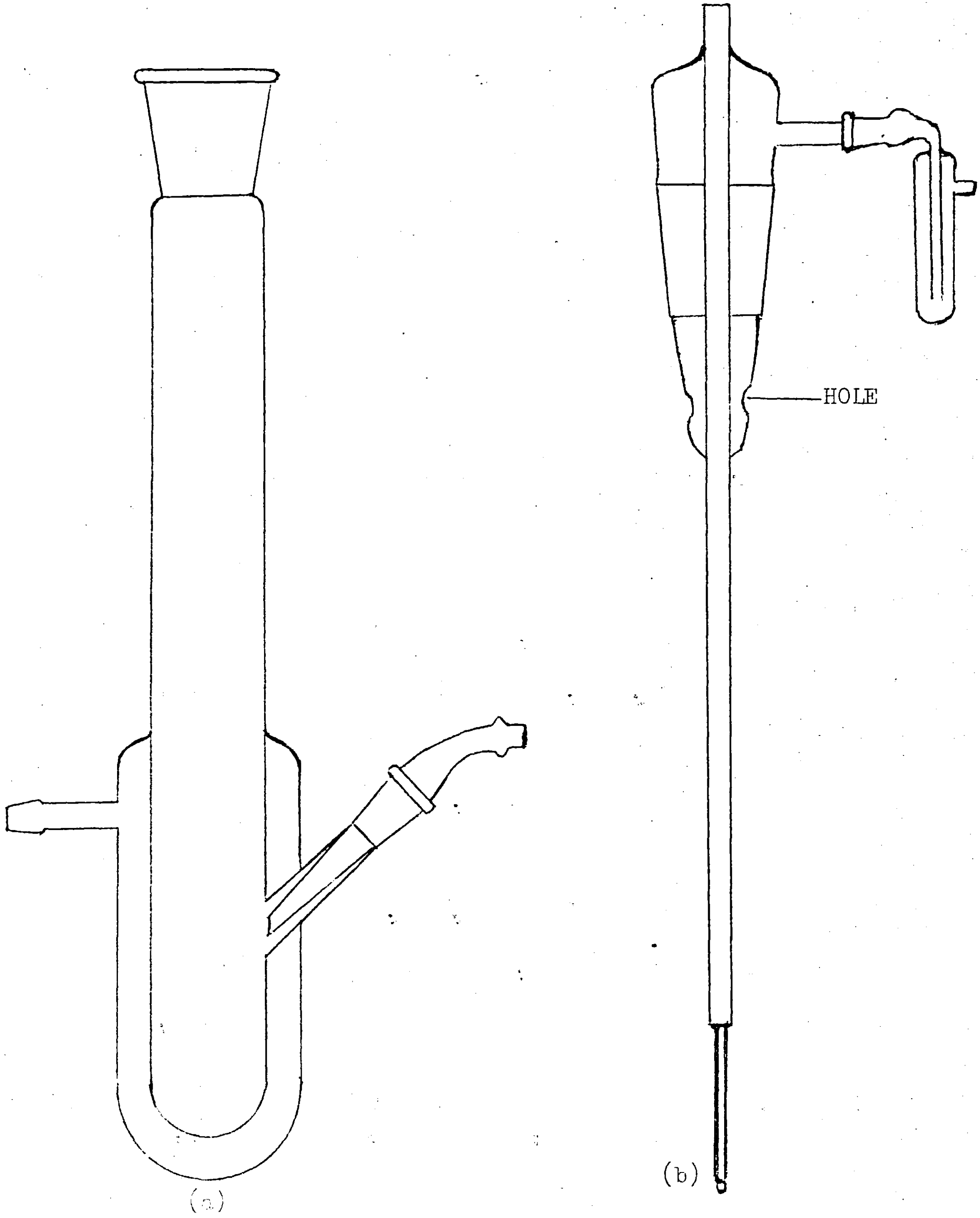


FIG. 2. (a) CRYOSCOPIC CELL AND (b) THERMISTOR

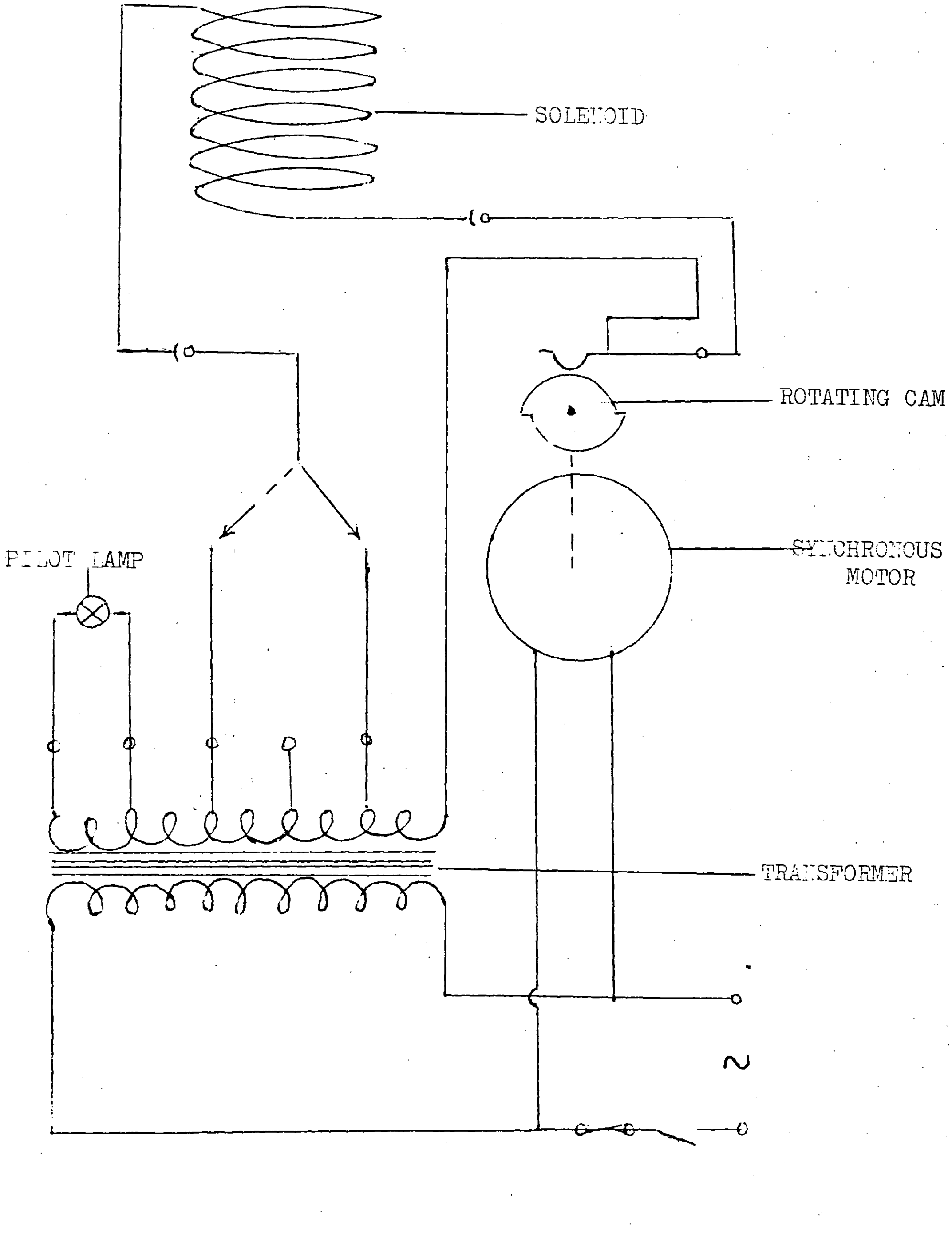


FIG. 3. MAGNETIC STIRRING CIRCUIT FOR CRYOSCOPE

constant (k) in the experimental equation,

$$M_2 = k \frac{m_2}{\Delta R}$$

where M_2 = Molecular weight of naphthalene.

m_2 = Concentration of naphthalene (g/10 ml. of benzene).

ΔR = Depression of the freezing point (in ohms).

The above equation is derivable from the Clausius-Clapeyron equation and the Raoult's Law, with the ideal dilute solution assumption.[110]

Thus, by determining the depression of freezing point (in ohms), at different concentrations, and plotting it against concentration, we obtain the calibration constant (k) for the specific solvent used with naphthalene as the reference compound. Naphthalene was used for the cryoscopic calibration, because it gives an ideal mixture up to almost eutectic concentrations in benzene.[111]

The reproducibility and accuracy of the results largely depends upon the purity and stability of the compounds rather than on the apparatus or the experimental method.[108]

PROCEDURE

(i) The cell was cleaned thoroughly and dried in an oven (110°C) overnight. It was cooled and flushed with dry nitrogen (oxygen-free). Cryoscopic solvent (10 ml.) was added, the thermistor introduced and the circuit connected.

(ii) The cell was lowered into a freezing mixture (ice + salt, -10°C) to approximately 2 cm. above the solvent level. The stirrer was started and the resistance reading (R_0) was taken, when the equilibrium between the frozen and liquid solvent was established.

(iii) In an accurately weighed syringe, made from precision glass tubing and the precision glass rod, the desired amount of the substance was compressed to form a pellet. The pellet was then dropped into the cryoscope, through the B10 socket and the B10 stopper (with B10 teflon sleeve) was replaced at once. The syringe was re-weighed accurately to determine the exact weight of the sample used.

(iv) When the sample had been added, the solution was stirred and allowed to warm until the sample had completely dissolved and the solvent had completely melted. The freezing point of this solution was then recorded using the above procedure.

(v) The sequence of operations was repeated over the desired concentration range and a graph of concentration (g/10 ml. solvent) vs. freezing point (ohms) was constructed. The molecular weight was computed, using the experimental equation $M = k \frac{m}{\Delta R}$, and the calibration constant (k). The results are reported in Section 5 page 122.

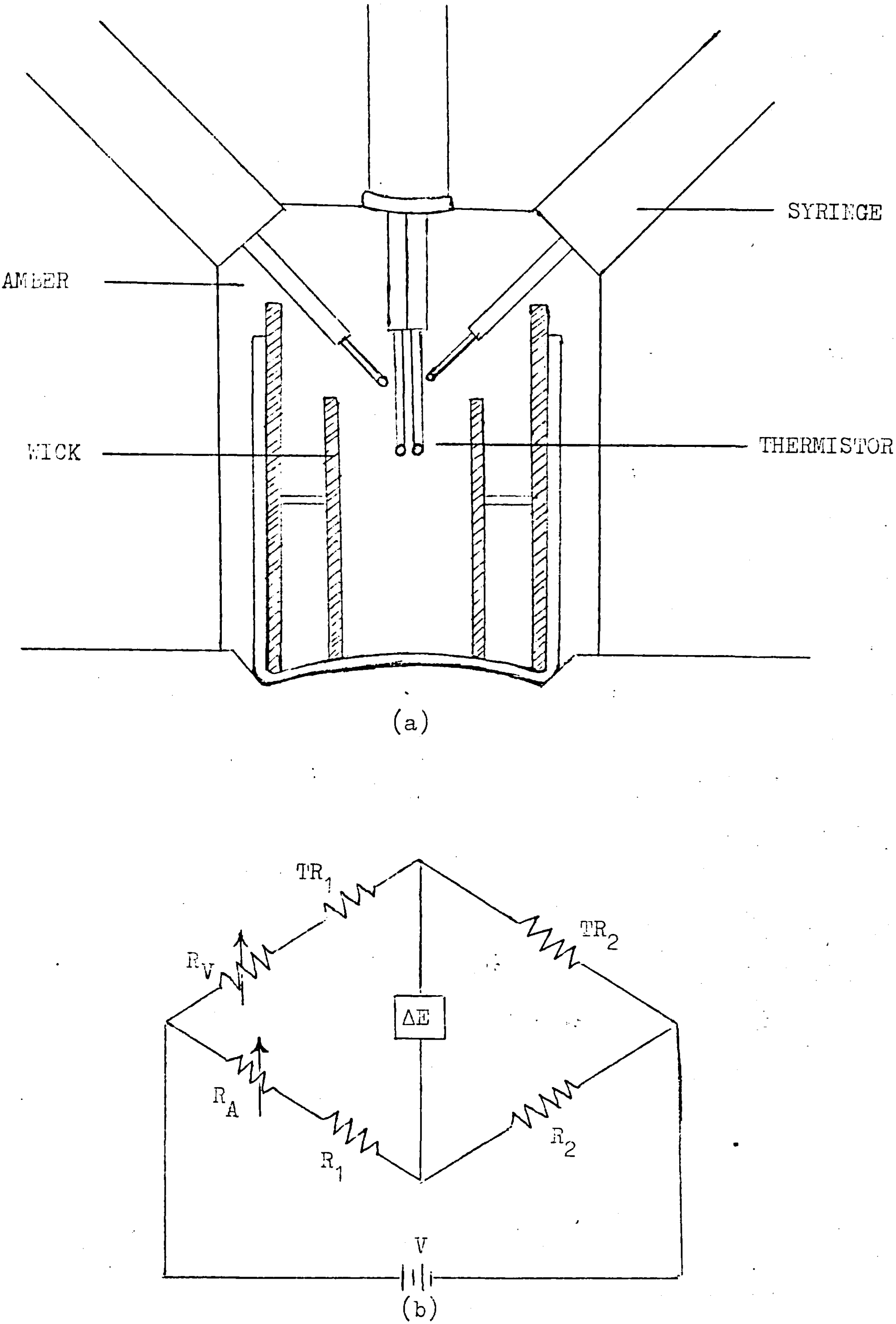
(ii) Differential vapour pressure method.

The Hewlett Packard Model 302, Vapour Pressure Osmometer was used to determine the molecular weights. The apparatus is shown in Fig. 4 consists of two bead thermistors suspended in a precisely thermostatted chamber saturated with the solvent vapour. The beads, which undergo a large change in resistance (ΔR) for a relatively small change in temperature, form two arms of a Wheatstone bridge.

PROCEDURE

The apparatus was maintained at the desired temperature ($25^{\circ}C$) for about 4-5 hours. The solvent cup was filled with pure dry solvent (benzene). Two of the syringes were filled with the same solvent while the other four were filled with the solutions of different concentrations.

A drop of solvent was placed on the reference thermistor and a drop of solution was placed on the measuring thermistor. Due to the lower vapour pressure of the solution drop, some



V = BRIDGE VOLTAGE

ΔE = UNBALANCED BRIDGE POTENTIAL

$R_1 = R_2$ = FIXED RESISTORS

R_V and R_A = ADJUSTABLE RESISTORS

$TR_1 = TR_2$ = THERMISTORS WITH EQUAL RESISTANCE

FIG. 4 (a) VAPOUR PRESSURE OSMOMETER (CHAMBER) and (b) WHEATSTONE CIRCUIT solvent condensed on the solution drop and increased its temperature. The bridge was imbalanced and the balance was restored by adjustment of the decade resistances, until equilibrium was achieved when ΔR (in ohms) was noted. This solution drop was now washed away with several drops of pure solvent. A drop of higher concentration was then placed on the solution-thermistor and ΔR measured as above. In the same way ΔR was measured for the remaining solutions of different concentrations and a graph of $\Delta R/c$ against the respective concentrations was plotted to obtain a straight line which was extrapolated to zero concentration. The molecular weight was determined by the following equation.

$$M.W. = \frac{k}{\left(\frac{\Delta R}{c}\right)_{c \to 0}}$$

where c = concentration in g. litre^{-1}

and k = calibration constant.

The apparatus was first calibrated with a known molecular weight solute (e.g. naphthalene) for each solvent used to determine molar constant (k) mentioned above. This molar constant was then used in the above equation for the determination of molecular weight of the unknown substance. The results are reported in Section 5 page 122a.

(C) DETERMINATION OF HEAT OF VAPORIZATION.

The heats of vaporization of dihaloboranes were calculated from measurements of vapour pressure at various boiling temperatures, using a semi-micro-ebulliometer which was constructed in the laboratory with minor modifications from Hoover's design.[112]

The apparatus is simple in construction, Fig. 5, and consists of a boiling pot, a column, a side arm and a thermometer tube. The only critical dimension is that which places the thermometer tube just below the lip of the boiling pot.[112] A partial shield of asbestos around the apparatus was found to increase temperature stability.

Procedure

The ebulliometer was thoroughly cleaned and dried in an oven (110°C), cooled and flushed with dry (oxygen-free) nitrogen, loaded with ca. 2 ml. of the sample (using a dry-box containing dry oxygen-free nitrogen). The thermometer tube was located and the apparatus was then clamped in a stand and connected to a vacuum line, through a Cartesian manostat (manufactured by Edwards High Vacuum Ltd.). A small amount of mercury, to cover the bulb of the thermometer, was placed in the thermometer tube and a 30 mm. immersion

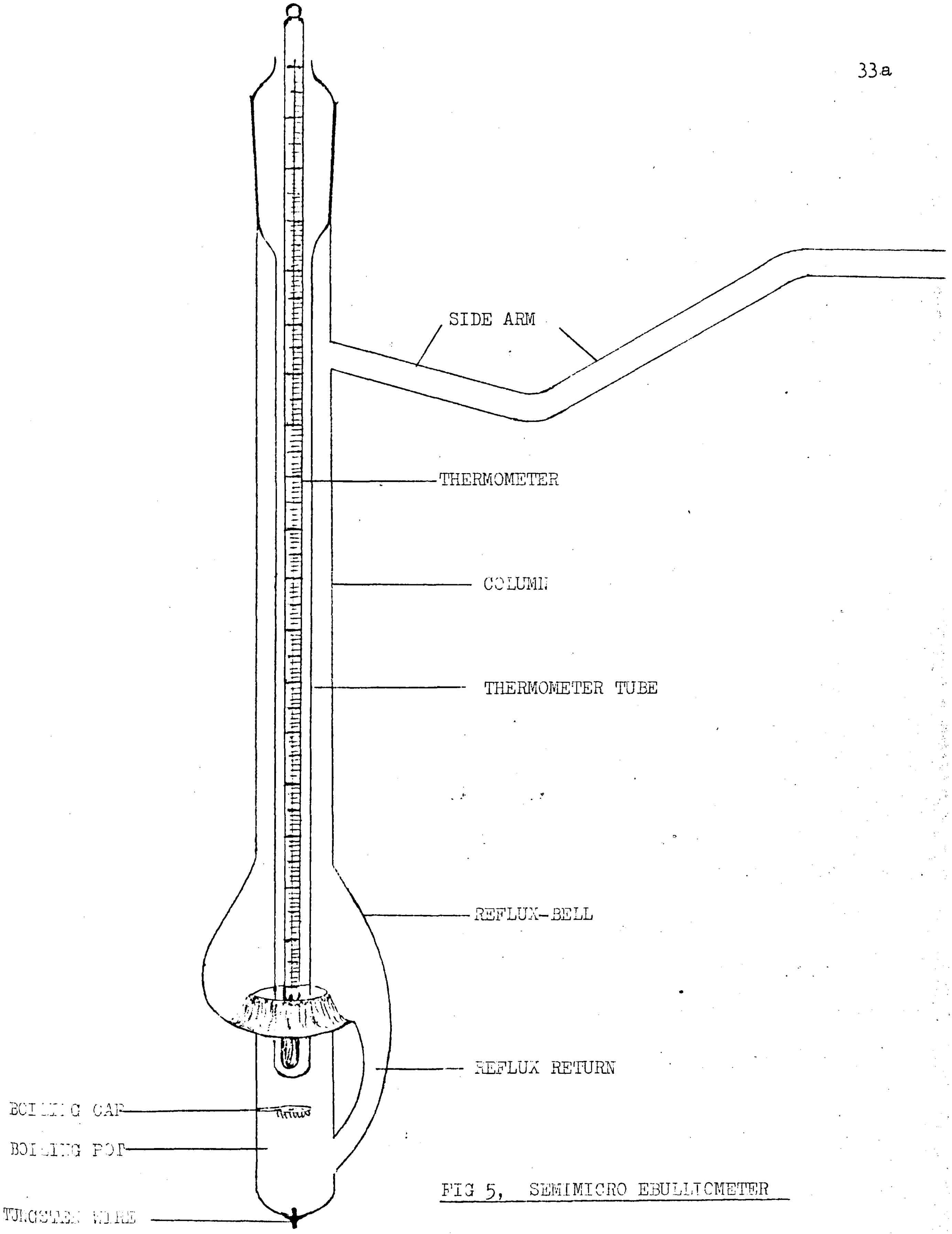


FIG 5, SEMIMICRO EBULLIOMETER

thermometer (0-150°C or 140-300°C) was slipped in. The boiling pot was placed on a rigid asbestos sheet, with a small hole in the middle, and heated by a micro-burner.

The pressure was stabilized initially at low value (ca. 10 mm.) and heating was started. The liquid began to reflux and the temperature increased. When refluxing reached above the mercury level and the temperature reading was constant for about five minutes, the reading was noted and the burner removed. The pressure was then stabilized at a higher value and a further reading taken in the similar manner. The sequence of these operations gave various boiling temperatures at known pressures.

A graph of $\log_{10}P$(mm.) vs. $10^3/T$ (°K) was plotted and gave a straight line. The gradient of this line, when multiplied by 2.303R (gas constant), gave the heat of vaporization (kcal.mole^{-1}) of the liquid over the range of the experimental temperatures. The data were then converted to 298.15°K using Watson's equation (see page 36).

The apparatus was first checked by measuring the vapour pressures of standard liquids (e.g. water and propionic acid) at various temperatures and calculating the heats of vaporization. The results were in agreement with literature values:

H_2O	$\Delta H_v 298.15^oK$ =	10.4 ± 0.2 kcal.mole^{-1} (lit.[114] = 10.48 kcal.mole^{-1})
CH_3CH_2COOH	$\Delta H_v 298.15^oK$ =	12.4 ± 0.2 kcal.mole^{-1} (lit.[115] = 12.46 kcal.mole^{-1})

THEORY

The change of vapour pressure (P) is related to the temperature (T^oK) by Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H_{vap.}}{T.\Delta V}$$

where T = temperature (degrees Kelvin)

P = vapour pressure (mm.)

$\Delta H_{vap.}$ = Heat of vaporization (cal./mole)

ΔV = Change in volume (per mole) accompanying vaporization ($V_g - V_l$)

If the vapour is considered to be a perfect gas and the molar volume of the liquid (V_l) is assumed to be negligible compared with that of the vapour (V_g), then we have

$$\frac{d \ln P}{d(1/T)} = -\frac{\Delta H_{vap.}}{R}$$

Assuming ΔH to be constant over the given temperature interval, the equation may be integrated to give

$$\log_e P = A - \frac{B}{T} = A - \frac{B}{(t + 273.15)}$$

where t = temperature in degrees centigrade.

If now $\log_{10} P$ is plotted against $10^3/T^oK$, then

$$B = \frac{\Delta H \text{ vap. (kcal.mole}^{-1})}{2.303R}$$

where B is the slope of the line obtained.

The heat of vaporization derived by the above method refers to the mean temperature of the range over which measurements were taken. These values were "corrected" to 298.15°K, using an empirical equation devised by Watson.[115]

$$\frac{\Delta H \text{ vap. } (T^oK)}{\Delta H \text{ vap. } (298.15^oK)} = \left[\frac{1 - T/T_c}{1 - 298.15/T_c}\right]^{0.38}$$

where T = temperature in degrees Kelvin

T_c = Critical temperature (°K).

The value of T_c for different compounds can be estimated by the method of Meissner and Redding.[116,117]

The boiling temperature, which is required for this estimation, was obtained by extrapolation of the $\log_{10}P$(mm) vs. $10^3/T$ graphs to 760 mm. vapour pressure.

Meissner and Reddings equations give estimated values within 5% agreement of the experimental values.[117] The results are given in Section 4 page 99.

SECTION 3

SYNTHESIS AND ANALYSIS

(a) Aryldihydroxyboranes and tri-arylboroxines.

These compounds were prepared by the reaction of arylmagnesium halides and trimethoxyborane, in dry ether, at -60°C, according to the following equations.[119,120]

$$ArMgX+B(OMe)_3+3H_2O \longrightarrow ArB(OH)_2+3MeOH+Mg(X)OH \quad \ldots (1)$$

$$2Mg(X)OH+H_2SO_4 \longrightarrow MgX_2+MgSO_4+2H_2O \quad \ldots (2)$$

$$3ArB(OH)_2 \xrightarrow{-3H_2O} (ArBO)_3 \quad \ldots (3)$$

A conventional Grignard procedure[121] was used to prepare the arylmagnesium halides. This is as follows:[122]

A three necked, one litre (Quickfit, round-bottom, pyrex-glass) flask was fitted with a mechanical stirrer (with mercury seal), a reflux condenser with a drying tube (anhyd. $CaCl_2$) and a dropping funnel with a gas adaptor for the passage of nitrogen. The flask was initially warmed, to remove air and oxygen-free dry nitrogen (anhyd. $CaCl_2$ and P_2O_5) was allowed to pass through the apparatus at a constant slow rate. Bright magnesium turnings (0.5 mol.) were placed in the flask and covered with dry ether (anhyd. $CaCl_2$ and sodium wire, 100 ml.). Then 20 ml. solution of the arylhalide (0.5 mol. in 300 ml. dry ether) was dropped onto the magnesium and the flask warmed gently, till the reaction became rapid. [If the reaction did not start within 20 minutes, iodine (0.5 g.) or ethylbromide (1 ml.) was added to initiate the reaction]. The reaction-rate was controlled with an ice-bath, the stirring was started, and the rest of the arylhalide solution was added dropwise, maintaining a rapid refluxing of the ether. When all of the arylhalide solution had been added, the mixture was stirred for half an hour and then refluxed for a further 30 minutes. The reaction mixture was then allowed to settle and cool down to room temperature, filtered through a sintered (No. 1) glass funnel, under the presence of dry (oxygen-free) nitrogen and estimated by a standard procedure.[123]

The dihydroxyboranes were prepared from the reaction of arylmagnesium halides with trimethoxyborane in dry ether at -60°C, according to the modified procedure of Washburn et al.[119,120] The following procedure was used;

A three-necked, one litre (Quickfit, round-bottom, pyrex-glass) flask was fitted with a mechanical stirrer (with mercury seal) and two graduated (500 ml.) dropping funnels, with pressure equalizing side arms. A constant supply of dry (oxygen-free) nitrogen, at a slow rate, was maintained throughout the apparatus while dry ether (100 ml.) was added to the flask, and the stirring started. Freshly prepared (filtered and estimated) arylmagnesium halide solution (0.5 mol. in 500 ml. dry ether) was transferred (under the pressure of dry nitrogen) to one of the dropping funnels. The calculated amount (0.5 mol., estimated) of trimethoxyborane (distilled) in 100 ml. dry ether was added to the second graduated funnel. The stirring and the pressure of nitrogen were slightly increased and the contents of the flask were cooled to -80°C (solid CO_2 + acetone). Then 20 ml. solution of trimethoxyborane was added to the flask followed by the rapid simultaneous dropwise addition of the solutions of arylmagnesium halide and trimethoxyborane in the ratio of 1:3 trimethoxyborane to arylmagnesium halide solution. The temperature of the flask was maintained at -60°C with the help of a cooling bath (solid CO_2 + acetone). All of the reagents were added within ten minutes and stirring was continued for a further 30 minutes. The mixture was then hydrolysed with 100 ml. cold (ice) distilled water, added over a period of ten minutes, and H_2SO_4 solution (100 ml. 10%) was added dropwise during a five minute period with stirring. The mixture was allowed to separate into two layers and the ethereal layer was separated. The water layer was extracted (several times) with 100 ml. portions of ether and the extract was mixed with the main ethereal solution. The ether was then removed by the following procedure:

A two-necked Quickfit pyrex-glass round-bottom flask was fitted with a modified Claisen head, a mechanical stirrer (with mercury seal), a condenser and a dropping funnel (250 ml.). The ethereal solution was transferred to the dropping funnel and then added to the flask. Stirring was started and the ether was allowed to distil at 34°C, using an electric heating mentle. When one third of the total ether had been distilled, 200 ml. of distilled water was added, dropwise, to the flask, and the temperature was increased when the remaining ether distilled. When the temperature (attached to the still-head) reached 100°C, heating was stopped and the heating mantle was removed, but the stirring was continued till the solution cooled down to 10°C (cooling by an ice-bath). The aryldihydroxyboranes crystallised and were filtered through a sintered glass (No. 1) funnel and washed with petroleum ether (40-60°C). The resulting crude products were then purified according to the methods given in the literature.

Phenyldihydroxyborane $[C_6H_5B(OH)_2]$

Bromobenzene (39.25 g., 0.25 mol., in 100 ml. dry ether) was reacted with bright magnesium turnings (6.0 g., 0.25 mol.) in the presence of nitrogen (dry, oxygen-free) to give phenylmagnesium bromide (0.22 mol., 90% theor. in 300 ml. dry ether).

Trimethoxyborane (distilled, 22.4 g., 0.22 mol. in 100 ml. dry ether) and phenylmagnesium bromide (0.22 mol. in 300 ml. dry ether) were added simultaneously to ether (100 ml.) in a reaction flask at -60°C and in the presence of (oxygen-free, dry) nitrogen. The reaction mixture on hydrolysis (H_2SO_4, 10%, 100 ml.) and removal of solvent by distillation gave a white, crystalline crude product (24.0 g., 86%). The crude product was washed with petroleum ether (40-60°C) and twice recrystallised from boiled distilled water to give pure (white, shining, long needles) phenyldihydroxyborane (20 g., 70% theor.) m.pt. 206°C (lit. 216).[43]
Analysis: Found, B(9.1%), calc. B (8.87%).

Triphenylboroxine $(C_6H_5BO)_3$

Phenyldihydroxyborane (20.0 g.) was heated at 110°C (in an oven) for eight hours at atmospheric pressure, then ground to a fine powder, and dehydrated at 40°C and 0.1 mm pressure, to give triphenylboroxine (15.0 g., 83%) m.pt. 215°C (lit. 214-216°C).[42]
Analysis: Found B(10.33), calc. B(10.41%).

<u>p-Fluorophenyldihydroxyborane</u> [p-$FC_6H_4B(OH)_2$]

p-Fluorobromobenzene (43.7 g., 0.25 mol., in 100 ml. dry ether) was allowed to react with shining magnesium turnings (6.0 g., 0.25 mol.) in presence of iodine and dry oxygen-free nitrogen, to give p-fluorophenylmagnesium bromide (0.15 mol. 60%, in 300 ml. dry ether).

Trimethoxyborane (distilled, 15.6 g., 0.15 mol.) and p-fluorophenylmagnesium bromide (0.15 mol., in 300 ml. dry ether) were added simultaneously to dry ether (100 ml.) in a reaction flask at -60°C, in the presence of dry oxygen-free nitrogen. The reaction mixture, after hydrolysis (10% H_2SO_4) and distillation, gave a white crystalline crude product (12.0 g., 57% theor.).

The crude substance was washed with petroleum ether (40-60°C) and crystallised, twice, from boiled distilled water and, once, from benzene, to give pure (white, crystalline, needles) p-fluorophenyldihydroxybenzene (10.0 g. 50% theor.) m.pt. 240°C. lit. 265-266°C.[42]

Analysis: Boron, found (7.9) calc. (7.73).

<u>Tri-p-fluorophenylboroxine</u> [(p-$FC_6H_4BO)_3$]

p-Fluorophenyldihydroxyborane (10.0 g.) was dehydrated at 40°C and 0.1 mm pressure, for twenty four hours, ground to a fine powder and further dehydrated at 40°C and 0.1 mm pressure, for twelve hours, to give a white powder (9.0 g, 91% theor.) m.pt. 246°C, lit. 265-266°C.[42]

Analysis: Found, C(58.95), H(3.4), F(15.72), B(8.48).
Calc., C(59.1), H(3.3), F(15.58), B(8.87).

p-Chlorophenyldihydroxyborane [$p\text{-ClC}_6\text{H}_4\text{B(OH)}_2$]

Bright magnesium turnings (6.0 g., 0.25 mol.) and p-chlorobromobenzene (48.12 g, 0.25 mol.) were reacted (in the conventional Grignard-type apparatus) in the presence of iodine (0.5 g.), dry ether (300 ml.) and dry (oxygen-free) nitrogen, to give p-chlorophenylmagnesium bromide (0.22 mol. approx. 90% theor.).

Trimethoxyborane (distilled, 22.5 g., 0.22 mol. in 100 ml. dry ether) and p-chlorophenylmagnesium bromide were added simultaneously to dry ether (100 ml.) at -60°C, in the presence of dry (oxygen-free) nitrogen. The reaction mixture, after hydrolysis (10% H_2SO_4) and distillation, gave a white, crystalline, crude product (42.0 g. about 80% theor.).

The crude substance was washed with petroleum ether (40-60°C) and, twice, crystallised from boiled distilled water, to give pure, (white, shining plates), p-chlorophenyl dihydroxyborane (m.pt. 265°C lit. 261-263°, 80%, 42 g.).[42]

Analysis: Boron, found (7.2%)calc. (6.9).

Tri-p-chlorophenylboroxine [$(p\text{-}ClC_6H_4BO)_3$]

p-chlorophenyldihydroxyborane (20.0 g.) was dehydrated at 40°C and 0.1 mm pressure for 24 hours, ground to a fine powder and further dehydrated at 40°C and0.1 mm pressure for twelve hours, to give tri-p-chlorophenylboroxine [16.0 g. 90% theor.] m.pt. 265°C lit. 261-263°C.[42]

Analysis, Found, B(8.0), C(51.94), H(2.72), Cl(25.59).

Calc. B(7.82), C(52.0), H(2.91), Cl(25.6).

p-Bromophenyldihydroxyborane [$p\text{-}BrC_6H_4.B(OH)_2$]

Bright magnesium turnings (6.0 g., 0.25 mol.) and p-dibromobenzene (59.0 g., 0.25 mol., in 100 ml. dry ether) were reacted (in a conventional Grignard-type apparatus) in the presence of iodine (0.5 g), dry ether (300 ml.) and dry (oxygen-free) nitrogen to give p-bromophenylmagnesium bromide (0.19 mol., 75% theor.).

Trimethoxyborane (distilled, 0.19 mol., 20 g. in 100 ml. dry ether) and p-bromophenylmagnesium bromide (0.19 mol. in 300 ml. dry ether) were added simultaneously to dry ether (100 ml.) at -60°C, in the presence of dry, oxygen-free nitrogen. The reaction mixture, after hydrolysis (10% H_2SO_4) and distillation, gave a white crystalline crude product (13.0 g., 30% theor.).

The crude substance was washed with petroleum ether

(40-60°C), crystallised (twice) from boiled distilled water, (once) from benzene, (once) from ethanol and then from n-hexane to give pure p-bromophenyldihydroxyborane (white needles, m.pt. 272°C, lit. 276-281°C).[42]

Analysis, Boron, found (5.81%), calc. (5.4%).

Tri-p-bromophenylboroxine $[(p\text{-}BrC_6H_4BO)_3]$

The purified p-bromophenyldihydroxyborane was dehydrated at 40°C and 0.1 mm pressure for 24 hours, ground to a fine powder and further dehydrated at 40°C at 0.1 mm pressure for another twenty four hours, to give p-tribromophenylboroxine m.pt. 282°C (lit. 274-282°C).[42]

Analysis, Found, C(39.46), H(2.34), B(6.5), Br(43.55).

Calc. C(39.4), H(2.2), B(5.91), Br(43.7).

p-Tolyldihydroxyborane $[p\text{-}CH_3C_6H_4B(OH)_2]$

Shining magnesium turnings (6.0 g., 0.25 mol.) and p-bromotoluene (45.0 g., 0.25 mol. in 100 ml. dry ether) were reacted (in a conventional Grignard-type apparatus) in the presence of iodine (0.5 g.), dry ether (300 ml.) and dry (oxygen-free) nitrogen to give p-tolylphenylmagnesium bromide (0.21 mol.,85%).

p-Tolylmagnesium bromide (0.21 mole, in 300 ml. dry ether) and trimethoxyborane (distilled, 0.21 mol., 22.0 g. in 100 ml. dry ether) were added simultaneously to dry ether (100 ml.) at -60°C, in the presence of (oxygen-free, dry) nitrogen. The reaction mixture after hydrolysis (10% H_2SO_4) and distillation, gave a white, crystalline, crude product (20.0 g., 53% theor.).

The crude substance was washed with petroleum ether, twice crystallised with boiled distilled water to give pure p-tolyldihydroxyborane (12.0 g., 70% theor.) m.pt. 245°C, lit. 246-248°.[42]

Analysis: Boron, found (8.1), calc. (7.8).

Tri-p-tolylboroxine [$(p\text{-}CH_3C_6H_4BO)_3$].

The purified p-tolyldihydroxyborane (12.0 g.) was dehydrated at 0.1 mm pressure and room temperature for thirty six hours, ground to a fine powder and again dehydrated at 40°C for twelve hours, to give tri-p-tolylboroxine (white, long needles) m.pt. 245°, lit. 246-248°C.[42]

Analysis, Found, C(70.91), H(6.06), B(9.3).
Calc. C(71.3), H(5.98), B(9.16).

o-Tolyldihydroxyborane [$o\text{-}CH_3C_6H_4B(OH)_2$]

o-Bromotoluene (42.5 g, 0.25 mol. in 100 ml. dry ether) and shining magnesium turnings, were reacted (in a conventional Grignard-type apparatus) in the presence of iodine (0.5 g.), dry ether (300 ml.) and dry (oxygen-free) nitrogen to give o-tolylmagnesium bromide (0.19 mol., 300 ml. dry ether) 75% theor.).

o-Tolylmagnesium bromide (0.19 mol., 300 ml. dry ether) and trimethoxyborane (distilled, 0.19 mol. 20.0 g. in 100 ml. dry ether) were added simultaneously to dry ether (100 ml.) at -60°C, in the presence of dry (oxygen-free) nitrogen. The reaction mixture, after hydrolysis (10% H_2SO_4) and distillation, gave a white crystalline crude product (15 g. 60% theor.).

The crude substance was washed with petroleum ether (40-60°C), twice crystallised with boiling distilled water and recrystallised (once) from toluene, to give pure o-tolyldihydroxyborane (12.0 g., 80% theor.) white, needles, m.pt. 160°C, lit. 160-161°C,[46] and 160°C[37] or 171°C.[41]

Analysis, Boron, found, (8.0%), calc. (7.8%).

Tri-o-tolylboroxine $[(o\text{-}CH_3C_6H_4BO)_3]$

o-Tolyldihydroxyborane (12.0 g.) was dehydrated at 0.1 mm pressure and room temperature for 24 hours, ground to a fine powder and again dehydrated at 80°C and 1.0 mm pressure, for twelve hours, to give tri-o-tolylboroxine, m.pt. 169°C, lit. 160-161°C.[46]

Analysis, Found, C(70.91), H(6.06), B(9.3).

Calc. C(71.3), H(5.98), B(9.16).

p-Anisyldihydroxyborane [p-$CH_3OC_6H_4B(OH)_2$]

Bright magnesium turnings (8.0 g., 0.38 mol.) and p-anisylbromide (0.33 mol., 63.0 g., in 100 ml. dry ether) were reacted (in the conventional Grignard-type apparatus) in the presence of iodine (0.5 g.), dry ether (300 ml.) and dry (oxygen-free) nitrogen to give, p-anisylmagnesium bromide (0.26 mol., 80% theor. in 300 ml. dry ether).

Trimethoxyborane (distilled, 0.26 mol., 27.0 g., in 100 ml. dry ether) and p-anisylmagnesium bromide (0.26 mol., filtered, estimated, in 300 ml. dry ether) were added simultaneously to dry ether (100 ml.) at -60°C (solid CO_2 + acetone) in the presence of dry, oxygen-free, nitrogen. The reaction mixture, after hydrolysis (10% H_2SO_4) and distillation, gave a white, crystalline, crude product (25.0 g., 60% theor.).

The crude product was washed with petroleum ether (40-60°C), twice crystallised from boiled distilled water, crystallised once from ethanol (extra dry, distilled over Mg & I_2) and then finally crystallised from n-hexane (64-65°C, dried over sodium), to give pure p-anisyldihydroxyborane (12.0 g., 50% theor.) m.pt. 205, lit. 204-207°C.[42]

Analysis: Boron, found (7.5%), calc. (7.1%).

Tri-p-anisylboroxine [$(p\text{-}CH_3OC_6H_4BO)_3$]

p-Anisyldihydroxyborane (12.0 g.) was dehydrated at 0.1 mm pressure and room temperature, for 36 hours to give p-trianisylboroxine, white crystals, which were ground to a fine powder and further dehydrated at 40°C and 0.1 mm pressure, for 5 hours. m.pt. 206°C, lit. 204-207°C.[42]

Analysis, Found, C(63.5), H(5.35), B(8.08)

Calc. C(62.78), H(5.26), B(8.06).

p-Trifluoromethylphenyldihydroxyborane [$p\text{-}CF_3C_6H_4B(OH)_2$]

Magnesium (bright turnings, 0.25 mol. 6.0 g.) and p-trifluoromethylbromobenzene (37.0 g., 0.25 mol. in 100 ml. dry ether) were reacted together (in a conventional Grignard-type apparatus) in the presence of iodine (0.5 g.), dry ether (300 ml.) and dry (oxygen-free) nitrogen to give p-trifluoromethylphenylmagnesium bromide (0.22 mol., in 300 ml. dry ether, 90% theor.).

Trimethoxyborane (distilled, 0.22 mol., in 100 ml. dry ether) and p-trifluoromethylphenylmagnesium bromide (0.22 mol., in 300 ml. dry ether) were added simultaneously to dry ether (100 ml.) at -60°C, in the presence of dry-oxygen-free, nitrogen. The reaction mixture on hydrolysis (10% H_2SO_4) and distillation, gave a white, crystalline, crude product (14.0 g., 40% theor.).

The crude product was washed with petroleum ether (40-60°C), twice crystallized from boiled distilled water to give p-trifluoromethylphenyldihydroxyborane (9.0 g., 60% theor. white long needles) m.pt. 243°C.

Analysis; Boron, found (5.9), calc. (5.7).

Tri-p-trifluoromethylphenylboroxine [$(p\text{-}CF_3C_6H_4BO)_3$]

p-Trifluoromethylphenyldihydroxyborane (9.0 g.) was dehydrated at 0.1 mm pressure and room temperature for 24 hours, ground and again heated at 80°C and 1.0 mm pressure for ninety minutes to give tri-p-trifluoromethylphenylboroxine (7.0 g., 90%) m.pt. 245°C.

Analysis, Found, C(46.32), H(2.94), B(6.4), F(31.26).
Calc., C(48.8), H(2.34), B(6.29), F(33.16).

p-Biphenyldihydroxyborane [$p\text{-}C_6H_5C_6H_4B(OH)_2$]

Magnesium (bright turnings, 0.25 mol., 6.0 g.) and p-phenylbromobenzene (58.0 g., 0.25 mol., 150 ml. dry ether) were reacted together (in a conventional Grignard-type apparatus) in the presence of ethylbromide (1.0 ml.), dry ether (300 ml.) and dry (oxygen-free) nitrogen, to give (0.12 mol., 50% theor.) p-biphenylmagnesiumbromide (in 300 ml. dry ether).

Trimethoxyborane (distilled, 0.12 mol., 12.5 g., in

100 ml. dry ether) and p-biphenylmagnesium bromide (0.12 mol., in 300 ml. dry ether) were added simultaneously to dry ether (100 ml.) at -60°C, in the presence of dry, oxygen-free, nitrogen. The reaction mixture on hydrolysis (10% H_2SO_4) and distillation, gave a white, crystalline, crude product (20.0 g., 80% theor.).

The crude substance was washed with petroleum ether (40-60°), was twice crystallised from 25% ethanol (absolute), and once from benzene (AnalaR distilled and dried over sodium) to give p-biphenyldihydroxyborane, (white plates, 7.7 g., 38% theor.), m.pt. 230-232°C (lit. 232°- 234°).[41]
Analysis, Found, C(72.76), H(5.6), B(5.6).
Calc. C(72.63), H(5.63), B(5.7).

p-Biphenyldihydroxyborane, even on heating at 40°C, and 0.1 mm pressure for 36 hours, did not show any sign of dehydration.

t-Butylbenzene

$$Me_3CCl+C_6H_6 \xrightarrow[\text{(anhyd.)}]{AlCl_3} Me_3CC_6H_5+HCl$$

In a three-neck round bottom, flask (fitted with mechanical stirrer, a reflux condenser and a dropping funnel) were placed aluminium chloride (25.0 g. anhydrous, powdered) and dry benzene (sodium wire, AnalaR, 100 ml.). The mixture was cooled to 0°C (ice + salt), and stirring was started followed by the addition of t-butyl chloride (25.0 g., dropwise, over 45 min.) keeping the temperature of the mixture at 0-5°C. The mixture was stirred for a further 45 min., when distilled water (150 ml. ice-cold) was added and allowed to attain the room temperature. Two layers were separated. The upper organic layer was transferred to a flask, dried (anhyd. $MgSO_4$), filtered and fractionally distilled through a 30 cm. column (packed with helices and insulated with asbestso-string). t-Butylbenzene (40%) was collected at 165-170°C.

p-t-Butylbromobenzene

t-Butylbenzene (14.0 g.) bromine (16.0) and pyridine (0.25 mol.) were mixed in a 1 litre, round bottom, flask . Hydrogen bromide (gas), which was evolved, was collected in a trap (-196°C). When hydrogen bromide evolution ceased an equal volume of ether (30.0 ml.) was added, and the solution was washed with dilute alkali followed with distilled water. The ethereal solution was separated, dried (anhyd. $MgSO_4$) and fractionally distilled at reduced pressure. The fraction at 100-102°C/12 mm was collected (yield 44%) (lit. b.p. 80-81/2 mm., 228-229/740 mm).[123]

p-t-Butylphenyldihydroxyborane [$p\text{-}Me_3CC_6H_4B(OH)_2$]

Magnesium (bright turnings, 0.25 mol., 6.0 g.) and p-t-butylbromobenzene (0.25 mol., 53.0 g. in 100 ml. dry ether) were reacted (in a conventional Grignard-type apparatus) in presence of iodine (0.5 g.), dry ether (300 ml.) and dry (oxygen-free) nitrogen to give p-t-butylphenylmagnesium bromide (0.18 mol. 38.4 g. 70% theor.).

Trimethoxyborane (distilled, 0.18 mol. 19.0 g., in 100 ml. dry ether) and p-t-butylphenylmagnesium bromide (0.18 mol. 38.4 g. in 300 ml. dry ether) were added simultaneously to dry ether (100 ml.) at -60°C, in the presence of (dry, oxygen-free) nitrogen. The reaction mixture on hydrolysis (10% H_2SO_4) and distillation, gave a white crystalline crude product (20.0 g. 60% theor.).

The crude product was washed with petroleum ether (40-60°C), twice crystallised from 10% ethanol (aqueous) and then from benzene (dry, AnalaR) to give p-t-butylphenyldihydroxyborane (10.0 g., 50% theor.) white plates, m.pt. 196°C. Analysis; Boron, found (6.5%) calc. (6.1%).

Tri-p-t-butylphenylboroxine [$(p\text{-}(CH_3)_3CC_6H_4BO)_3$]

p-t-Butylphenyldihydroxyborane (10.0 g.) was dehydrated at 40°C and 0.1 mm pressure for 24 hours, ground to a fine powder, and further dehydrated at 40°C and 0.1 mm pressure for another 24 hours to give p-t-Butylphenylboroxine m.pt.198°C.

Analysis; Found, C(75.36), H(8.11), B(6.76).

Calc., C(75.5), H(8.12), B(6.8).

p-Carboxyphenyldihydroxyborane [$p\text{-}COOHC_6H_4B(OH)_2$]

This compound was prepared by the oxidation of p-tolyldihydroxyborane with alkaline potassium permanganate according to the following equation.[46]

$$2p\text{-}CH_3C_6H_4B(OH)_2 \xrightarrow[(KMnO_4,\ alk.)]{2O_2} 2p\text{-}COOHC_6H_4B(OH)_2 + 2H_2O$$

p-Tolyldihydroxyborane (5.0 g.) was dissolved in aqueous sodium hydroxide (containing 30.0 g., as a 10% solution), and 15 ml. distilled water was added to it. The solution was filtered (sintered funnel) into one litre, two neck, round bottom flask, fitted with a mechanical stirrer and a dropping funnel. Distilled water (200 ml.) was added to the solution and stirring was begun. Aqueous potassium permanganate (12.2 g., saturated solution) was added dropwise (the next drop of $KMnO_4$ solution was added when the first one was decolourized). When all of the $KMnO_4$ solution had been added, the mixture was further stirred for fifteen minutes and then heated, on a water bath at 50-60°C, for twenty minutes.

The colourless liquid was filtered from MnO_2 (brown ppt), and was concentrated to about 300 ml. Hydrochloric acid (conc) was added (in excess) to precipitate the p-carboxyphenyldihydroxyborane. The mixture was cooled and filtered.

The white crystals were recrystallised from hot distilled water. The filtrate and the mother liquor were collected, concentrated, extracted with ethanol (150 ml.). The ethanol solution was concentrated to give further white crystals, which were also recrystallised from boiled distilled water to give p-carboxyphenyldihydroxyborane as white needles m.pt. 225°C (lit. 225°C).[46]

Analysis; Found, C(50.79, H(4.49), B(6.68).
Calc., C(50.66), H(4.25), B(6.51).

p-Carboxyphenyldihydroxyborane did not give the corresponding boroxine on heating at 40°C and 0.1 mm pressure for 24 hours.

p-Aldehydophenyldihydroxyborane [$p\text{-}CHO.C_6H_4B(OH)_2$]

This compound was prepared by the oxidation of p-tolyldihydroxyborane with benzoyl peroxide in chloroform solution.[128]

$$p\text{-}CH_3C_6H_4B(OH)_2 \xrightarrow[(C_6H_5COO)_2]{O_2} p\text{-}CHOC_6H_4B(OH)_2+H_2O$$

Chloroform (dry, 150 ml.), N-bromsuccinimide (5.0 g.) and benzoyl peroxide (0.65 g.) were mixed in a 500 ml. (two-neck, round bottom) flask fitted with a dropping funnel and a reflux condenser. The mixture was refluxed for three hours in the presence of light from a tungsten lamp (500 watts) placed at a distance of about 30 cm.

Hexamine (Hexamethylenetetramine, 7.0 g. in 75 ml. chloroform) was then added and the refluxing continued for a further one hour. The chloroform solution was decanted and the solid residue was extracted with dilute hydrochloric acid. (pH 4, 40.0 ml.). The aqueous solution was separated and refluxed for one hour. The hot solution was poured into a beaker and HCl (10.0 ml. conc.) was added to it and the solution was cooled. White needles separated and were recrystallised from hot water. (yield, 1.2 g., 25%), m.pt. 250°C (lit. 230-240°C).[128]

Analysis; Found, C(55.1), H(4.9), B(7.4).

Calc., C(56.0), H(4.7), B(7.2).

(b) ARYLDIHALOBORANES

These were prepared according to the following sequence of reactions.

$$\mathrm{ArX + Mg \xrightarrow{THF} ArMgX} \quad \ldots \quad \text{(i)}$$

$$\mathrm{ArMgX + HgCl_2 \xrightarrow{THF} ArHgCl + MgClX}.. \quad \text{(ii)}$$

$$\mathrm{ArHgCl + BCl_3 \xrightarrow{C_6H_6} ArBCl_2 + HgCl_2}.. \quad \text{(iii)}$$

Arylmagnesium halides:- These were prepared by the method of Ramsden et al.[124]

Arylhalides (0.5 mole) and magnesium (0.5 mole) were reacted together (in a conventional Grignard type apparatus) in tetrahydrofuran (1.5 mol, purified and dried over sodium) in an atmosphere of dry (oxygen-free) nitrogen and in the presence of ethylbromide (1 ml) as an initiator.

The solution (arylmagnesium halide) was diluted to 500 ml (dried THF) and estimated by a standard procedure.[125]

Arylmercuric chlorides: These were prepared by the following procedure.[126]

Mercuric chloride (150.0 g, 0.55 mol.) and tetrahydrofuran (400 ml. dry) were mixed in a two litre (3-neck, round bottom) flask fitted with a mechanical stirrer, a reflux condenser and a dropping funnel in presence of a regulated stream of nitrogen (dry, oxygen-free). The stirring was started and the mercuric chloride was dissolved to give a clear solution when the arylmagnesium halide solution (0.5 mol./500 ml. THF filtered and estimated) was added dropwise. The mixture was allowed to reflux, by the heat of reaction, and was cooled only when necessary (ice-bath). A white precipitate was produced. The mixture was stirred for a further 30 min. and then left overnight. The precipitate was filtered and washed with THF. The filtrate, combined with washings, were distilled to dryness (water bath) to leave a white solid which was treated with N/HCl (700 ml.) and filtered through a No.1 sintered glass funnel. The crude substance was washed with dilute HCl and crystallized from THF. The white crystals, obtained on cooling the solution, were filtered and dried at 80°C (oven). The mother liquor was concentrated to give a further crop of arylmercuric chloride.

Aryldichloroboranes:- These were prepared according to the method of Gerrard et al.[65]

The arylmercuric chlorides (0.5 mol.) were refluxed with boron trichloride (0.5 mol.) in dry benzene (150 ml.) in an atmosphere of nitrogen (dry, oxygen-free) and using a Jackson condenser (Dry ice + acetone). The insoluble mercuric chloride was filtered off and the filtrate fractionally distilled (50 cm. column) to give aryldichloroboranes.

Phenyldichloroborane: This compound was synthesised according to the method of Gerrard et al.[67]

$$(C_6H_5)_4Sn + 4BCl_3 \longrightarrow 4\ C_6H_5BCl_2 + SnCl_4$$

Tetraphenyltin (51.4 g., 0.12 mol.) was placed in a round bottom flask (1 litre, 2 neck) equipped with a Jackson condenser (-80°C) and a nitrogen inlet. Nitrogen (dry, oxygen-free) was flushed through the apparatus and the flask cooled to -80°C (solid CO_2 + acetone) and boron trichloride (56.5 g, 0.12 mol., cooled to -80°C) was added. The condenser (cold finger) was charged with cooling mixture (solid CO_2 + acetone). The contents of the flask were allowed to attain the room temperature. When boron trichloride began to reflux (first rapidly and then vigorously) and the tetraphenyltin dissolved to give a homogeneous solution. The solution was refluxed (170°C) for four hours and then fractionally distilled (through 30 cm. column, packed with helices and insulated with asbestos string). The fraction with boiling range 80-120°C at 100 mm. was collected and refractionated to give phenyldichloroborane, b.pt. 112°C/140 mm. (lit. 57-58/10 mm.).[67]

Analysis: Boron, found (6.9), calc. (6.8).

Chlorine, found (46.84), calc. (47.7).

<u>p-Tolyldichloroborane</u> (p-$CH_3C_6H_4BCl_2$)

p-Tolylmagnesium chloride (0.5 mol.,) was prepared (using the usual Grignard techniques) from magnesium (14.0 g., 0.53 mol.), p-chlorotoluene (72.0 g., 0.57 mol.)

and tetrahydrofuran (500 ml., dry) in an atmosphere of nitrogen (dry, oxygen-free) and in the presence of ethylbromide as an initiator. It was then reacted with mercuric chloride (0.5 mol., 136.0 g. in 500 ml. THF) to give p-tolylmercuric chloride (120.0 g., 70%) m.pt. 238°C, lit. 238-9°C.

p-Tolylmercuric chloride (65.0 g., 0.20 mol.), boron trichloride (25.0 g., 0.21 mol.) and benzene (60.0 ml. dry) were refluxed together in an atmosphere of (dry, oxygen-free) nitrogen, using a Jackson condenser (solid CO_2 + acetone) for four hours. The solution was fractionally distilled (through a 30 cm. column, packed with helices and insulated with asbestos) and the fraction of b.pt. 90-110°C/35 mm., was collected. On refractionation it gave p-tolyldichloroborane, b.pt. 112°/40 mm., lit. 92°C/10 mm.,[65] m.pt. 27°C (18.0 g., 60%).

<u>o-Tolyldichloroborane</u> (o-$CH_3C_6H_4BCl_2$)

Magnesium (12.0 g., 0.50 mol.) and o-bromotoluene (86.0 g., 0.5 mol.) were reacted together, using the usual Grignard techniques, in tetrahydrofuran (500 ml. dry) in the presence of ethyl bromide (1.0 ml.) as an initiator and in an inert atmosphere (dry, oxygen-free nitrogen) to give o-tolylmagnesium bromide (0.38 mol., 75%). On reaction with mercuric chloride (105 g., 0.38 mol. in 400 ml. THF) it gave o-tolylmercuric chloride (90.0 g., 72% theor.) m.pt. 145°C (lit. 146°C).[178]

o-Tolylmercuric chloride (65.0 g., 0.20 mol.) was refluxed with boron trichloride (25.0 g. 0.21 mol.) and benzene (dry, 60.0 ml.) in an atmosphere of nitrogen (dry, oxygen-free) using a Jackson condenser (solid CO_2 + acetone), for four hours. The solution was fractionally distilled (30 cm. column) to give a crude product at 65-75°C/6 mm., which on refractionation gave o-tolyldichloroborane (16.0 g. b.pt. 71°C/6 mm. (lit. 88-92/12 mm.).[65]

Analysis: Boron, found (6.5), calc. (6.25).
Chlorine, found (40.28), calc. (41.08).

Mesityldichloroborane (2,4,6 $Me_3C_6H_2BCl_2$)

Mesitylmagnesium bromide (0.5 mol., 75%) was prepared by the reaction of magnesium (14.0 g., 0.58 mol.) and bromomesitylene (109.0 g., 0.58 mol.) in tetrahydrofuran (500 ml.), using usual Grignard techniques, in an atmosphere of nitrogen (dry, oxygen-free) and in the presence of ethylbromide (1.0 ml.) as an initiator. It was reacted with mercuric chloride to yield mesitylmercuric chloride (130.0 g., 74%) m.pt. 200°C (lit. 200°C).[178]

Mesitylmercuric chloride (79.0 g., 0.20 mol.) and boron trichloride (0.21 mol., 25.0 g.) were refluxed together, for four hours, in dry benzene (60.0 ml.), using a Jackson condenser (solid CO_2 + acetone) in an atmosphere of nitrogen (dry, oxygen-free). The solution was fractionally distilled (30 cm. column) to give a crude product with b.pt. 150-152°C/250 mm., which on refractionation gave mesityldichloroborane, b.pt. 114°/40 mm (and 100°C/30 mm for next fractionation).

Attempted preparation of 2:6 dimethyl-phenyldichloroborane:- ($2,6\text{-}Me_2C_6H_3BCl_2$).

2:6-Dimethylphenylmagnesium bromide (0.49 mol. 75% theor.) was prepared by the reaction of magnesium (14.0 g., 0.58 mol.) with 2:6 dimethylbromobenzene (100.0 g. 0.54 mol.) in tetrahydrofuran (500 ml. dry), using conventional Grignard techniques in an atmosphere of (dry, oxygen-free) nitrogen and in the presence of ethylbromide as an initiator, It was treated with mercuric chloride (136.0 g., 0.50 mol., 500 ml. THF) to give 2:6 dimethylphenylmercuric chloride (150.0 g., 88% theor.) m.pt. 130°C.

2,6-Dimethylphenylmercuric chloride (68.0 g., 0.20 mol.) was refluxed with boron trichloride (25.0 g., 0.21 mol.) in dry benzene (60 ml.) for four hours in an atmosphere of nitrogen (dry, oxygen-free) using a Jackson condenser (solid CO_2 + acetone). The solution was filtered (No.1 sintered glass funnel) and fractionally distilled (30 cm. column) and several liquid fractions (b.pt. 80°C - 134°C/ 760 mm.) were obtained, which did not contain chlorine or boron and were possibly unsaturated hydrocarbons. The solid residue (hygroscopic) contained a polymeric bright yellowish-white substance (m.pt. 300° dec.) with no boron, and a white substance (m.pt. 160-170°C) containing boron. Identification of the products was not achieved. Possible reasons for the failure of the synthesis are discussed on page 95.

SECTION 4

RESULTS AND DISCUSSION

TRIARYLBOROXINES

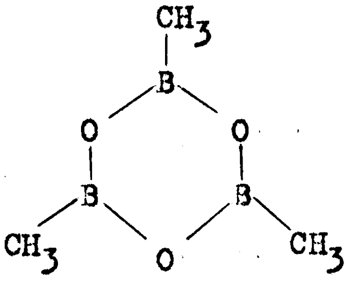
Boroxines are in general the (trimeric) anhydrides of the corresponding dihydroxyboranes and are given a formula $(RBO)_3$, where R can be H, alkyl, alkoxy or an aryl group. Thus,

$$3RB(OH)_2 \xrightarrow{-3H_2O} (RBO)_3$$

The simplest molecule, where R = H, is called "boroxine", while the other compounds (R different from H) are its derivatives.

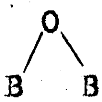
The trimeric formula for boroxines has been proved by various physical methods; cryoscopic,[127] ebullioscopic,[128] electron diffraction,[129] Raman spectroscopic[130] etc.

Electron diffraction studies on boroxine[131] $(H_3B_3O_3)$ and trimethylboroxines[132] have proved a planar, six-membered, ring structure, with alternating boron and oxygen atoms. In the case of trimethylboroxine, even the methyl group, bonded to boron atom, is in the plane of the ring.

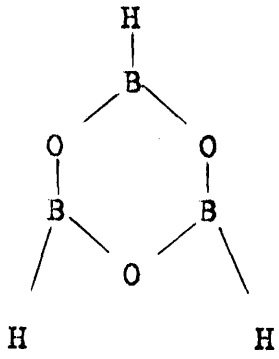


$B - O = 1.39 \pm 0.02 A^\circ$

$B - C = 1.57 \pm 0.03 A^\circ$

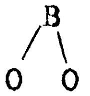


$= 112 \pm 4^\circ$



$B - H = 1.192 \pm 0.017 A^{\circ}$

$B - O = 1.375 \pm 0.002 A^{\circ}$



$= 120^{\circ} \pm 0.64^{\circ}$

Recently triphenylboroxine has also been shown to be a planar ring[133] and it appears that other substituted arylboroxines also have the same structure.

Most of the arylboroxines are high-melting solids and some of the physical and chemical properties of these compounds have been reviewed by Lappert.[10]

Preparation of arylboroxines:

All of the arylboroxines were prepared by the dehydration of the respective aryldihydroxyboranes, which were obtained by the reaction of Grignard reagents with trimethoxyborane, as shown by the following equations.

$$ArX + Mg \xrightarrow{Et_2O} ArMgX$$

$$Ar\ MgX + (CH_3O)_3B \xrightarrow[H_2O]{Et_2O} ArB(OH)_2 + 3CH_3OH + MgX(OH)$$

$$3ArB(OH)_2 \xrightarrow[-3H_2O]{} (ArBO)_3$$

The dehydration procedure consisted of one or more of the following steps:

(i) Keeping at 0.1 mm. pressure and room temperature for 24 hours.

(ii) Heating at 110°C in an oven, for 6-8 hours.

(iii) Heating at 40°C at 0.1 mm. for 24 hours.

(iv) Heating at 80°C at 1.0 mm. for 1 hour.

(v) Azeotropic distillation with dry solvents like toluene[135] (or EtCl).[134]

(vi) Dehydration in presence of a desiccating agent like H_2SO_4, P_2O_5, $SOCl_2$.[136]

The steps used for individual compounds are described in section 3.

The other possible procedures, not used in this work, for the preparation of arylboroxines are:

(1) Refluxing of Ar_3B in presence of B_2O_3:

$$Ar_3B + B_2O_3 \longrightarrow (ArBO)_3$$

(2) Controlled hydration of aryldichloroboranes,

$$3ArBX_2 + 3H_2O \longrightarrow (ArBO)_3 + 6HCl$$

The above two methods are not very useful for the preparation of substituted arylboroxines, because

(a) several steps are involved in the preparation of reactants, which usually are not commercially available.

(b) decomposition of the reactants may take place at higher temperatures or in the absence of an inert atmosphere.

Some of the dehydrating procedures are not very satisfactory because decomposition of the compounds may take place at higher temperatures in the absence of an inert atmosphere. The initial dehydrating (step (i)) at reduced pressure (0.1 mm.) at room temperature is quite useful, and further dehydrating can be effected at moderate temperatures at reduced pressure.

The purity of arylboroxines depends upon the purity of the parent aryldihydroxyboranes, which were properly crystallized from various dry and oxygen-free solvents (for individual compounds see section 3).

The criteria of purity for arylboroxines was their elemental analyses which are tabulated below. (Table 1).

We report in this thesis two new boroxines, i.e. $(p.{}^{t}BuPhBO)_3$ and $(p.CF_3PhBO)_3$ (see section 3 for synthesis and physical constants). Molecular weight studies on these compounds indicate their trimeric nature (page 122). Molecular weight studies of other arylboroxines have also been carried out in various solvents.[127] Dioxane and cyclohexane, in general, seem to be more suitable solvents for cryoscopic determinations, while in benzene the results are

TABLE 1

R in $(R\text{-}Ph\text{-}BO)_3$	ANALYSIS							
	Calculated				Found			
	C	H	B	Hal.	C	H	B	Hal.
pF-	59.1	3.3	8.87	15.58	58.95	3.4	8.48	15.72
pCl-	52.0	2.91	7.82	25.6	51.94	2.72	8.0	25.59
pBr-	39.4	2.2	5.91	43.7	39.46	2.34	6.5	43.55
pCH_3-	71.3	5.98	9.16		70.91	6.06	9.3	
oCH_3-	71.3	5.98	9.16		71.24	6.00	9.28	
pCH_3O-	62.8	5.26	8.06		63.5	5.35	8.08	
$pC(Me)_3$-	75.5	8.12	6.8		75.36	8.11	6.76	
pCF_3-	48.88	2.34	6.29	33.16	46.32	2.94	6.4	31.26

variable. The differential vapour pressure method seems to be excellent even in benzene as a solvent. Results are tabulated on page 122.

The infrared spectra of boroxines indicates a strong absorption band at 680 ± 20 $cm.^{-1}$, which is ascribed to the presence of the boroxine ring (out-of-plane deformation). This band is also present in the spectra of p.tri-t-butylphenylboroxine and p.tri-trifluoromethylphenylboroxine but at higher wave numbers, 596 and 694 cm.$^{-1}$ respectively.

Calorimetry:

The enthalpy of formation of arylboroxines is obtained by studying the oxidative hydrolysis in excess aqueous base.[83] The reactions were carried out in a constant-temperature-environment calorimeter (for details see Part 2, section 4, page 164).

The reaction is as follows:

$$[\mathrm{ArBO}]_3,\text{cryst.} + [3\mathrm{H_2O_2} + 3\mathrm{H_2O}]\text{a.e.b.} \longrightarrow [3\mathrm{ArOH} + 3\mathrm{H_3BO_3}]\text{a.e.b.}$$

Therefore,

$$\Delta H_f^o[\mathrm{ArBO}]_3,\text{cryst.}=3\Delta H_f^o[\mathrm{ArOH+H_3BO_3}]\text{ae.b.} - 3\Delta H_f^o[\mathrm{H_2O_2+H_2O}]\text{a.e.b.}$$

$$3\Delta H_f^o[(\mathrm{H_2O_2})\text{a.e.b.}]-3[\mathrm{H_2O},l]-\Delta H_{obs}.$$

Here ΔH_{obs} is the experimental heat of reaction; a.e.b. ≡ excess aqueous base.

The phenols were not oxidized under the calorimetric conditions, since the heat of neutralization of phenols with 1.0N sodium hydroxide was the same in the absence or in the presence of hydrogen peroxide.

The reaction conditions were chosen in such a way that a nearly equivalent rise in temperature occurred for every reaction. The volume of the calorimetric fluid was kept to 125-150 ml. and the amount of the substance was only changed to get the desired temperature difference. The effect of dilution was always found to be negligible.

The calorimetric liquid generally consisted of 1.0N or 0.1N sodium hydroxide solution. The thermal effect of the decomposition of hydrogen peroxide by concentrated alkali solution (1.0N NaOH), under calorimetric conditions was found to be negligible. This was checked by analysis by a standard iodimetric procedure,[138] as follows:

$$H_2O_2 + 2Kl + H_2SO_4 \longrightarrow I_2 + K_2SO_4 + 2H_2O$$

Sodium hydroxide solution (150 ml, 1.0N) was loaded in the calorimeter with stirring. 2.0 ml. of H_2O_2 solution (30%) was added; 25.0 ml. of the calorimetric liquid were then immediately transferred to an Erlenmeyer flask containing 160 ml. 2.0N sulphuric acid solution, 10 ml. of KI solution (10%) and three drops of ammonium molybdate solution (3%, to catalyse the reaction) with constant stirring. After five minutes the liberated iodine was titrated with 0.1 sodium thiosulphate solution. The same procedure was repeated after four hours, eight hours, and twenty-four hours, when there was only 7% decomposition of hydrogen peroxide.

The triarylboroxines, which were stored in an atmosphere of dry, oxygen-free nitrogen, were filled in glass ampoules in a dry-box in dry, oxygen-free nitrogen and were weighed accurately, using standardized weights. The average measured heats of reactions for arylboroxines (at 298.15K) are as follows, (see detailed results in section 5, page 116).

TABLE 2

COMPOUND R in $(RBO)_3$	N	* $\Delta H_{obs.}$ kcal.mole^{-1}
p,F-	10516	-274.2 ± 2.3
p,Cl-	13087	-296.7 ± 1.5
p,Br-	25130	-306.9 ± 2.7
p,CH_3-	13887	-274.9 ± 2.3
o,CH_3-	26317	-307.3 ± 1.8
p,CH_3O	15141	-275.5 ± 1.7

Ancillary data:-

For a general reaction:

$$A + B \longrightarrow C + B; \quad \Delta H_{obs} \text{ or}$$

$$\Delta H_f^o A = \Delta H_f^o C + \Delta H_f^o D - \Delta H_f^o B - \Delta H_{obs}$$

The heat of formation of the products and reactants (except A) under the conditions of the reaction are required.

Generally, heats of formation of various reactants and products are available in the literature in their standard states (the state at 1 Atm. pressure and 298.15K temperature). If not available, these may be experimentally determined, or estimated from some known data, applying simple assumptions and approximations.

Consider the following equation:

$$\Delta H_f^o[(ArBO)_3, \text{cryst.}] = 3\Delta H_f^o[(ArOH)\text{a.e.b.}] + 3\Delta H_f^o[(H_3BO_3)\text{a.e.b.}]$$
$$-3\Delta H_f^o[(H_2O_2)\text{a.e.b.}] - 3\Delta H_f^o[(H_2O)\text{l}] - \Delta H_{obs}.$$

The standard heat of formation (ΔH_f^o) of arylboroxines (cryst.) can be calculated if the following data are available:

(1) ΔH_{obs}; the heats of reactions, which were determined experimentally and are given in Table 23 section 5 (Part I)

(2) $\Delta H_f^o[(H_3BO_3)\text{a.e.b.}]$. This datum is available in the literature.[83]

(3) $\Delta H_f^o[(ArOH)\ \text{a.e.b.}]$. The standard heats of formation of some of the phenols are available in the literature,[139] while for the rest of the phenols estimation according to the procedure described later was made. The heat of reaction of the respective phenols with excess aqueous base was determined by solution reaction calorimetry (Table 26, page 119). This, together with $\Delta H_f^o[(ArOH)$, gave the heats of formation of phenols in excess aqueous base.

(4) $\Delta H^o_f[(H_2O_2)$ a.e.b.$]$. The standard heat of formation of hydrogen peroxide $[H_2O_2,]$ and its heat of solution in water is available in the literature.[140] It is, however, assumed that the heat of dilution of hydrogen peroxide in excess aqueous base is equal to that in water. This assumption is justified, because the ionic product of H_2O_2 in aqueous solution is ca. 1.5×10^{-12} (20°C).[141]

(5) Heat of formation of liquid water; this is available in the literature.[140]

(6) Heat of mixing of various reaction products (ArOH and H_3BO_3 etc.) are assumed to be negligible.

In order to determine the heat of formation of a compound in the gaseous state, the latent heat of vaporization, ΔH_v, (if liquid) or the latent heat of sublimation ΔH_s, (if solid) is required. Thus:

$$[(ArBO)_3 \text{ cryst.}] \xrightarrow{\Delta H_s} [(ArBO)_3, g]$$

or

$$\Delta H^o_f[(ArBO), g] = \Delta H^o_f[(ArBO), \text{cryst.}] + \Delta H^o_s$$

Since ΔH_s of $[(ArBO)_3\text{cryst.}]$ is difficult to determine, the assumption is therefore made, that the heat of sublimation of triarylboroxines is equivalent to the heat of sublimation of triarylbenzenes. The heat of sublimation of 1,3,5 triphenylbenzene is 31.5 ± 0.5 kcal.mole^{-1} [142] while that of substituted arylbenzenes is assumed to be 32.0 ± 2.0 kcal.mole^{-1}. Thus the heat of sublimation for all the arylboroxines is taken as 32.0 ± 2.0 kcal.mole^{-1}.

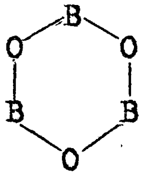
Various bond energy terms can be calculated from the standard heat of formation of a compound in the gaseous state, if the standard heats of formation of the hypothetical dissociation products are known. Thus for arylboroxines the equation;

$$[(ArBO)_3,g] \longrightarrow 3Ar(g) + (BO)_3g; \quad 3\bar{D}(C_{Ar} - B)$$

$$\text{or } 3\bar{D}(C_{Ar}-B) = 3\Delta H_f^o[Ar,g] + \Delta H_f^o[(BO)_3g) - \Delta H_f^o[(ArBO)_3g]$$

can give the dissociation energy of the (aryl) carbon-boron bond, $\bar{D}(C_{Ar}-B)$, when the heat of formation of aryl radicals (gas) and that of boroxine ring (gas) is available. The only aryl radical standard heat of formation available in the literature is that of the phneyl radical^{97}, while for the rest of the radicals these data were calculated, as shown later. The heat of formation of the boroxine ring was estimated from a knowledge of $\bar{D}$(B-O), $\Delta H_f^o B(g)$ and $\Delta H_f^o O(g)$, since:

$$\Delta H_f^o(BO)_3(g) = 3\Delta H_f^o B(g) + 3\Delta H_f^o O - 6\bar{D}(B-O)$$



The overall ancillary data used here are, therefore, reported as follows:

TABLE 3

Heat of neutralization of phenols with 1.0N NaOH.

$$\text{ArOH} \xrightarrow{\text{a.e.b.}} [\text{ArOH}]\text{a.e.b.} \; ; \; \Delta H_{\text{obs.}}$$

Compound	N	$\Delta H_{\text{obs.}}$ kcal.mole^{-1}
$pF.C_6H_4.OH$	749	3.60 ± 0.1
$pCl.C_6H_4.OH$	924	3.60 ± 0.2
$pBr.C_6H_4.OH$	924	3.20 ± 0.04
$pCH_3.C_6H_4.OH$	727	4.07 ± 0.08
$oCH_3.C_6H_4.OH$	901	3.8 ± 0.1
$p.CH_3O.C_6H_4OH$	772	2.2 ± 0.1
$p.COOH.C_6H_4OH$	1904	15.9 ± 0.3
$2,4,6\ Me_3.C_6H_2.OH$	1242	3.1 ± 0.1

TABLE 4

Heat of formation of phenols [ΔH_f^o (ArOH), a.e.b.]

Compound	ΔH_f^o(cryst.) kcal.mole^{-1}	Reference	ΔH_f^o(a.e.b.) kcal.mole^{-1}
$p.F.C_6H_4OH$	-89.9 ± 2.0	This work	-93.5 ± 2.0
$p.Cl.C_6H_4OH$	-50.3 ± 2.0	" "	-53.9 ± 2.0
$p.Br.C_6H_4OH$	-34.6 ± 2.0	" "	-37.8 ± 2.0
$p.CH_3OC_6H_4OH$	-80.7 ± 2.0	" "	-82.9 ± 2.0
2,4,6 $Me_3C_6H_2OH$	-65.0 ± 2.0	" "	-68.55
$p.CH_3C_6H_4OH$	-47.64 ± 2.0	139	-51.71
$o.CH_3C_6H_4OH$	-48.91 ± 2.0	"	-52.71
$p.COOH.C_6H_4OH$	-142.0	144	-157.9

TABLE 5

Standard heat of formation of (gaseous) aryl radicals, calculated from the given compounds.

Compound	ΔH_f^o g kcal.mole^{-1}	Reference	ΔH_f^o radical$_{(g)}$ (calc.) kcal.mole^{-1}
C_6H_5-H	+ 19.82	100	71.7 ± 2.0
$F.C_6H_4$-H	- 27.1	"	24.8 "
$Cl.C_6H_4$-H	+ 12.5	"	64.4 "
Br C_6H_4-H	+ 27.2	"	79.0 "
$CH_3.C_6H_4$-H	+ 11.95	"	63.85 "
$CH_3O.C_6H_4$-H	- 18.0	"	34.0 "
2,4,6 $Me_3C_6H_2$-OH	- 46.1	Calc. (this work)	49.7 "

TABLE 6

Other ancillary data

Compound	State (298.15H)	ΔH_f^o kcal.mole^{-1}	Reference
H_3BO_3	crystal	-261.47	140
	a.e.b.	-266.8	83
H_2O	liquid	-68.32	140
H_2O_2	gas	-32.53	83
	a.e.b.	-45.7	83
B	gas	132.8 ± 4.0	26
O	gas	59.8	145
OH	gas	9.3	145
H	gas	52.1	145

TABLE 7

Bond energies

Bond	Energy kcal.mole^{-1}	Reference
$C_{Ar} - H$	104	97
$C_{Ar} - OH$	104	calc.
$B - O$	124.4	146
$C_{Ar} - B$	105.0	147
$C - B$	88.0	147

Calculation of ancillary data

Phenols. Although the standard heats of formation of phenols,[139] the cresols[139] and xylenols[139] have been reported, much data are absent from the literature. In order to utilize our experimental results, an attempt was made to calculate some of the desired data on the basis of reasonable assumptions and approximations.

According to Benson[94] $E(C_{Ph}-H) = E(C_{Ph} - OH) = 103$ kcal. mole^{-1} and the value of the standard heat of formation of the gaseous phenyl radical $\Delta H_f^o[(Ph),g]$ is 71 kcal.mole^{-1}. Recently, Kerr[97] recommended that $E(C_{Ph}-H)$ be taken as 104 kcal.mole^{-1} and $\Delta H_f^o[(Ph),g]$ as 72 kcal.mole^{-1}. Taking $\Delta H_f^o[(PhOH)g]$ as 23.05 kcal.mole^{-1}, the value of $E(C_{Ph}-OH)$, according to Kerr's data, becomes 104 kcal.mole^{-1}. Therefore, as a first approximation, we take $E(C_{Ar}-H) = E(C_{Ar}-OH) =$ 104 kcal.mole. The notations C_{Ph} and C_{Ar} represent the carbon atoms of the phenyl group and the substituted phenyl groups respectively. The above assumption is difficult to justify. However, we consider that the substitution in the phenyl group brings about a change in the resonance energy of the carbon skeleton only, and that the corresponding values of $E(C_{Ar}-H)$ and $E(C_{Ar}-OH)$ are not much affected.

Now considering the following equations:

$\Delta H_f^o[(ArOH)g] \longrightarrow \Delta H_f^o[(Ar)g] + \Delta H_f^o[(H),g]-E[C_{Ar}-OH]$ ... (i)

$\Delta H_f^o[(ArH)g] \longrightarrow \Delta H_f^o[(Ar),g]+\Delta H_f^o[(H),g]-E[C_{Ar}-H]$ ... (ii)

and subtracting (ii) from (i):

$\Delta H_f^o[(ArOH),g] = \Delta H_f^o[(Ar-H),g] + \Delta H_f^o[(OH),g] - \Delta H_f^o[(H),g]$

The standard heats of formation of various substituted benzenes in the gaseous state, $\Delta H_f^o[(OH),g]$ and $\Delta H_f^o[(H),g]$ are available in the literature.[100] $\Delta H_f^o[(ArOH),g]$ was therefore calculated from the above equation.

In order to obtain $\Delta H_f^o[(ArOH)cryst.]$, a suitable heat of sublimation, obtained by comparison of the data for compounds with similar structure, was, therefore, subtracted from the calculated value of $\Delta H_f^o[(ArOH),g]$. The results have been tabulated earlier (see Table 4).

Some of the calculated and experimental heats of formation of gaseous phenols are compared as follows:

$\Delta H_f^o[(PhOH),g]$ calc. = -23.1 kcal.mole^{-1}

exp. = -23.05 kcal.mole^{-1} [139]

$\Delta H_f^o[(pCH_3C_6H_4OH),g]$ calc. = -30.8 kcal.mole^{-1}

exp. = -30.0 kcal.mole^{-1} [139]

$\Delta H_f^o[(o.CH_3C_6H_4OH),g]$calc. = -30.8 kcal.mole^{-1}

exp. = -30.7 kcal.mole^{-1} [139]

The standard heat of formation of mesitol (2,4,6, $Me_3C_6H_4OH$) in the gaseous and the crystalline states was calculated from the following data.

TABLE 8

Compound (s.s.)	ΔH_f^o (gas) kcal.mole^{-1}	ΔH^o subl. kcal.mole^{-1}
$C_6H_5OH(c)$	-23.05 ± 0.15	16.40 ± 0.12
$4,CH_3-C_6H_4-OH(c)$	-29.97 ± 0.36	17.67 ± 0.35
$2,6\ Me_2C_6H_3OH(c)$	-38.68 ± 0.13	18.07 ± 0.04

Thus the standard heat of formation of 2,4,6 $Me_3C_6H_2OH$ was calculated according to the following equations:

$$\Delta H_f^o[(2,4,6,Me_3C_6H_2OH)g] = \Delta H_f^o[(2,4\ Me_2C_6H_3OH)g] + \Delta H_f^o[(4,CH_3C_6H_4OH)g] - \Delta H_f^o[(C_6H_5OH),g] = -45.60\ \text{kcal.mole}^{-1}$$

$$\Delta H^o_{subl.}[(2,4,6\ Me_3C_6H_2,cryst.] = \Delta H^o_{subl.}[(2,6,Me_2C_6H_3OH),cryst.] + \Delta H^o_{subl.}[(4,MeC_6H_4OH),cryst.] - \Delta H^o_{subl.}[(C_6H_5OH),cryst.] = 19.34$$

Hence, $\Delta H_f^o[(2,4,6\ Me_3C_6H_2OH)cryst.] = -65.0 \pm 1.0$ kcal. mole^{-1}

The error ± 1.0 is applied to adjust the uncertainties in the actual value.

Aryl radical

The standard heats of formation of aryl radicals in the gaseous state were also calculated from the standard heat of formation of the respective substituted benzenes, applying the same assumption, mentioned above, that:

$$\bar{D}(C_{Ar}-H) = \bar{D}(C_{Bz}-H)$$

Thus

$$[Ar-H]g \longrightarrow Ar(g) + H(g)\ ;\ \bar{D}(C_{Ar}-H)$$

or

$$\Delta H_f^o[(Ar),g] = \Delta H_f^o[(Ar-H),g] - \Delta H_f^o[(H)g] + \bar{D}[C_{Ar}-H]$$

and so,

$$\Delta H_f^o[(Ph),g] = \Delta H_f^o[(C_6H_6)g] - \Delta H_f^o[(H),g] + \bar{D}(C_{Bz}-H)$$

$$= (+19.82) - (+52.1) + (+104)$$

$$= 71.7 \text{ kcal.mole}^{-1} \text{ (lit. } 72.0 \text{ kcal.mole}^{-1}\text{).}$$

since $\Delta H_f^o[(2,4,6,Me_3C_6H_2-H)g]$ is not available, this data was calculated from the estimated $\Delta H_f^o[(2,4,6-Me_3C_6H_2-OH)g]$, as

$$\Delta H_f^o[(2,4,6-Me_3C_6H_2-)g] = \Delta H_f^o[(2,4,6-Me_3C_6H_2-OH)g] - \Delta H_f^o[(OH),g] + E[C_{Ar}-OH]$$

$$\text{or} \quad = (-45.0) - (9.3) + (104)$$

$$= 49.7 \text{ kcal.mole}^{-1}.$$

Results

The standard heats of formation of arylboroxines, in both crystalline and gaseous states, were calculated using the ancillary data discussed above. The errors are spread and are considered within the range of ± 2-3 kcal.mole^{-1}. The results are tabulated as follows.

TABLE 9

Compound	ΔH_f^o crystals kcal.mole^{-1}	ΔH_f^o gas kcal.mole^{-1}
$(p.F\ C_6H_4BO)_3$	-464.7	-432.2
$(p.ClC_6H_4BO)_3$	-323.4	-291.0
$(p.BrC_6H_4BO)_3$	-264.8	-232.3
$(p.CH_3C_6H_4BO)_3$	-338.53	-307.0
$(o.CH_3C_6H_4BO)_3$	-309.23	-277.2
$(p.CH_3OC_6H_4BO)_3$	-431.6	-399.1
$(C_6H_5BO)_3$	-299.0	-267.5

A more useful interpretation can be obtained by calculating the overall difference in energy from the calculated and experimental heats of formation of the arylboroxines in the gaseous state. This difference in energy can be represented by a factor P and is given by the following equation:

$$P = \Delta H^o_f C_{(g)} + \sum_i Ei - \Delta Ha$$

where

ΔHa = sum of the standard enthalpies of formation of gaseous atoms or groups comprising the molecule under consideration at 298°K.

$\Delta H^o_f C_{(g)}$ = standard enthalpy of formation of the compound in the gas phase at 298°K.

$\sum_i Ei$ = Energy of the i^{th} bond at 298°K.

Assuming that $E(B-O) = 124.4$ kcal.mole^{-1} 146 and that $E(C_{Ar}-B) = 105$ kcal.mole^{-1}. Values of the factor P are reported

TABLE 10

Compound	P
$(p.F.C_6H_4BO)_3$	-22.7
$(p.Cl.C_6H_4BO)_3$	+ 0.3
$(p.Br.C_6H_4BO)_3$	+12.2
$(p.CH_3.C_6H_4BO)_3$	-14.4
$(o.CH_3.C_6H_4BO)_3$	+15.3
$(p.CH_3OC_6H_4BO)_3$	-16.6
$(C_6H_5BO)_3$	+1

Assuming a constant aromaticity in the boroxine rings i.e. the standard heat of formation of [B_3O_3,g] is constant and derivable from data for $(PhBO)_3$, values of E(C_{Ar}-B) for the remaining boroxines were evaluated. These are shown in Table 11.

However, the exact distribution of the stabilization (or destabilization) energy between the B-C bond and the aromaticity of the boroxine ring cannot be evaluated from these data.

In considerating the C-B bond energies, the σ-contributions are assumed to be constant [i.e. 88 kcal.mole^{-1}, the value of E(C-B) in $(C_6H_{11})_3$]^{147}, and taking E(B-O) = 124.4 kcal.mole^{-1},^{146} the π-electronic contributions to E(C_{Ar}-B) bond were calculated. These are as follows:

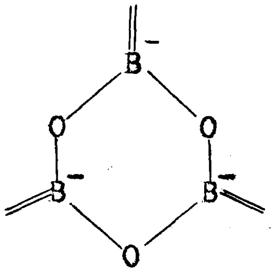
TABLE 11

Compound	E(C_{Ar}-B)kcal.mole^{-1}	π-E(C_{Ar}-B)kcal.mole^{-1}
$(p.F.C_6H_4BO)_3$	112	24
$(p.Cl.C_6H_4BO)_3$	105	17
$(p.Br.C_6H_4BO)_3$	101	13
$(p.CH_3C_6H_4BO)_3$	109	21
$(o.CH_3.C_6H_4BO)_3$	99	11
$(p.CH_3OC_6H_9BO)_3$	111	23
$(C_6H_5BO)_3$	105	17

DISCUSSION

Resonance stabilization of Arylboroxines.- The substitution of an aryl group on boron atom has been shown to increase to a considerable extent the $E(C_{Ar}-B)$ bond.[147] This was attributed to the resonance stabilization from the mesomeric structures.

Finch et al.[83] discussed the effect of substitution at a boron atom in the boroxine ring and showed that, when the substituent was a phenyl group, there was no appreciable change in the resonance stabilization energy of the boroxine ring. However, the effect of substituting the phenyl group appears quite marked. Here also the stability-contributing structure is:



It is apparent from the values of the factor P, calculated as above, which when negative indicate the extent of resonance stabilization, that the atoms or groups which enhanced mesormerism by hyperconjugation with the aromatic ring, increased the resonance stabilization of the boroxine rings. The observed order of stability contribution is,

$$p.F > p.CH_3O > p.CH_3 > p.Cl > H > p.Br > o.CH_3$$

Strength of the C_{Ar}-B bond in Arylboroxines

The effect of substituting the phenyl group in arylboroxines has been attributed to resonance stabilization of the boroxine rings. If, again, we assumed that the resonance energy of the boroxine ring is constant, (see page 86) then the increase or decrease in the strength of the C_{Ar}-B bond can be evaluated. The strength of C_{Ar}-B in triphenylborane has been experimentally determined as 105 kcal.mole^{-1}.[147] In comparison with this bond energy, the results in arylboroxines are as follows:

The effect of substituents on the C_{Ar}-B bond strength is as follows:

$$p.F > p.CH_3O > p.CH_3$$

Substituents which do not affect the C_{Ar}-B bond are the chloro- and H-atoms, while the substituents decreasing the strength of C_{Ar}-B are in the order

$$o.CH_3 > p.Br$$

The decrease in the strength of the C_{Ar}-B bond upon substituting a methyl group in the ortho position seems to be due to a steric effect. The increased size of the substituted atoms also decreases the C_{Ar}-B bond strength.

π-Electronic contributions from C_{Ar}-B Atom

The E(C-B) bond due to a σ-bonding is taken as 88.0 kcal. mole^{-1}, when the boron atom is bonded to three cyclohexane rings [i.e. E(C-B) in $(C_6H_{11})_3B$].[147] The increase in E(C_{Ar}-B), over this value was taken as the contribution due to π-electronic contributions:

$$p.F > pCH_3O > p.CH_3 > H > p.Cl > p.Br > o.CH_3$$

The decreased π-electronic contributions in the case of the ortho-methyl substituent indicates a strong steric effect.

We propose, according to available evidence, that the contribution to E(B-O) of the boroxine is least affected by substitution in the phenyl ring of the triphenylboroxine, and that overall contributions are mainly due to π-electronic contributions to the (C_{Ar}-B) bond. These results are supported by the infrared studies of Lappert et al.,[148] Makoza et al.[90], and Dale et al.[149]. Thus the following table indicates that ν_s(B-O) is nearly constant in alkyl and arylboroxines.

Alkylboroxines (Lappert et al.)

Group —	Me	Et	nBu	t-Bu
^{11}B-O	1370	1380	1387	1357
^{11}B-C	1253	1265	1236	1160
^{10}B-C	1222	1225	1202	1147

Arylboroxines (Makoza et al.)

Group —	H	oCH_3	mCH	pCH_3
B-O	1354	1350	1347	1352
B-O	1184	1201	1198	1186

Dale and Rush[149] indicated that ν_sB-O is nearly constant, even if unsaturated groups are substituted in the phenyl ring.

Perkin et al. calculated the π-electronic structures of some arylboroxines. They concluded that the substitution in a phenyl ring on the boron atom raises its electron density, but that this is due to π-contributions of the (B-O) bond. Santucci et al.[91], according to ultraviolet studies, reported that the π-electronic contributions of phenyl groups to the boron atoms of the boroxine ring are not negligible.

It is, therefore, concluded that the substitution of an aryl group at the boron atom in a boroxine ring affects the π-electronic contributions, and that the conjugating groups increase this effect considerably.

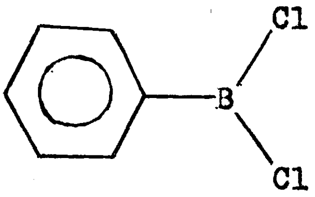
Substitution at the ortho-position in arylboroxines introduce a marked steric interaction and thus a decrease in $E(C_{Ar}-B)$.

Aryldihaloboranes.

Aryldihaloboranes are simple derivatives of aromatic hydrocarbons, in which one of the hydrogen atoms has been replaced by a dihaloboryl group. These compounds are mostly volatile, high-boiling liquids and are quite stable at moderate temperatures. At higher temperatures some of the compounds seem to decompose to aromatic hydrocarbons, especially in the presence of impurities.

Aryldihaloboranes are monomeric in the gaseous state, because the latent heats of vaporization of the substituted dichloroboranes are of the same order of magnitude as the corresponding figure for phenyldichloroborane.

Aryldihaloboranes are probably planar in the gaseous state. Thus the electron diffraction studies by Bauer et al.[150], definitely proved that the phenyldichloroborane is planar and that the B-Cl bond length is the same as in boron trichloride.



(C-C) ring = 1.39A°

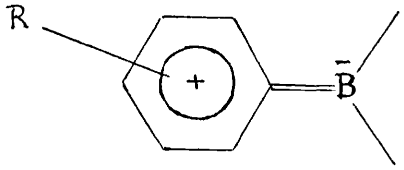
B-Cl = 1.72 ± 0.03A°

1.73 ± 0.02 BCl_3

$\angle$ClBCl = 118 ± 3°

C-B = 1.52 ± 0.07A°.

Thus the following mesomeric structure seems to contribute to phenyldihaloboranes.



Support for the contribution of this structure derives from the observed dipole moment of the compound in benzene, e.g. 3.07 ± 0.15 Debye.[150] A small difference in electron-sharing properties of the phenyl group and the chlorine atoms should result only in a small net moment. The large moment observed, therefore, could only be accounted for by a quinoid structure and the presence of a partial (phenyl-boron) double bond. Thus there must be a considerable $p\pi - p\pi$ bonding contribution.

The same type of conclusion was arried at by Stone et al.[151] from spectroscopic measurements on alkyl and aryldihaloboranes.

Lockhart,[113] on the basis of infrared and Raman spectroscopy, calculated the barrier to rotation about the boron-carbon link, in phenyl dichloroborane, as ca. 45 kcal.mole^{-1}, and thus established a considerable π-character in aromatic C-B bond.

Gerrard et al.[91] also studied the infrared spectra of substituted aryldihaloboranes and reported the presence of the usual band multiplicity associated with hyperconjugation of the methyl group in tolyldihaloboranes. They also supported the conjugation of the phenyl ring with the boron atom. The infrared spectra of our compounds (page 123) support the above results and indicate that ν_sB-Cl in p-tolyldichloroborane, ortho-tolyldichloroborane, and mesityldichloroborane is unaffected by substitution in the phenyl ring (910 ± 20 cm.$^{-1}$), (Fig. 7 - 10 page 123-126).

The results obtained by Eggers[88] on the magnetic resonance properties of substituted aryldihaloboranes were in disagreement to the H.M.O. calculations. On the basis of H.M.O. calculations he reported that the increase in the order of B-C bond in these above compounds was in the following order,

$$CH_3O > CH_3 > F > Cl > Br.$$

and as regards tolyldichloroboranes the order is

$$\text{ortho} > \text{para} > \text{meta}$$

We have not studied the meta-dichloroboranes but for ortho and para tolyldichloroboranes, the order of increase in (C_{Ar}-B) bond strength has been found to be:

$$\text{ortho} > \text{para}$$

which thus supports the above results.

Preparation of aryldihaloboranes

Several methods are available for the preparation of aryldihaloboranes; the more important are as follows:

$$(1)\quad \mathrm{Ar{-}H + BCl_3 \xrightarrow[\text{under pressure}]{\text{Al powder}} ArBCl_2 + HCl}$$

$$(2)\quad \mathrm{Ar_4Sn + 4BCl_3 \xrightarrow[\text{reflux}]{170^{\circ}C} 4ArBCl_2 + SnCl_4}$$

$$(3)\quad \mathrm{(ArBO)_3 + 3BCl_3 \xrightarrow[\text{reflux}]{200^{\circ}C} 3ArBCl_2 + (SOCl)_3}$$

$$(4)\quad \mathrm{ArHgX + BCl_3 \xrightarrow[\text{reflux}]{C_6H_6} ArBCl_2 + HgXCl}$$

The first procedure,[69] which requires special high pressure equipment, has the disadvantage of producing appreciable amount of isomeric products. The second method[50] is unsuitable for the preparation of substituted aryldihaloboranes because tetra-aryltin compounds are commercially unavailable, and their preparation involves additional steps. The third method,[137] although experimentally simple, suffers from the above defects and, further, the percentage yield is low.

The fourth method is, therefore, the best available method for the preparation of substituted aryldihaloboranes. It has the advantage of producing the least amount of isomeric products and offers reasonably pure products. However, mercury compounds are strong antiseptic and antibacterial agents and cause much damage to the skin, so they must be used cautiously.

The preparation of 2,6-dimethylphenyldichloroborane could not be effected by the above method and was not attempted by any other method. It seems that either the intermediate complex could not be formed during the reaction, or the product was quite unstable and decomposed under the reaction conditions. The probable steric effect of substituents in the ortho-position decreases the energy of the aryl-mercury bond. However, since we had prepared the corresponding arylmercury compound (2,6-dimethylphenylmercuric-chloride) it seems that the reaction would not take place with boron trichloride. Mowever, since we could not isolate any isomeric aryldihaloboranes it is concluded that isomerism does not take place in this procedure; this contradicts Egger's observation. We also could not find any ionizable chlorine in the liquid fractions, which seem to consist of unsaturated aromatic hydrocarbons (b.pt. 80°C - 134°C). The solid products were a mixture of unknown composition and consisted of a polymeric, light yellow, substance with no boron, and of m.pt. 300°C (dec.) together with a white substance (m.pt. 160-170°C) containing boron. The mixture absorbed moisture very readily and turned to a greyish mass. Further work on this preparation, therefore, was not carried out due to the above complexities.

The purity of aryldichloroboranes prepared for this work was evident from the results of boron and chlorine analysis, infrared spectra (pages 123-126) proton magnetic resonance spectra (page 127) and vapour pressure studies. The calculated and observed boiling points of the products were in agreement.

Analytical results are as follows:

TABLE 12

Compound	ANALYSIS			
	Calc.%		Found%	
	B.	Hal.	B.	Hal.
p.$CH_3C_6H_4BCl_2$	6.24	41.08	6.25	38.2
o.$CH_3C_6H_4BCl_2$	6.24	41.08	6.5	40.28
2,4,6 $Me_3C_6H_2BCl_2$	5.37	35.4	5.9	34.9

The other results are given in section 5, Part I.

Calorimetry

Phenyldichloroborane has been found to hydrolyse rapidly and quantitatively to phenyldihydroxyborane.[147]

$$ArBCl_2 + 2H_2O \longrightarrow ArB(OH)_2 + 2HCl$$

The reaction, however, occurs violently, causing the calorimetric fluid to be splashed on the sides of the calorimeter.

The reaction was therefore subdued by using a small amount of substance, but the heat of reaction is small, about 40 kcal.mole^{-1} at N = 2900.

Generally, arylboron compounds are readily oxidised to aromatic hydroxy-compounds (phenols) and orthoboric acid by hydrogen peroxide in a basic medium. This reaction was found useful in determining the heat of formation of aryldihaloboranes and can be written as follows:

$$ArBCl_2 + H_2O_2 + 2NaOH \xrightarrow{aq.} ArOH + B(OH)_3 + 2NaCl; \Delta H_{obs}$$

thermochemically the reaction is defined as:

$$\Delta H_f^o[(ArBCl_2)] = \Delta H_f^o[(ArOH)a.e.b.] + \Delta H_f^o[(B(OH))a.e.b.] +$$
$$2\Delta H_f^o[(NaCl)\ a.e.b.] - \Delta H_f^o[(H_2O_2)a.e.b.] - 2\Delta H_f^o[(NaOH)aq.] - \Delta H_{obs}$$

All of the ancillary data are therefore either available or can be calculated by using simple assumptions and approximations (see arylboroxines).

The standard state of p.tolydichloroborane is rather questionable. The compound, though completely liquid at 27°C, does not appear to be wholly crystallized at 25°C. The heats of reaction of this compound were therefore determined at two different temperatures, 22°C and 32°C. The standard state was, however, taken as a liquid, and so accordingly the results were corrected to 25°C. The other aryldichloroboranes were liquid at 25°C and presented no problem. The observed heats of oxidative hydrolysis of the aryl dichloroboranes are tabulated as follows.

TABLE 13

Compound	N	ΔH_{obs} kcal.mole^{-1}
p.CH_3 $C_6H_4BCl_2$(l)	16145	-165.4 ± 0.7
o.CH_3 $C_6H_4BCl_2$(l)	13044	-159.0 ± 0.5
2,4,6 $Me_3C_6H_2BCl_2$(l)	11840	-168.2 ± 0.7

Ancillary Data

Most of the ancillary data required here have been tabulated previously (see arylboroxines).

The heat of solution of NaCl in aqueous excess base was assumed to be the same as in pure water. The heat of mixing of various products was assumed to be negligible.

The heat of vaporization of aryldichloroboranes was determined experimentally using the John Hoover and Mellor's semi-micro ebulliometer (see section 2).

The results obtained by least square analysis of the experimental data and then corrected to 298°K, using Watson's equation (section 2), are tabulated as follows:

TABLE 14

Compound	ΔH vaporization (298.15°K kcal.mole^{-1}
$C_6H_5BCl_2$	11.3 ± 0.4
p.$CH_3C_6H_4BCl_2$	9.73 ± 0.31
o.$CH_3C_6H_4BCl_2$	11.2 ± 0.21
2,4,6, $Me_3C_6H_4BCl_2$	13.3 ± 0.5

The other ancillary data required are:

$\Delta H_f^o[(NaCl), aq] = -97.3$ kcal.mole^{-1} [140]

$\Delta H_f^o[(NaOH), aq] = -112.36$ kcal.mole^{-1} [140]

$\Delta H_f^o[(BCl_2), g] = -14.7$ kcal.mole^{-1} [107]

Results.

Using the reported ancillary data, the heat of formation of aryldichloroboranes in their standard liquid and gaseous state at 298.15K were calculated. These are as follows:

TABLE 15

Compound	ΔH_f^o(s.s.) kcal.mole^{-1}	ΔH_f^o(gas) kcal.mole^{-1}
$p.CH_3C_6H_4BCl_2(l)$	-77.3	-67.6 ± 0.5
$o.CH_3C_6H_4BCl_2(l)$	-84.71	-73.5 ± 0.5
2,4,6 $Me_3C_6H_2BCl_2(l)$	-90.8	-77.5 ± 1.0
$C_6H_5BCl_2(l)$	-71.9 ± 0.6	-60.6 ± 0.6

The (aryl)carbon-boron bond energies [$E(C_{Ar}-B)$] in these compounds were calculated according to the following thermochemical cycle.

$$\begin{tikzcd}
ArBCl_2 \arrow[rr, "E(C_{Ar}-B)"] & & Ar(g) + BCl_2(g) \\
& C(\text{graphite}) + H_2(g) + Cl_2(g) + B\ (\text{cryst.}) \arrow[ul, "\Delta H_f^o ArBCl_2(g)"] \arrow[ur, "\Delta H_f^o Ar(g) + \Delta H_f^o BCl_2(g)"'] &
\end{tikzcd}$$

or $E(C_{Ar}-B) = \Delta H_f^o[Ar,g] + \Delta H_f^o[BCl_2,g] - \Delta H_f^o[ArBCl_2,g]$

The bond energies calculated in this way are shown in the following table.

TABLE 16

Compound	$E(C_{Ar}-B)$ kcal.mole^{-1}	$E(C-B)$ kcal.mole^{-1}
$p.CH_3C_6H_4BCl_2$	117 ± 2.0	29.0
$o.CH_3C_6H_4BCl_2$	122 ± 2.0	34.0
2,4,6 $Me_3C_6H_2BCl_2$	112 ± 3.0	24.0
$C_6H_5BCl_2$	118 ± 2.0	30.0

Values of $E(C-B)$ were calculated by taking the $\sigma E(C-B)$ as 88.0 kcal.mole^{-1}.

Discussion

Thermochemical results indicate that the value of $E(C_{Ar}-B)$ in aryldichloroboranes increases in the following order:

o.tolyl > phenyl > p.tolyl > mesityl.

This order is supported by bond orders (H.M.O. calculations[88]) in the tolyldichloroboranes, i.e.

o-tolyl > p-tolyl > n-tolyl

We have not studied the meta-substituted aryldichloroboranes but the results support the following order:

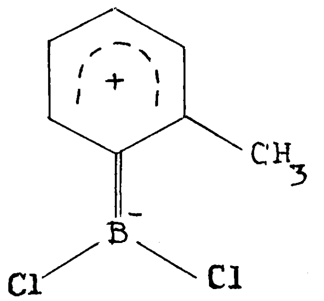
o.tolyl > p.tolyl.

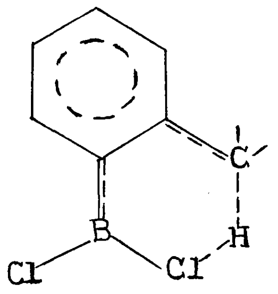
The increase in $C_{Ar}-B$ bond strength in ortho tolyldichloroboranes can be due to increased mesomerism or to σ-interaction of the methyl group with the chlorine atoms. However, 'H n.m.r. did not resolve the methyl proton feature.

The $\pi E(C_{Ar}-B)$ in aryldichloroboranes are quite appreciable and the order increases i.e.:

o-tolyl > phenyl > p.tolyl > mesityl

Thus it seems that the following structures may contribute to the stability of the ortho-tolyldichloroborane.





The substitution of an ortho methyl group can also induce steric interaction. In ortho-tolyldichloroborane this effect is not apparent but in mesityldichloroborane it is quite significant, since the value of $E(C_{Ar}-B)$ in this compound is lower than that in orthotolyldichloroborane.

It seems that steric interaction of other groups in the ortho-position may also have significant effects on the value of $E(C_{Ar}-B)$ in aryldihaloboranes. This effect will certainly be more pronounced in ortho-substituted triarylboranes, where the rings have already a symmetrical propeller configuration.[103]

Aryldihydroxyboranes

Aryldihydroxyboranes are the derivatives of the aromatic system, where one of the aromatic hydrogen atoms has been replaced by a dihydroxyboryl group. These are generally crystalline solids which dehydrate readily to the corresponding triarylboroxines. Although these compounds are quite stable to moisture and dry oxygen at ordinary temperature, they readily oxidized to phenols and boric acid in the presence of oxygenated water. Heating in presence of excess water also decomposes these compounds, giving an aromatic hydrocarbon and boric acid.

The aryldihydroxyboranes have been extensively investigated. The main purpose was to find their antiseptic, antibacterial and neutron-capture properties, and to relate them on the basis of observed chemical and physical properties.[29]

From a theoretical point of view these compounds are quite important. Branch et al.[41] related the dissociation constants of the substituted phenyldihydroxyboranes and their structures, especially in relation to the electronegativity of the substituted groups and the effect of mesomerism. Since we prepared two new aryldihydroxyboranes (p.t-Bu. and p.CF_3 derivatives), their dissociation constants were determined and are compared with other dissociation constants:

TABLE 17

Compounds	Dissociation constants*	Ref.
$B(OH)_3$	6.5×10^{-11} (H_2O)	41
	13.4×10^{-1} (25% EtOH)	"
$C_6H_5B(OH)_2$	1.37×10^{-10}(H_2O)	"
	1.97×10^{-10} (25% EtOH)	"
	1.32×10^{-10} (H_2O)	This work.
p.$FC_6H_4B(OH)_2$	3.66×10^{-10} (EtOH 25%)	41
p.$ClC_6H_4B(OH)_2$	6.30×10^{-10} (")	"
p.Br $C_6H_4B(OH)_2$	7.26×10^{-10} (")	"
p.CH_3 $C_6H_4B(OH)_2$	10.0×10^{-11} (25% EtOH)	"
o.CH_3 $C_6H_4B(OH)_2$	18.1×10^{-11} (H_2O)	"
m.$CH_3C_6H_4B(OH)_2$	14.0×10^{-11} (25% EtOH)	"
p.COOH $C_6H_4B(OH)_2$	I 3.56×10^{-5} (25% EtOH) KII(1.90×10^{-10})	"
	I 6.07×10^{-5} (25% EtOH) KII(1.90×10^{-9})	This work.
p.$CF_3C_6H_4B(OH)_2$	8.06×10^{-9} (H_2O)	
	3.25×10^{-9} (2% Acetone)	
p.t-Bu.$C_6H_4B(OH)$	5.5×10^{-11} (10% Acetone)	

* The dissociation constants were determined by potentiometric titrations, using the "half-neutralization" method. Activity coefficients were estimated from Guntelberg's formula.[186]

The kinetics of the bromo-deboronation and oxidative-deboronation of the substituted aryldihydroxyboranes were studied by Kuivila et al.[42] They related the rate constants with the Hammett's constants and obtained a linear relationship.

Beachell et al.[44] studied the "B & H n.m.r. spectra of these compounds and they also obtained a linear relationship from a plot of the change in chemical shifts (by the substituents) against the Hammett's constants.

The infrared spectra of these compounds has been studied by various groups of workers.[89] The results always reported were that ν_sB-O was least affected by substitution; moreover, these frequencies were of the same magnitude as in the alkylborates[151] or arylboroxines.[90]

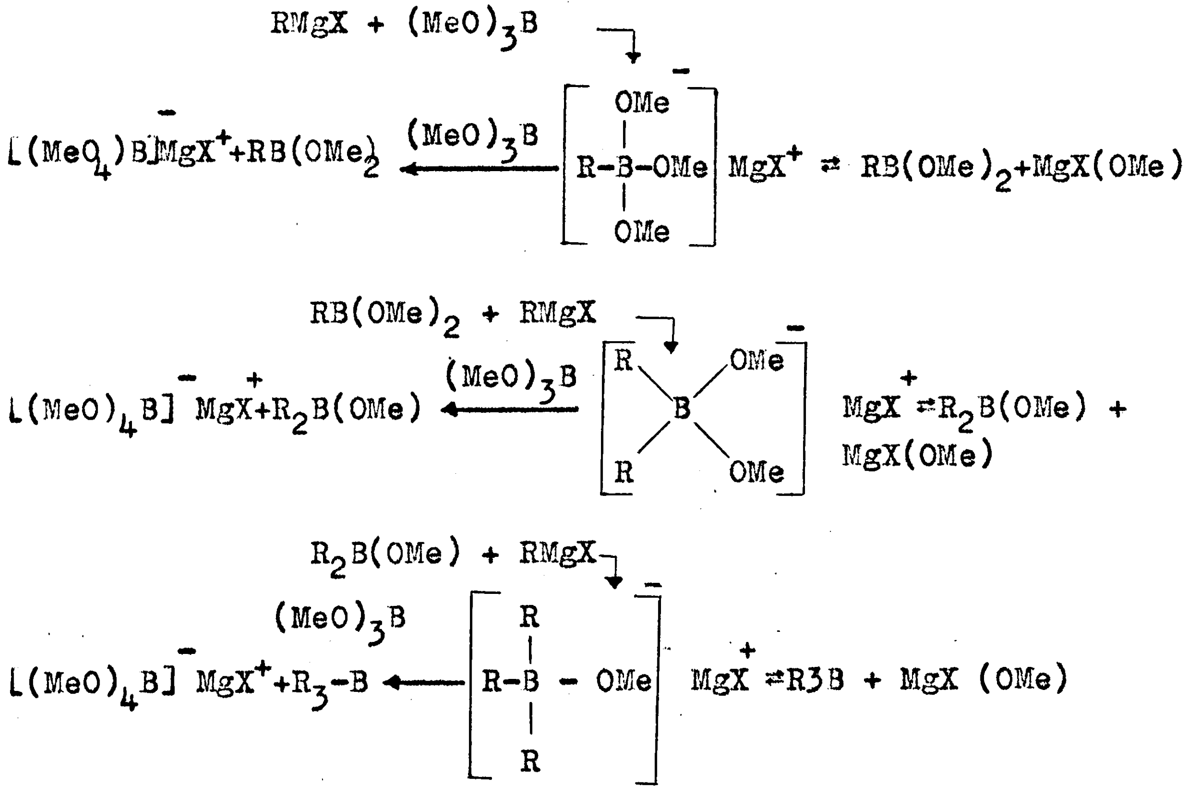
Molecular weight studies of these compounds show their monomeric nature in polar solvents.[172]

Possibly these compounds are also planar in the gaseous phase, like aryldihaloboranes, although no evidence is available. Their ready dehydration and decomposition at higher temperatures hinders electron diffraction studies and also the determination of heats of sublimations.

The only crystal structure reported is that of p.bromophenyldihydroxyborane, which is planar, and indicates a partial double bond character of the C_{Ar}-B bond (1.58 of 1.54Å).[98]

Preparation

The method of preparation has been reviewed earlier (see Introduction). The most suitable method for their preparation is through the reaction of a Grignard reagent on the trimethoxyborane, with subsequent hydrolysis. The method has been thoroughly investigated by Washburn et al.[43] and the following mechanism proposed:



The procedure, therefore, requires a careful estimation of Grignard reagents and the trimethoxyborane, because excess of Grignard reagent or methylborate will decrease the percentage yield of dihydroxyboranes and also will produce the diarylhydroxyborane and triarylboranes as impurities.

The procedure gives excellent results if the hydrolysis is carried out using fresh distilled water and if the distillation is performed in the absence of oxygen. The acids prepared by this method were crystallized by various solvents (see section 3 for individual compounds). Two or three crystallizations gave the pure aryldihydroxyborane. Their purity was checked by analysis of their boron contents and carbon and hydrogen analyses of the corresponding acids or anhydrides (see arylboroxines). The analyses are as follows:

TABLE 18

Compound	ANALYSIS					
	Calculated %			Found %		
	C	H	B	C	H	B
p.$CH_3C_6H_4B(OH)_2$			7.95			8.1
o.$CH_3C_6H_4B(OH)_2$			7.97			8.3
p.$COOHC_6H_4B(OH)_2$	50.7	4.3	6.5	50.79	4.49	6.7
p.$CHOC_6H_4B(OH)_2$	56.0	4.7	7.2	55.1	4.9	7.4
p.Ph-$C_6H_4B(OH)_2$	72.76	5.6	5.6	72.63	5.63	5.7

p.$COOHC_6H_4B(OH)$, p.$CHOC_6H_4B(OH)$ and p.Ph.$C_6H_4B(OH)$ do not dehydrate to the corresponding anhydrides.

Calorimetry

The oxidative hydrolysis of phenyldihydroxy borane had been reported[83] and found to be a useful thermochemical procedure. A basic oxidizing medium up to 1.0M was found quite suitable. The decomposition of hydrogen peroxide under these conditions has been found negligible. The reaction is represented as follows:

$$ArB(OH)_2 + H_2O_2 \xrightarrow{a.e.b.} ArOH + B(OH)_3$$

and the thermochemical equation becomes:

$$\Delta H_f^o[(ArB(OH)_2 cryst.] = \Delta H_f^o[(ArOH)a.e.b.] + \Delta H_f^o[B(OH)_3, a.e.b.] - \Delta H_f^o[(H_2O_2)a.e.b.] - \Delta H_{obs}.$$

We could not study a majority of aryldihydroxyboranes due to their low solubility or very slow reaction under the chosen calorimetric conditions. Thus p.$PhC_6H_4B(OH)_2$ did not respond to this reaction even in dioxane. p.CHO C_6H_4OH was found to give some side reaction (yellow colour) and in addition was also very slow. p.$CF_3C_6H_4B(OH)_2$ also gave a side reaction (green colour).

Since aryldihydroxyboranes are readily dehydrated, when exposed to the atmosphere, they were freshly crystallized from (oxygen-free) boiled distilled water and were kept in a water-saturated atmosphere at room temperature. The ampoules, for calorimetry, were filled in a static, moist, inert atmosphere of oxygen-free nitrogen. Two ampoules were filled together, one after the other, and accurately weighed. One was dehydrated to the anhydride, under reduced pressure, while the other was studied calorimetrically. The amount of acid used was, therefore, calculated on the basis of anhydride obtained. The results were quite uniform (see detailed results section 5) and are as follows:

TABLE 19

Compound	N	$\Delta H_{obs.}$
p.$CH_3C_6H_4B(OH)_2$	8968	-99.6 ± 0.6
o.$CH_3C_6H_4B(OH)_2$	11307	-74.9 ± 0.2
p.COOH $C_6H_4B(OH)_2$	10122	-113.3 ± 2.0

The reaction products, phenols, were not oxidized by hydrogen peroxide under experimental conditions.

Ancillary data.

Most of the ancillary data, required here, have been tabulated previously (see Arylboroxines).

The heats of sublimation of these compounds are impossible to determine and so it is assumed that their heat of sublimations are equal to the respective substituted benzoic acids.

These are as follows:

TABLE 20

Compound	$\Delta H_{subl.}$ kcal.mole^{-1}	Reference
p.$CH_3C_6H_4COOH$	21.7	200
o.$CH_3C_6H_4COOH$	21.3	"
p.$COOHC_6H_4COOH$ terphthalic Acid	33.3	104

Results

The heats of formation of the aryldihydroxyboranes were calculated using the above data, as follows:

TABLE 21

Compound	ΔH_f^o(cryst.)	ΔH_f^o(gas)
p.$CH_3C_6H_4B(OH)$	-173.2	-151.5
o.$CH_3C_6H_4B(OH)_2$	-198.9	-177.6
p.$COOHC_6H_4B(OH)_2$	-286.0	-252.7
$C_6H_5B(OH)_2$	-172.0	-151.1

Bond energies in these compounds were calculated according to the following thermodynamic cycle.

$$\begin{tikzcd}
ArB(OH)_{2(g)} \arrow[rr, "E(C_{Ar}-B) + 2E(B-O)"] & & Ar_{(g)}+B_{(g)}+2OH_{(g)} \\
& C(graphite) + H_2 + O_2 \arrow[ul, "\Delta H_f^o ArB(OH)_{2(g)}"] \arrow[ur, "{[\Delta H_f^o Ar_{(g)}+\Delta H_f^o B_{(g)}+2\Delta H_f^o (OH)_g]}"', "\Delta Ha"] &
\end{tikzcd}$$

The π-electronic contributions to $E(C_{Ar}-B)$ were calculated by assuming σ $E(C-B)$ as 88.0 $kcal.mole^{-1}$ [$E(C-B)$ in $(C_6H_{11})_3B$]. These are tabulated as follows:

TABLE 22

Compound	$E(C_{Ar}-B)$ $kcal.mole^{-1}$	π-$E(C_{Ar}-B)$ $kcal.mole^{-1}$
p.$CH_3C_6H_4B(OH)_2$	118	30
o.$CH_3C_4B(OH)_2$	144	56
p.$COOHC_6H_4B(OH)_2$	136	48
$C_6H_5B(OH)_2$	126	38

Discussion

Although the results reported here are not accurate, due to the non-availability of accurate ancillary data, (ΔH subl.), they are sufficiently precise for a discussion of the bond energy and structure relationship.

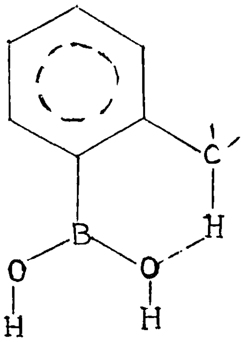
The thermochemical results indicate that the substitution of various groups in phenyldihydroxyborane changes the value of $E(C_{Ar}-B)$. This change of $E(C_{Ar}-B)$ with the substituents follows the order:

$$o.Me > p.COOH > H > p.CH_3$$

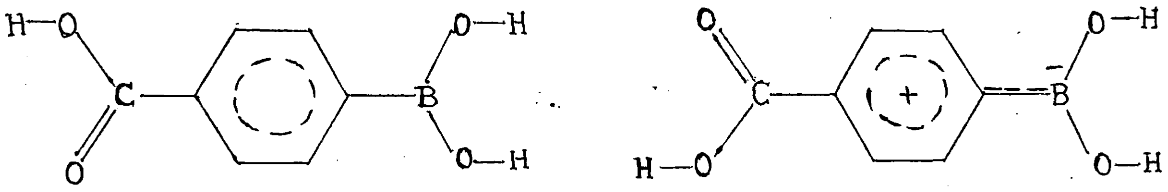
The same order is observed in the calculated π-electronic contributions, π-$E(C_{Ar}-B)$.

The higher $(C_{Ar}-B)$ bond strength in ortho-tolyldihydroxy borane again signifies some "extra energy", which may be is a result of σ-bond overlap of the ortho-methyl hydrogen atom and the oxygen atom. A sort of intramolecular hydrogen bonding in aryldihydroxyboranes has been proposed by Makoza et al.[90] by infrared studies, but ν_sB-O was of about the same order as in arylboroxines, irrespective of the position of the substituent in the phenyl ring. The same type of conclusion was derived by Dale and Rush.[149] They also suggested that steric interference takes place between two ortho-substituents in substituted aryldihydroxyboranes. The results are, however, confusing.

Since we have discussed a type of hydrogen-bonding in ortho-tolyldichloroboranes, we expect this effect in ortho-tolyldihydroxyborane to a considerable extent, because oxygen is more electronegative (3.5) than chlorine (3.0). O-tolyldihydroxyborane, therefore, can have the following structure.



In the case of p.COOHC$_6$H$_4$B(OH)$_2$, the mesomeric structures contribute much to the stability of the compound and hence there is an increase in the (C$_{Ar}$-B) bond strength and in the π-electronic contributions. The structures may be represented as follows:



Conclusion

The effect of substitution in the phenyl ring of triphenylboroxines, phenyldihydroxyboranes and phenyldichloroboranes is quite marked. The para-substituents that increase mesomerism increase the C_{Ar}-B bond strength. The order of this increase in bond strength has been thermochemically found to be:

$$p.F > p.CH_3O > o.CH_3 > p.CH_3 > p.Cl > p.Br$$

This order of bond strengths may be observed as a general case of substituting the phenyl ring at the boron atom.

The effect of ortho-substitution in the phenyl ring of the above compounds has been found quite interesting. While the ortho-substitution in the phenyl ring of the triphenylboroxine seems to decrease the C_{Ar}-B bond, possibly due to steric interaction, the effect is opposite to that in aryldihaloboranes and aryldihydroxyboranes.

For ortho-tolyldichloroboranes and ortho-tolyldihydroxyboranes, a sort of σ-overlap of chlorine or oxygen atoms with that of hydrogen atom of the methyl group is suggested.

DETAILED RESULTS

CALORIMETRIC RESULTS

All of the calorimetric results are reported in kcal.mole^{-1} at a temperature of 25.0 ± 0.1°C, unless otherwise indicated. The errors are quoted as twice the standard deviation from a single observation. N is the mole ratio of calorimetric fluid to compound. $\Delta H_{obs.}$ represents the heats of reaction for the equations presented.

TABLE 23

$$[(ArBO)_3,c]+3[(H_2O_2)+(H_2O),a.e.b.] \longrightarrow 3[(ArOH)+(H_3BO)_3,a.e.b.]; \quad \Delta H_{obs.}$$

Group Ar	N	$\Delta H_{obs.}$	Group Ar	N	$\Delta H_{obs.}$
C_6H_5-	10478	-291.6	$pF.C_6H_4-$	10275	-276.7
	10473	-292.4		12415	-271.4
	10167	-287.9		11408	-273.5
	10911	-292.6		7966	-275.1
Mean	10507	291.1±1.3	Mean	10516	274.2±2.3

TABLE 23 (continued)

Group Ar	N	$\Delta H_{obs.}$
$p.ClC_6H_4$	11919	-295.2
	17113	-297.5
	13921	-296.0
	11638	-297.0
	10766	-295.0
	13167	-299.3
Mean	13087	-296.7±1.5
$p.Br\ C_6H_4$	21274	-305.9
	24953	-309.5
	16109	-304.5
	31743	-307.7
	24337	-307.2
	22192	-203.6
	35300	-310.6
Mean	25130	306.9±2.7

Group Ar	N	$\Delta H_{obs.}$
$p.CH_3C_6H_4-$	15387	-276.7
	11636	-276.8
	14731	-272.5
	16533	-272.4
	11150	-276.3
Mean	13887	-274.9±2.3
$o.CH_3C_6H_4-$	11296	-306.6
	28952	-309.1
	23770	-305.0
	28188	-308.9
	22808	-310.9
	28813	-306.5
	27188	-306.3
	39520	-304.9
Mean	26317	-307.3±1.8
$p.CH_3OC_6H_9-$	12493	-277.4
	12639	-274.4
	14451	-274.3
	18730	-277.3
	17391	-273.9
Mean	15141	-275.5±1.7

TABLE 24

$$ArBCl_2+[(H_2O_2)+2NaOH),aq] \longrightarrow [(ArOH)+(H_3BO_3)a.e.b.]+[2NaCl, a.e.b.]; \ \Delta H_{obs.}$$

Temperature 32.0±0.1°C

Group R	N	$\Delta H_{obs.}$
$p.CH_3C_6H_9$-	15278	-163.3
	11521	-165.2
	9247	-164.1
	20670	-164.2
	15617	-164.3
	11335	-166.1
	13014	-165.0
Mean	13812	-164.6±0.7
$p.CH_3C_6H_4$	Temperature -22.0±0.1°C	
	20006	-165.3
	21305	-165.5
	17239	-166.8
	19276	-164.6
	12823	-165.9
	19618	-165.8
Mean	18378	-165.6±0.7

Group R	N	$\Delta H_{obs.}$
$o.CH_3C_6H_9$-	8484	-159.4
	13109	-158.5
	13879	-159.2
	14674	-159.4
	14674	-158.3
Mean	13044	-159.0±0.5
2,4,6-$Me_3C_6H_2$	9500	168.6
	17983	169.0
	13807	167.6
	8808	168.7
	9104	167.3
Mean	11840	168.2±0.7

TABLE 25

$ArB(OH)_2 + [(H_2O_2), a.e.b.] \longrightarrow [(ArOH) + (H_3BO_3), a.e.b.]; \Delta H_{obs.}$

Group R	N	$\Delta H_{obs.}$
p.$CH_3C_6H_9$	9528	-99.2
	8818	-100.0
	8201	-98.9
	7800	-100.2
	9148	-99.7
	9403	-98.8
	9879	-99.9
Mean	8968	-99.6±0.6
o.$CH_3C_6H_4$-	15326	-75.0
	14423	-74.4
	11872	-75.0
	9897	-75.1
	9804	-75.5
	6520	-74.3
Mean	11307	-74.9±0.2

Group R	N	$\Delta H_{obs.}$
p.COOH C_6H_4-	10592	111.8
	9833	114.2
	9948	116.5
	10273	110.8
	9966	113.4
Mean	10122	113.3±2.0

TABLE 26

$$\text{ArOH} \xrightarrow{\text{a.e.b.}} [(\text{ArOH}),\ \text{a.e.b.}];\quad \Delta H_{obs.}$$

Group Ar	N	$\Delta H_{obs.}$	Group Ar	N	$\Delta H_{obs.}$
p.F C_6H_4	741	3.7	p.$CH_3C_6H_4$-	738	4.13
	720	3.5		656	4.15
	775	3.5		737	3.98
	761	3.7		776	4.04
Mean	749	3.6±0.1	Mean	727	4.07±0.08
p.ClC_6H_4-	882	3.8	o.$CH_3C_6H_4$	979	3.7
	928	3.5		860	3.7
	976	3.7		884	3.8
	850	3.4		925	3.9
Mean	924	3.6±0.2		855	3.9
p.BrC_6H_4	904	3.23	Mean	901	3.8±0.1
	673	3.23	2,4,6-Me_3	1372	3.2
	565	3.17	C_6H_2-	1247	3.2
	665	3.14		1182	3.0
	587	3.21		1166	3.1
Mean	924	3.20±0.04	Mean	1242	3.1±0.1

TABLE 26 (continued)

Group Ar	N	$\Delta H_{obs.}$	Group Ar	N	$\Delta H_{obs.}$
$p.CH_3OC_6H_4-$	820	2.2	$p.COOHC_6H_4-$	1935	15.6
	856	2.1		1891	16.2
	763	2.2		2037	15.7
	651	2.1		1755	16.1
Mean	772	2.15±0.05		1904	15.6±0.2

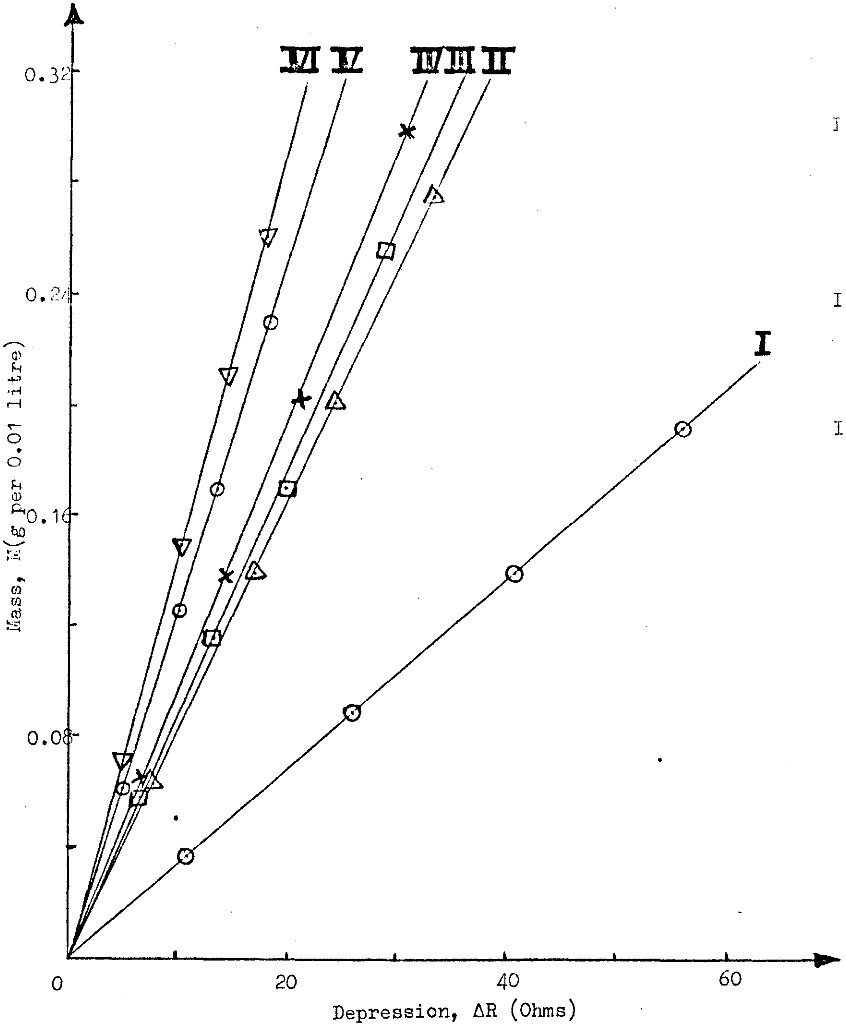
VAPOUR PRESSURE RESULTS

TABLE 27

Compound	Pressure (mm)	Temperature (°K)	Compound	Pressure (mm)	Temperature (°K)
H_2O.	40	285.7	propionic Acid $CH_3.CH_2.COOH$	40	338.2
	70	315.7		70	349.7
	100	324.2		100	358.2
	250	345.2		250	374.7
	400	354.9		400	390.7
	550	362.7		550	402.7
	757	372.7		757	414.2
			$pCH_3.C_6H_4-BCl_2$	80	411.2
				100	417.7

TABLE 27 (continued)

Compound	Pressure (mm)	Temperature (^oK)	Compound	Pressure (mm)	Temperature (^oK)
$C_6H_5BCl_2$	28	350.2	o.$CH_3C_6H_4$-BCl_2	10	346.2
	40	354.2		20	358.2
	50	361.2		30	369.7
	70	368.2		40	379.2
	80	373.2		50	387.2
	100	379.2		60	391.2
	130	383.7		70	395.2
	170	397.7		80	399.2
	210	403.2		100	404.7
	250	405.2		150	418.7
	300	412.7		200	433.7
	350	417.7		250	439.2
	400	423.2	2,4,6-$Me_3C_6H_2BCl_2$	20	358.2
	450	425.7		30	364.7
	500	430.7		40	370.2
	550	436.7		50	376.2
	600	438.7		100	390.2
p.$CH_3C_6H_9$-	20	364.7		150	403.2
	30	373.2		200	421.2
	40	385.2		250	427.2
	50	395.2			
	60	399.2			
	70	405.2			



I. Naphthalene

M(Molecular Weight) = 128
K = 3.71 x 10^{-4}

II Triphenylboroxine

M(Exp.) 311.8 (c.f. 311.4)

III. Tri-o-tolylboroxine

M(Exp.) 330, (c.f. 353)

IV. Tri-p-tolylboroxine

M(Exp.) 368 (c.f. 353)

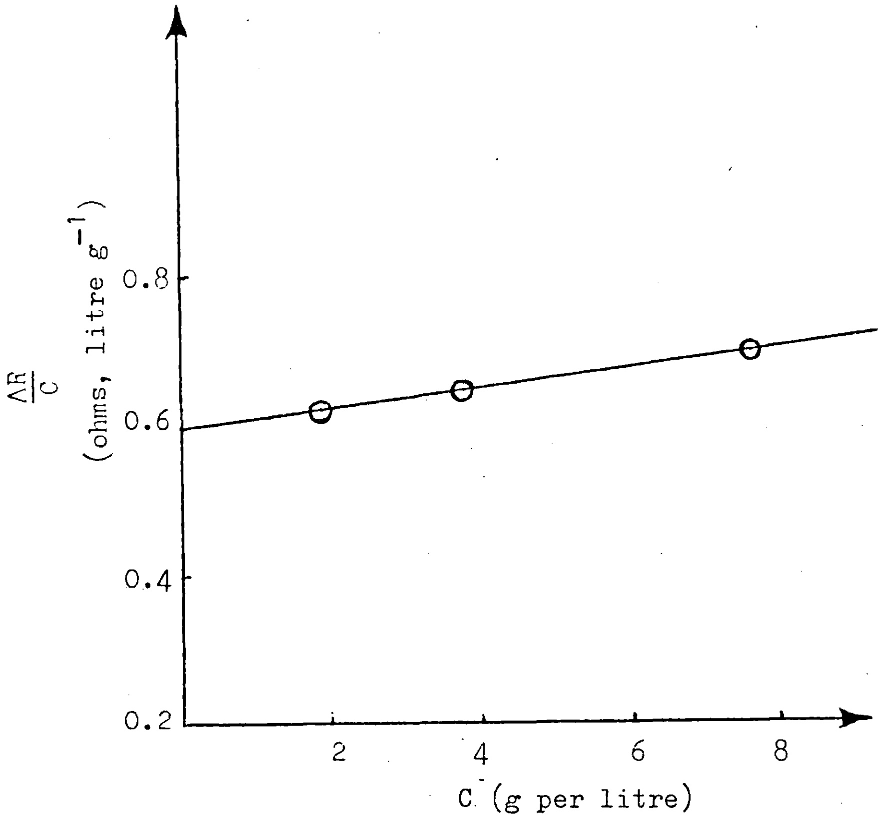
V. Tri-p-t-butylphenylboroxine

M(Exp.) 467 (c.f. 480)

VI. Tri-p-trifluoromethylphenylboroxine

M(Exp.) 520 (c.f. 516)

FIG. 6(a) CRYOSCOPIC MOLECULAR WEIGHTS IN DIOXANE



C(g/L)	ΔR(ohms)	$\frac{\Delta R}{C}$ (ohms Litre g^{-1})
7.67	5.4	0.70
3.83	2.6	0.65
1.91	1.18	0.62

When $C = 0$, $\frac{\Delta R}{C} = 0.6$

K (for C_6H_6) = 289 at 25°C

$$M = \frac{K}{\frac{\Delta R}{C}} = \frac{289}{0.6} = 481 \text{ (c.f. 480)}$$

FIG. 6(b) MOLECULAR WEIGHT OF TRI-p-t-BUTYLPHENYLBOROXINE BY VAPOUR PRESSURE OSMOMETRY

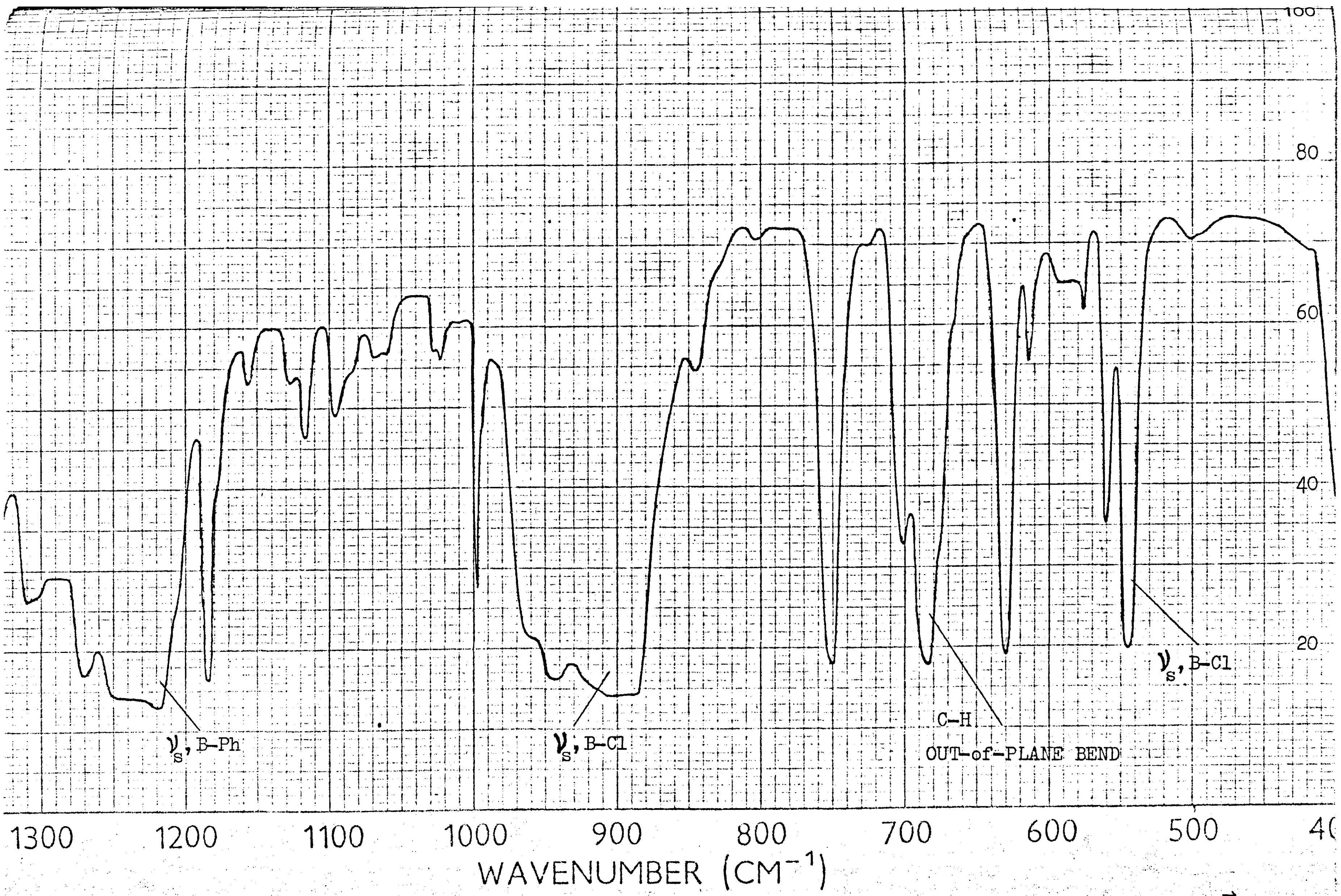


FIG. 7(a) PHENYLDICHLOROBORANE(LIQ. FILM)

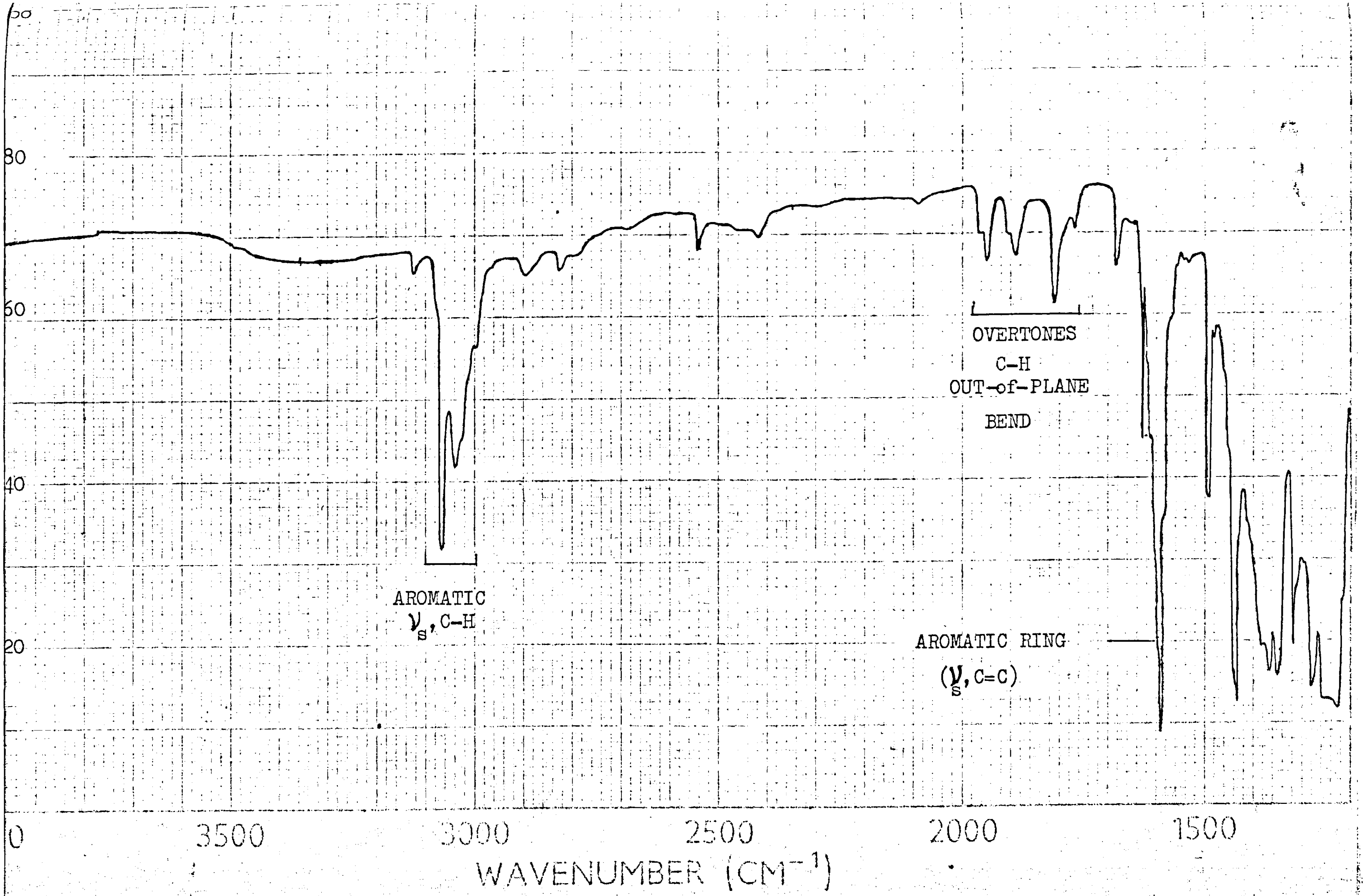


FIG. 7(b) PHENYLDICHLOROBORANE (LIQ. FILM)

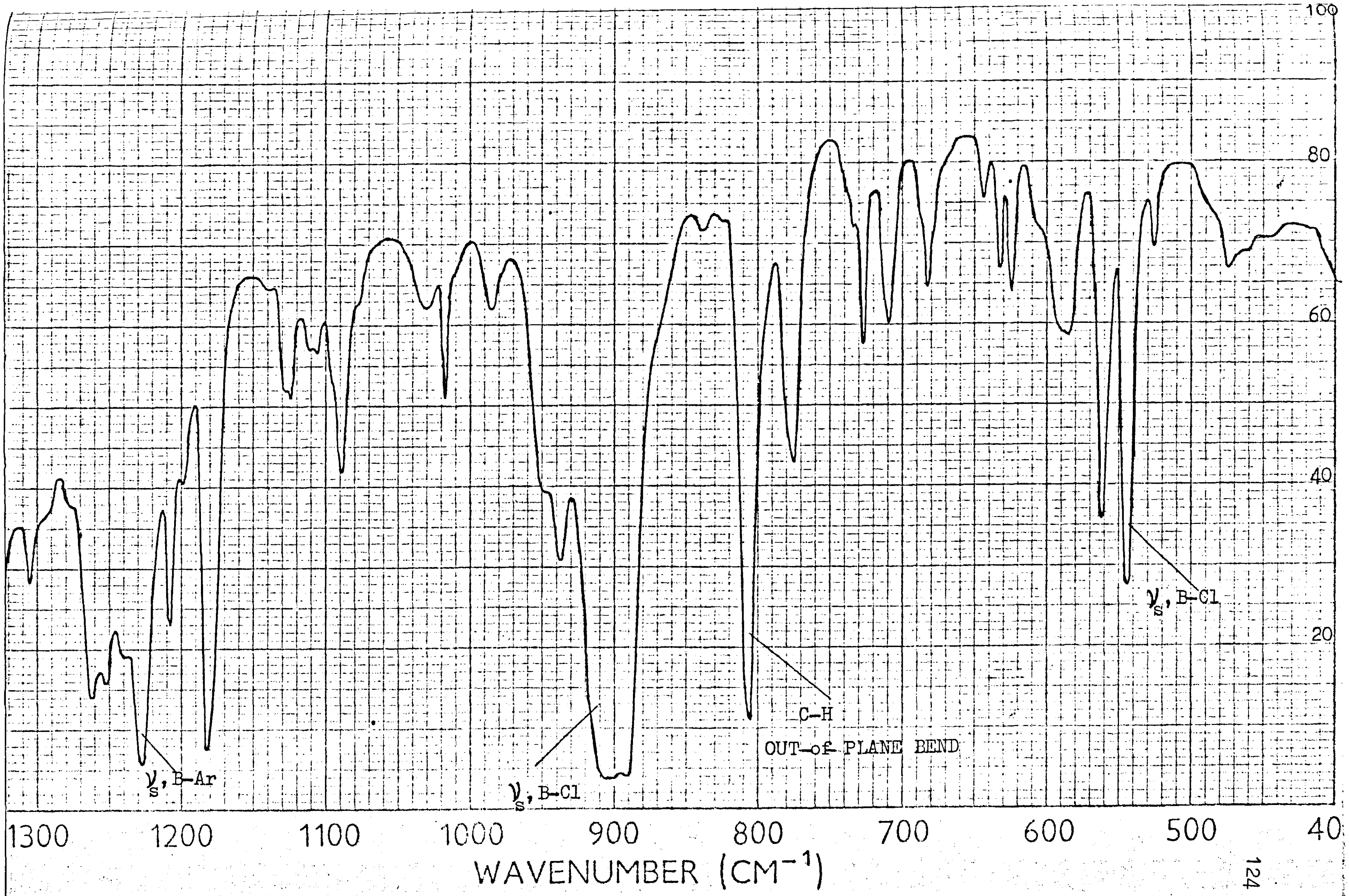


FIG. 8(a) p-TOLYLDICHLOROBORANE (LIQ. FILM)

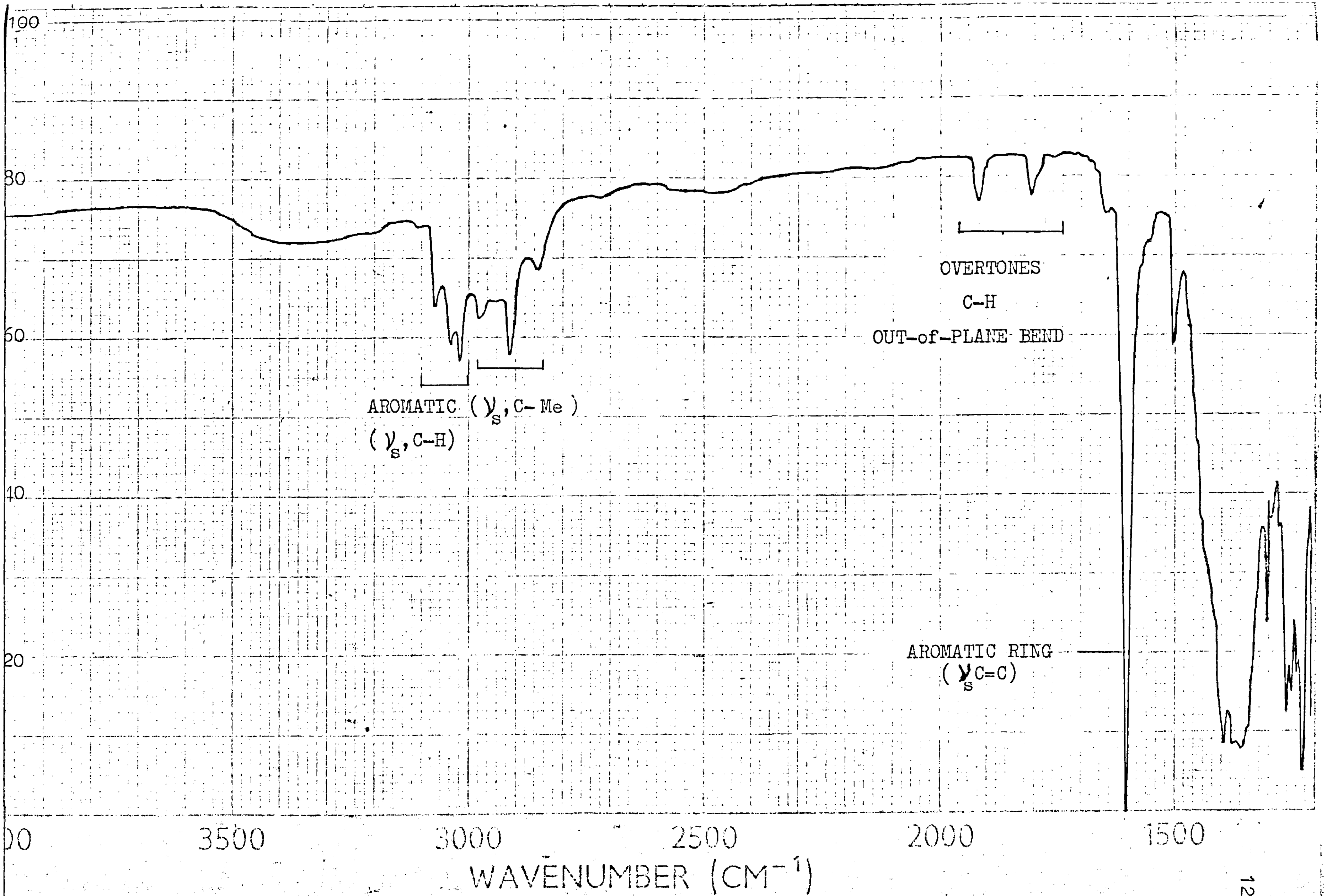


FIG. 8(b) p-TOLYLDICHLOROBORANE (LIQ. FILM)

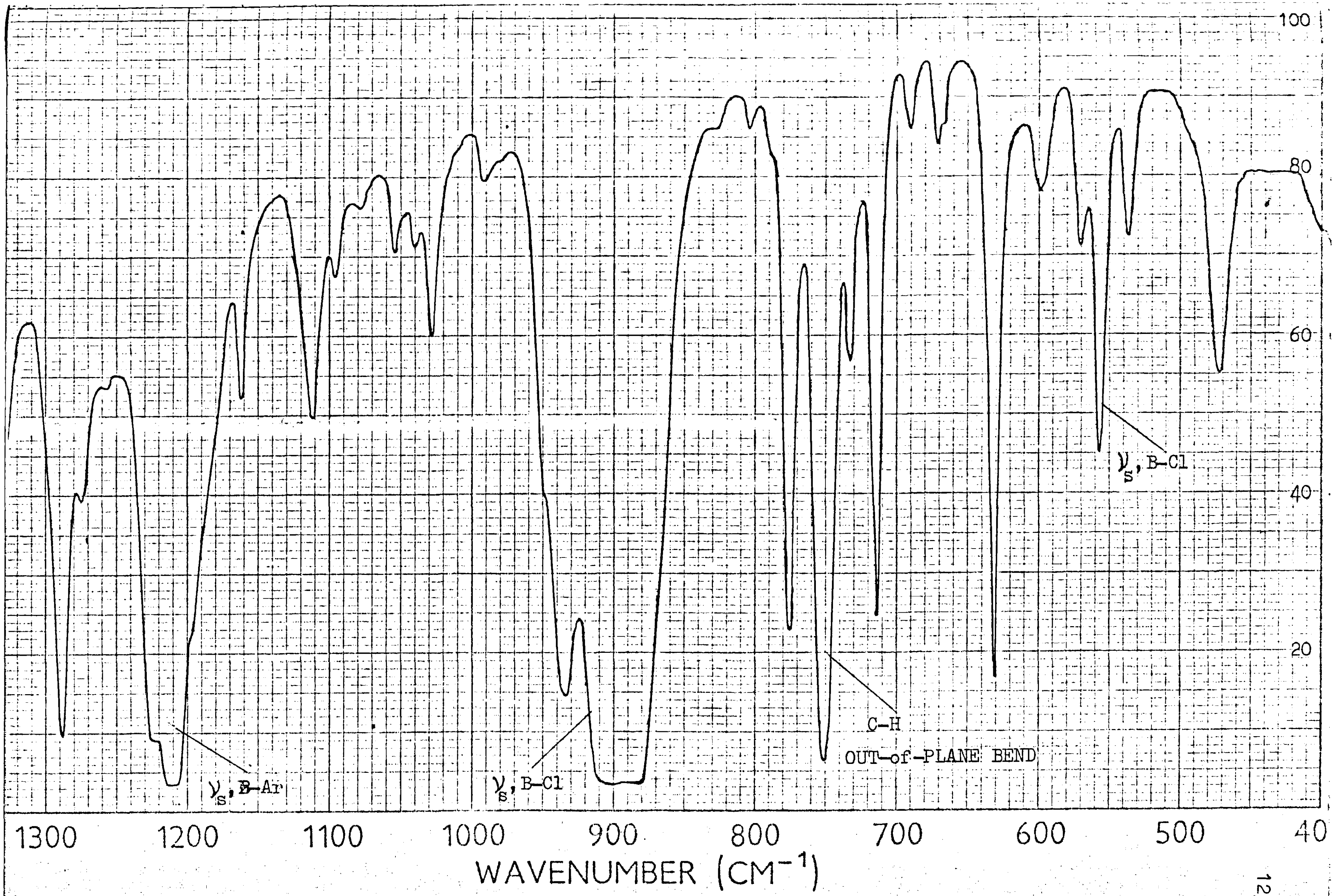


FIG. 9(a) o-TOLYLDICHLOROBORANE (LIQ. FILM)

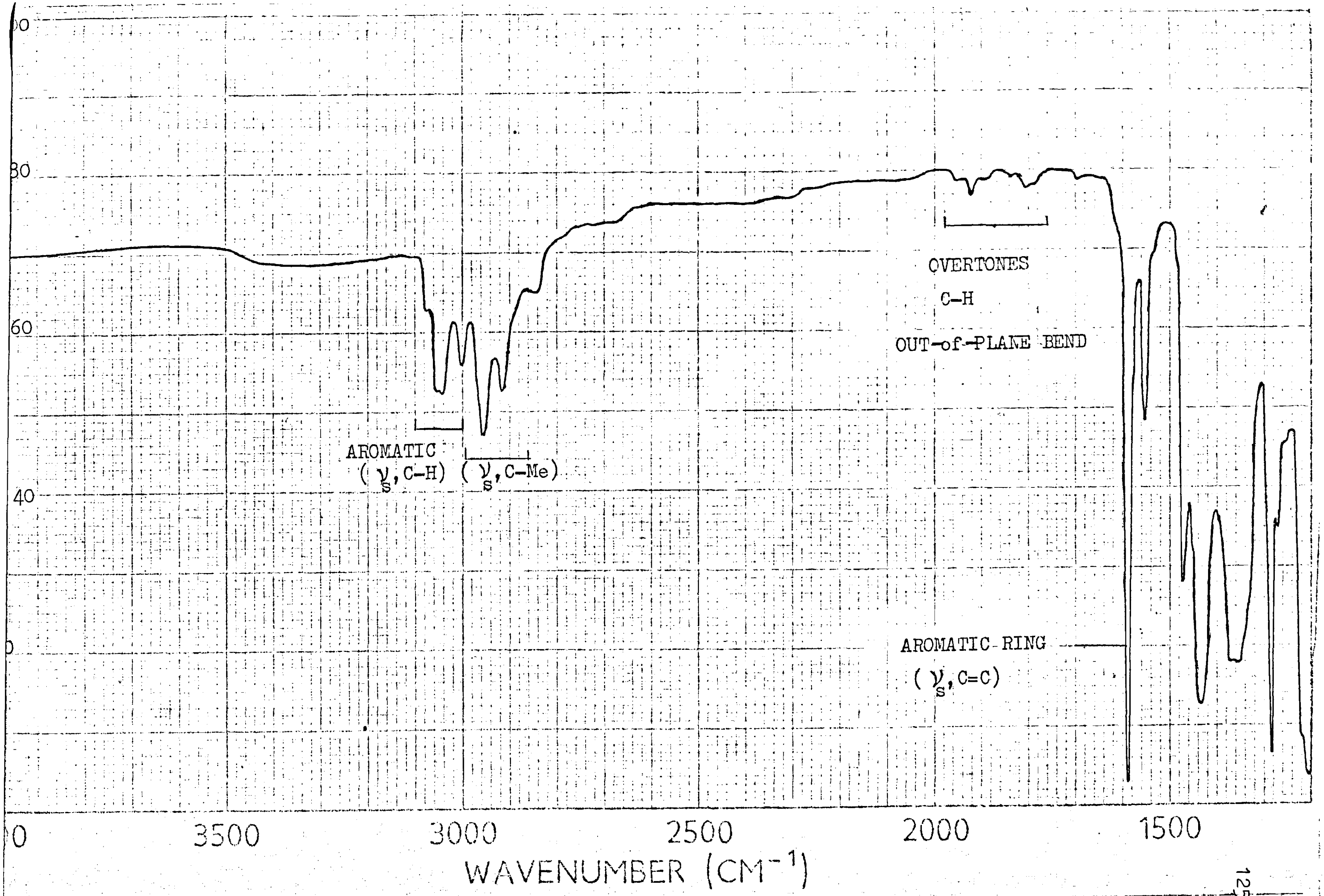


FIG. 9(b) o-TOLYLDICHLOROBORANE (LIQ. FILM)

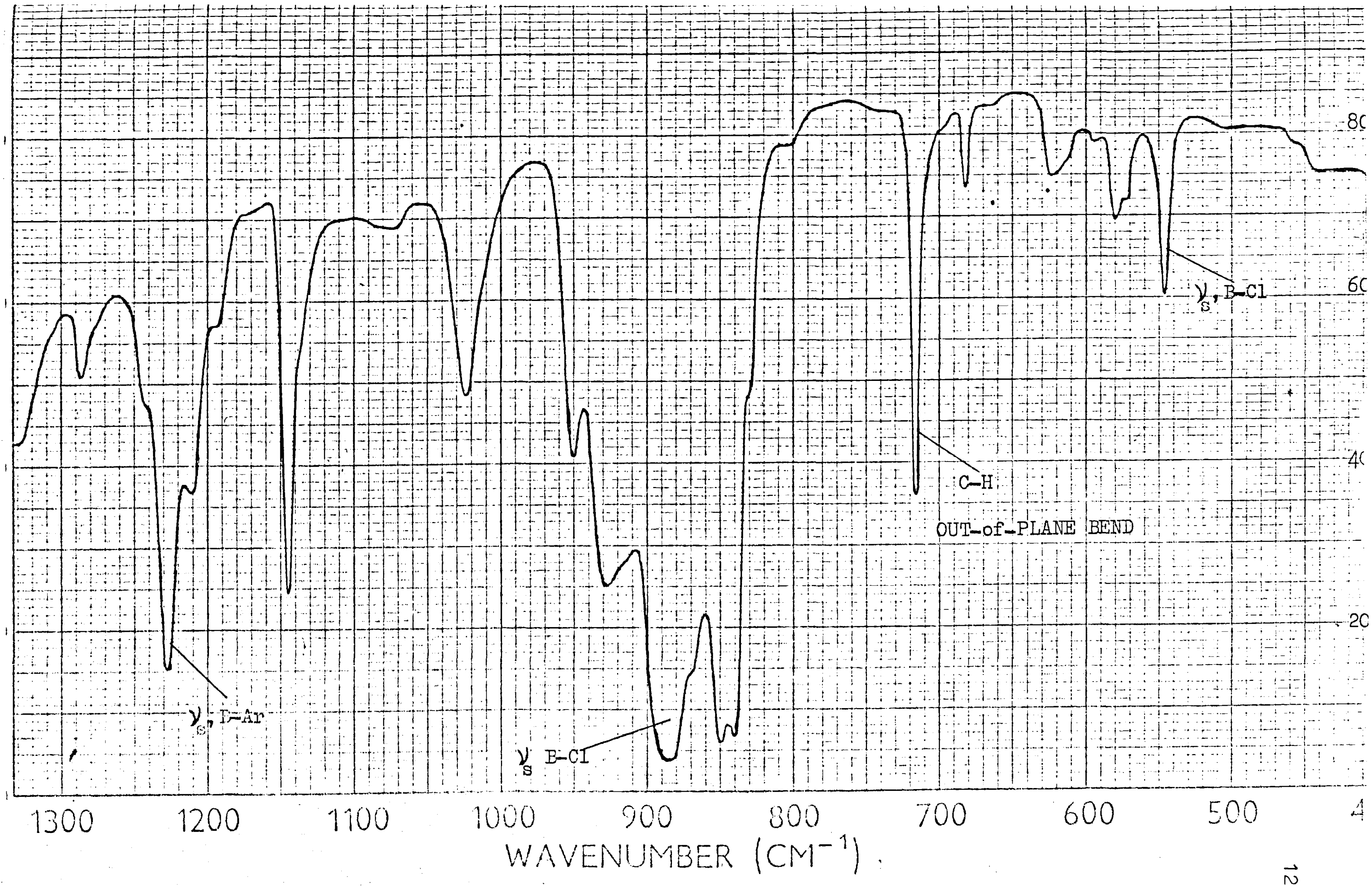


FIG. 10(a) MESITYLDICHLOROBORANE (LIQ. FILM)

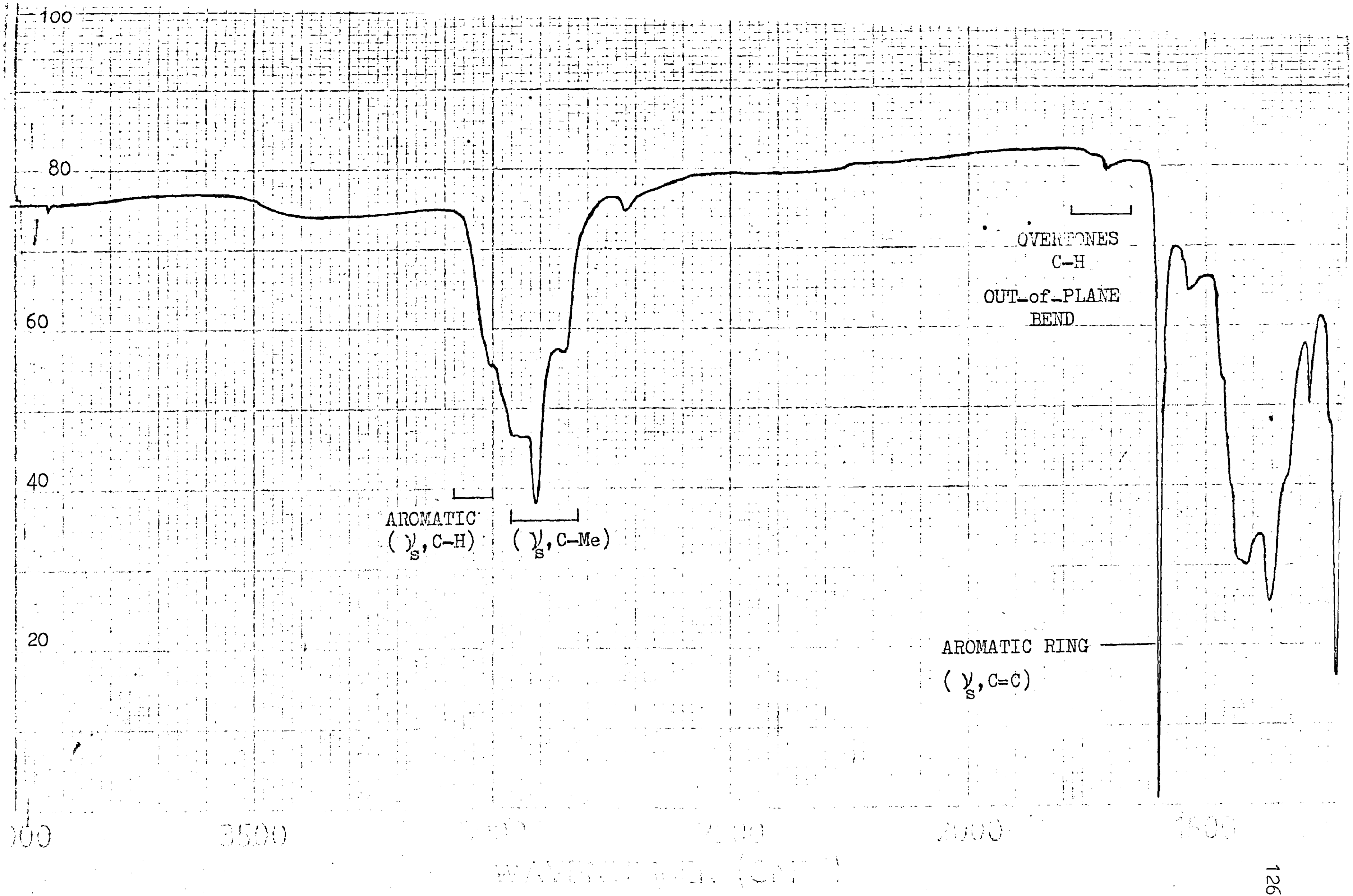


FIG. 10(b) MESITYLDICHLOROBORANE (LIQ. FILM)

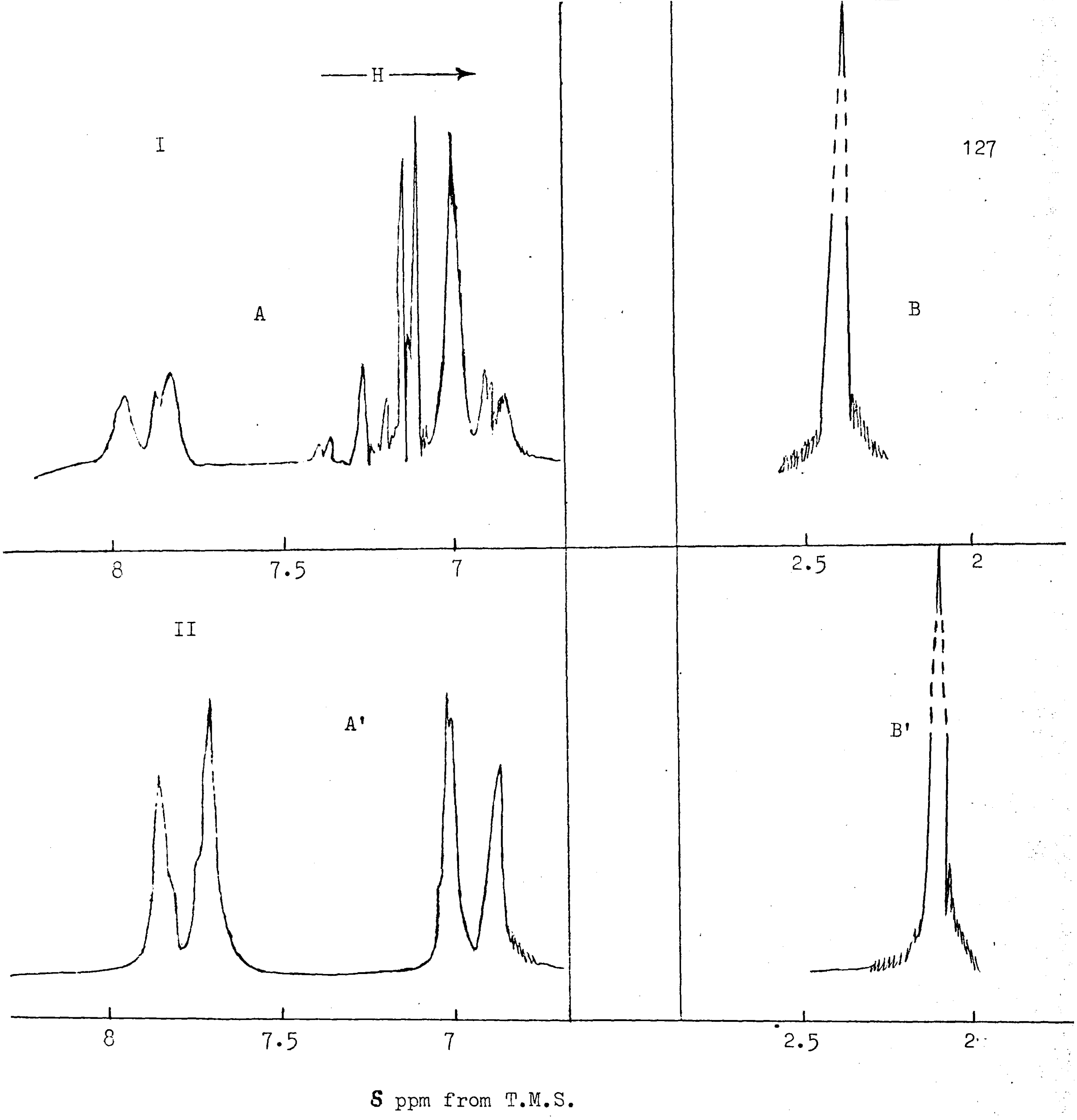
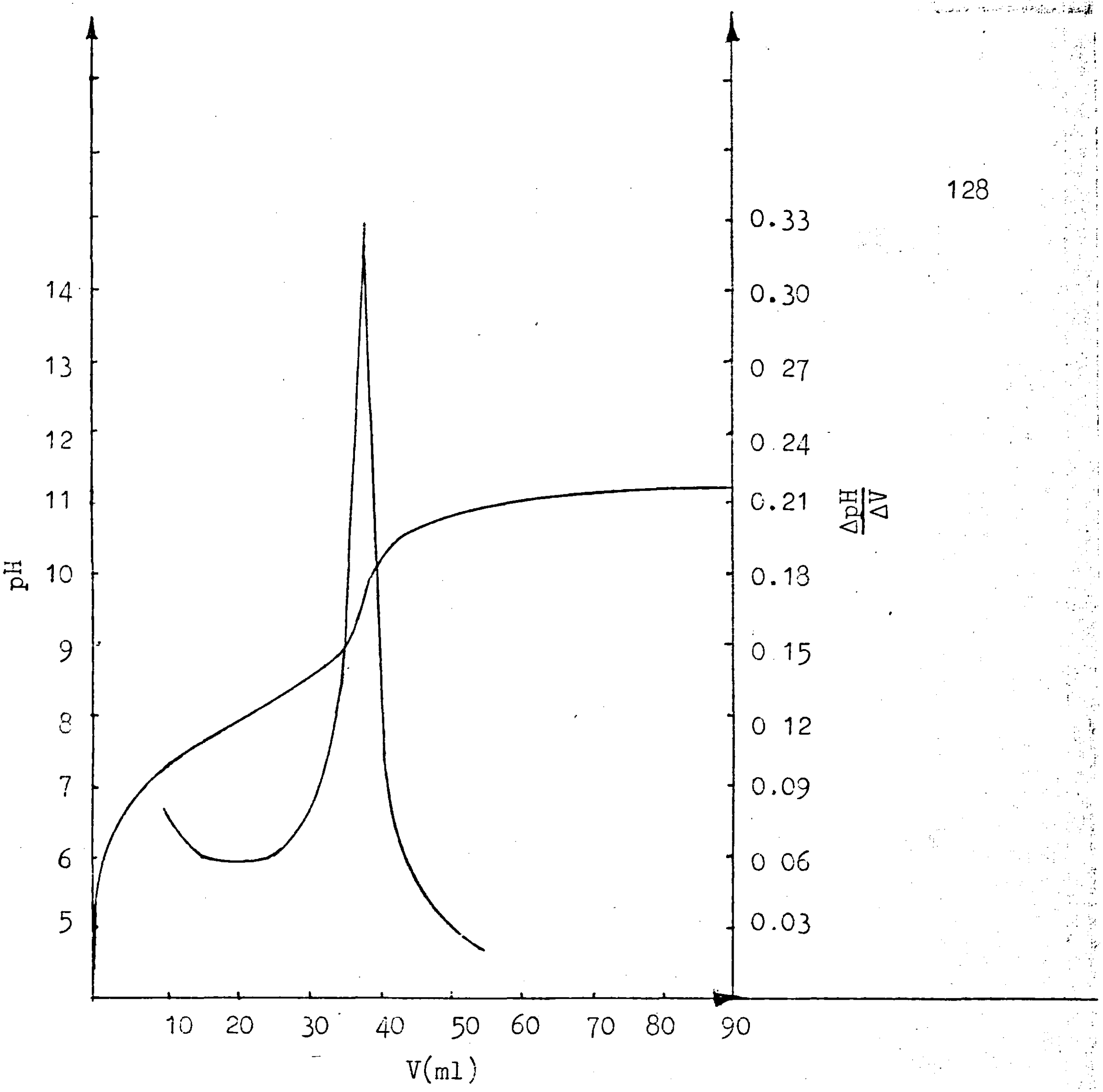


FIG. 11 PROTON MAGNETIC RESONANCE SPECTRA, I, o-TOLYLDICHLOROBORANE II, p-TOLYLDICHLOROBORANE; A, A' = AROMATIC PROTON RESONANCES B, B' = METHYL PROTON RESONANCES



Normality of NaOH = 0.1; Molarity of Acid = 0.10

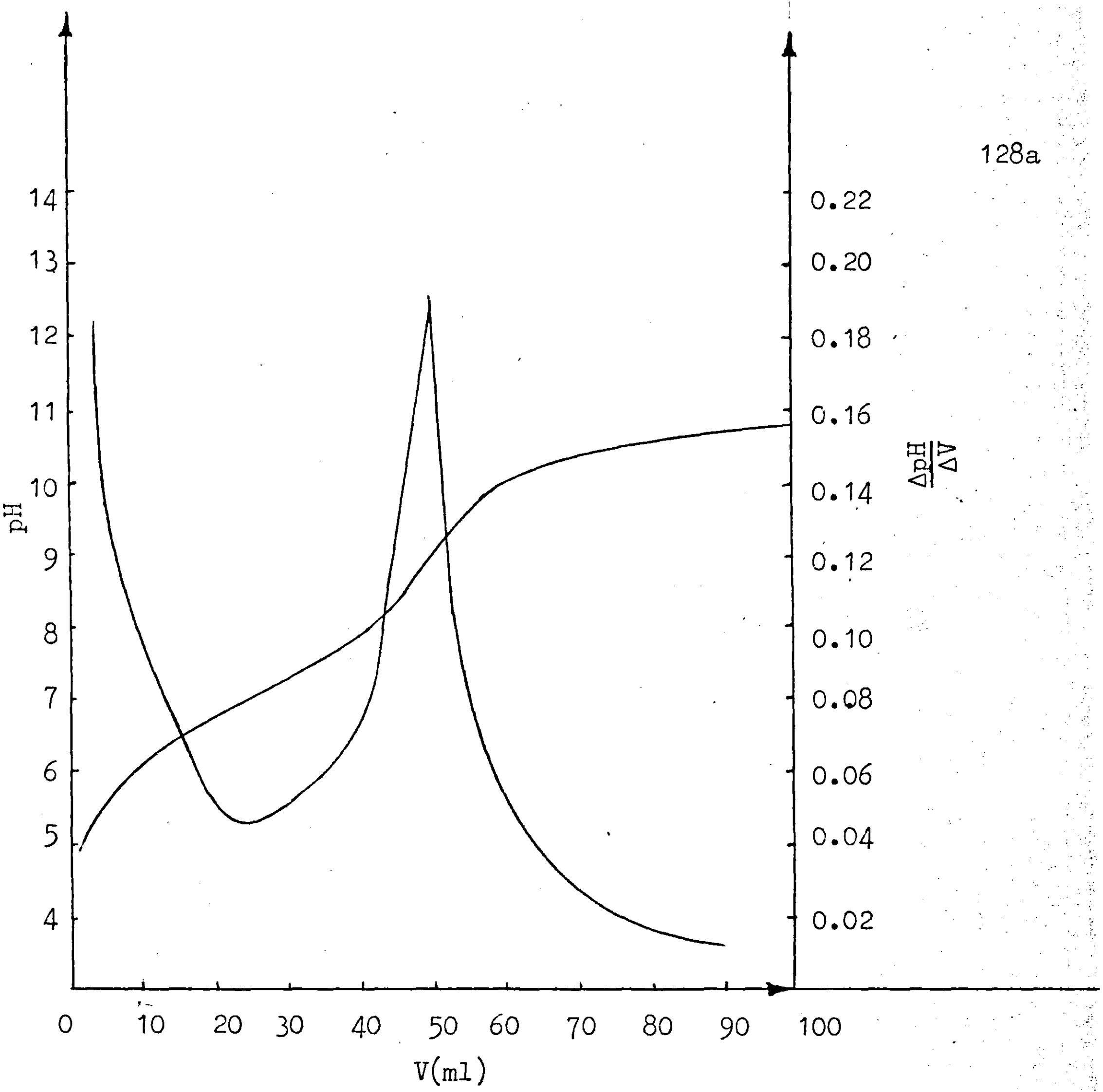
pH at half neutralization = 8.85; K(classical) = 1.41 x 10^{-9}

Ionic Strength (μ) = 0.05; Activity Coeff.($f_{\pm}$) = 0.8661

K(Thermodynamic) = 1.32 x 10^{-9}

FIG. 12(a) POTENTIOMETRIC TITRATION OF PHENYLDIHYDROXYBORANE

(Water) PLOT OF pH AND $\frac{\Delta pH}{\Delta V}$ AGAINST VOLUME OF ALKALI(V)



Normality of NaOH = 0.01; Molarity of the Acid = 0.004

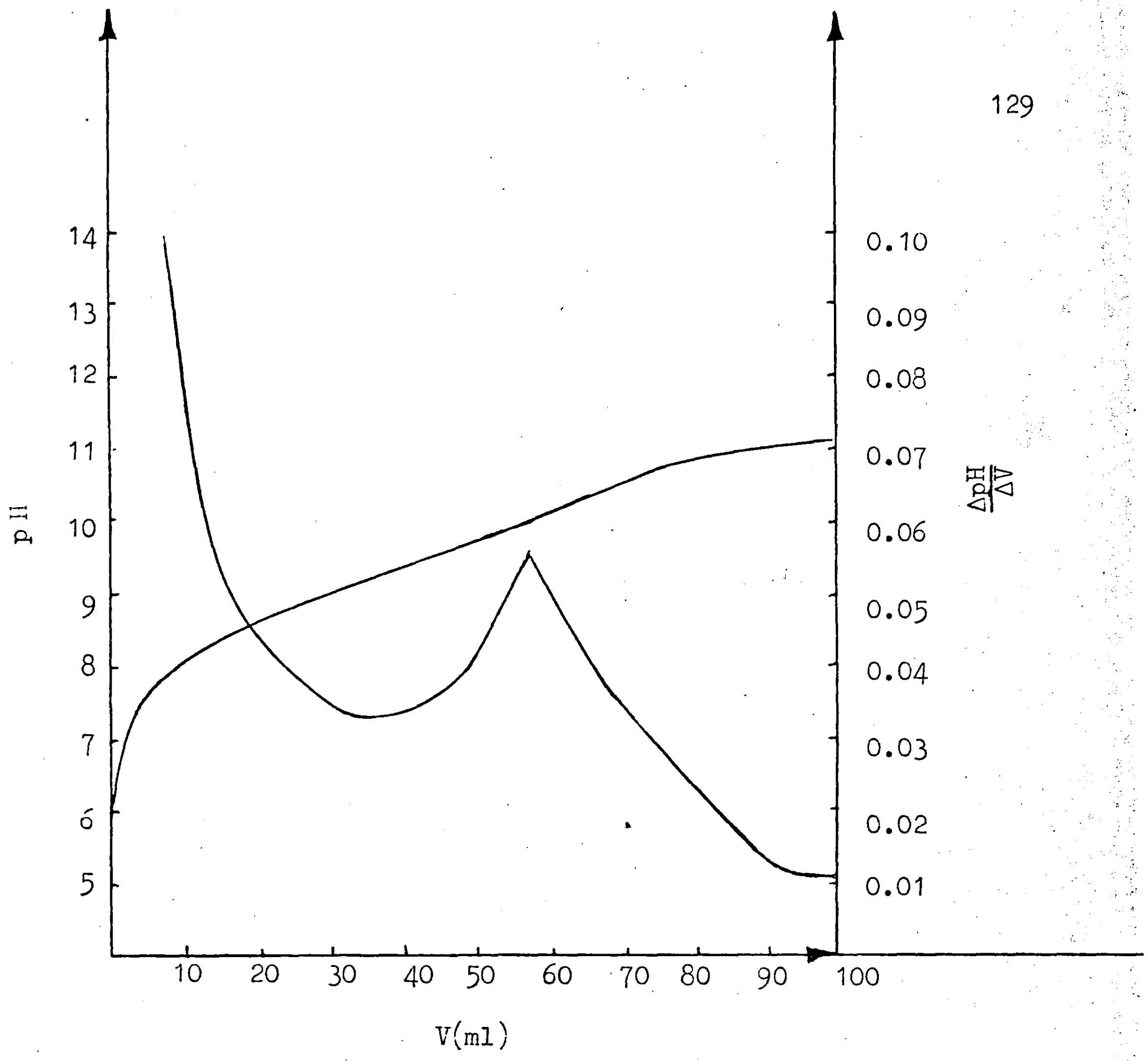
pH at half neutralization = 7.05, K(classical) = 8.9×10^{-9}

Ionic Strength (μ) = 0.002; Acticity Coeff.($f^{\pm}$) = 0.9519

K(Thermodynamic) = 8.064×10^{-9}

FIG. 12(b) POTENTIOMETRIC TITRATION OF p-TRIFLUOROMETHYL-PHENYLDIHYDROXYBORANE (Water)

PLOT OF pH AND $\frac{\Delta pH}{\Delta V}$ AGAINST VOLUME OF ALKALI(V)



Normality of NaOH = 0.01; Molarity of the Acid = 0.008

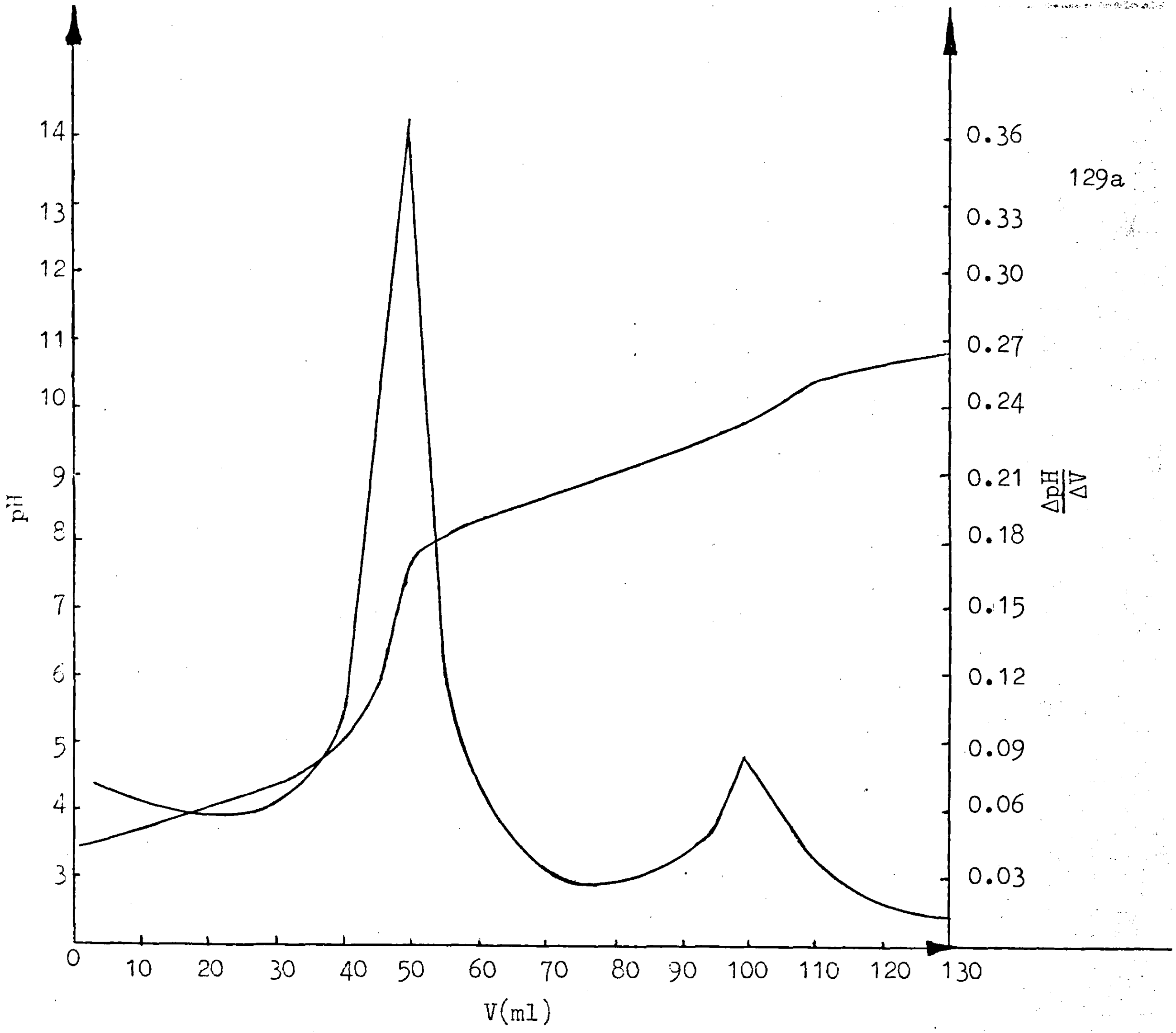
pH at half neutralization = 8.95, K(classical) = 1.1 x 10^{-10}

Ionic Strength (μ) = 0.004; Activity Coeff.($f^{\pm}$)=0.5012

K(Therm.) = 5.5 x 10^{-11}

FIG. 12 (c) POTENTIOMETRIC TITRATION OF p-t-BUTYLPHENYL-DIHYDROXY BORANE (ACETONE 10%)

PLOT OF pH and $\frac{\Delta pH}{\Delta V}$ AGAINST VOLUME OF ALKALI (V)



Normality of NaOH = 0.01; Molarity of the Acid = 0.013

pH at half neutralization (I) = 4.15; (II) = 8.7

K_I(classical) = 7.1 x 10^{-5}; K_{II}(classical) = 2.0 x 10^{-9}

Ionic Strength (μ) = 0.065; Activity Coeff ($f^{+}-$) = 0.8681

K_I (Therm.) = 6.07 x 10^{-5}; K_{II}(Therm.) = 1.90 x 10^{-9}

FIG. 12(d), POTENTIOMETRIC TITRATION OF p-CARBOXYPHENYL-DIHYDROXYBORANE (EtOH 25%)

PLOT OF pH AND $\frac{\Delta pH}{\Delta V}$ AGAINST VOLUME OF ALKALI (V)

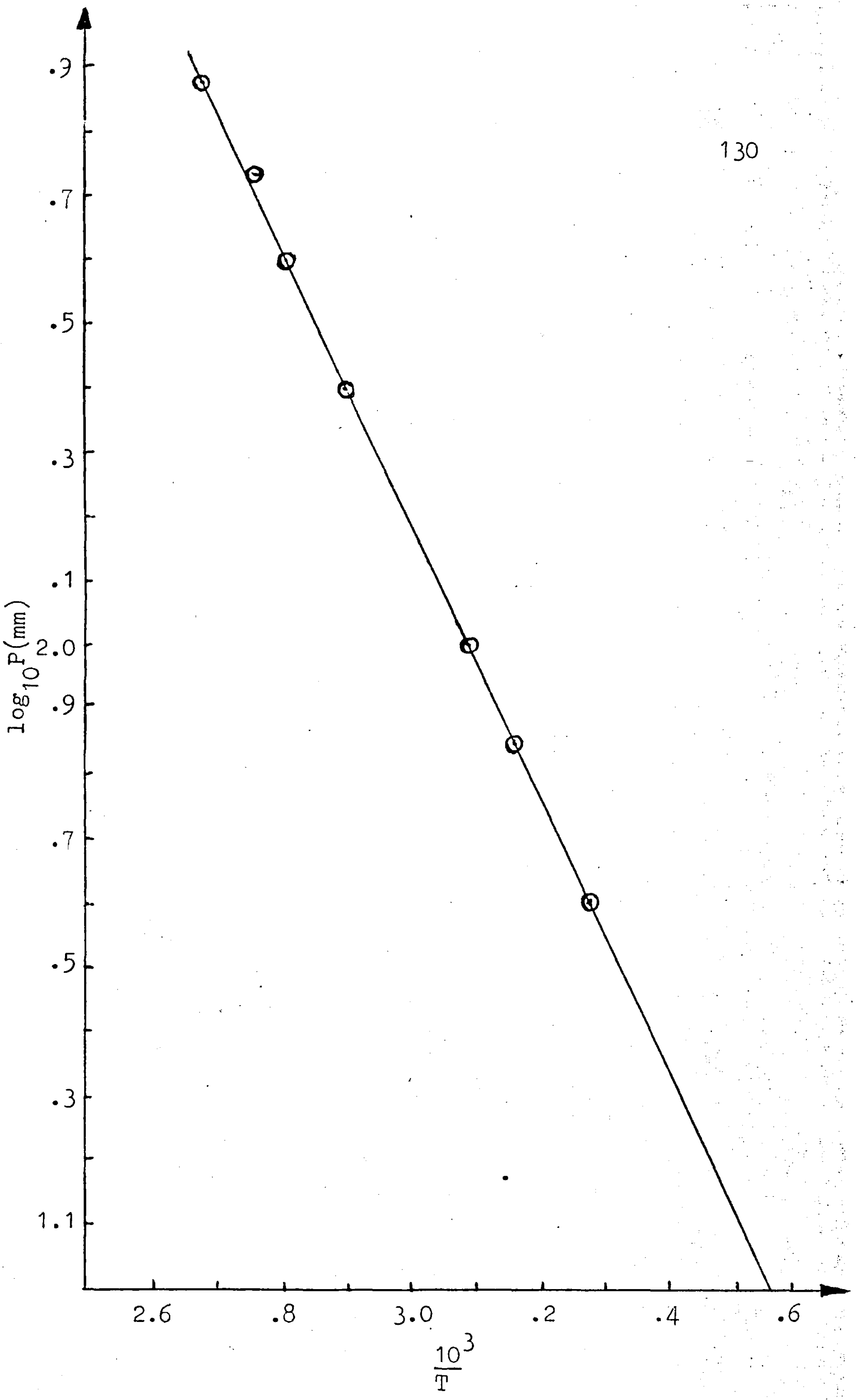


Fig. 13(a) Plot of $\mathrm{Log}_{10}P$ vs $\frac{10^3}{T}$ for WATER

OVER THE RANGE 305K - 373K

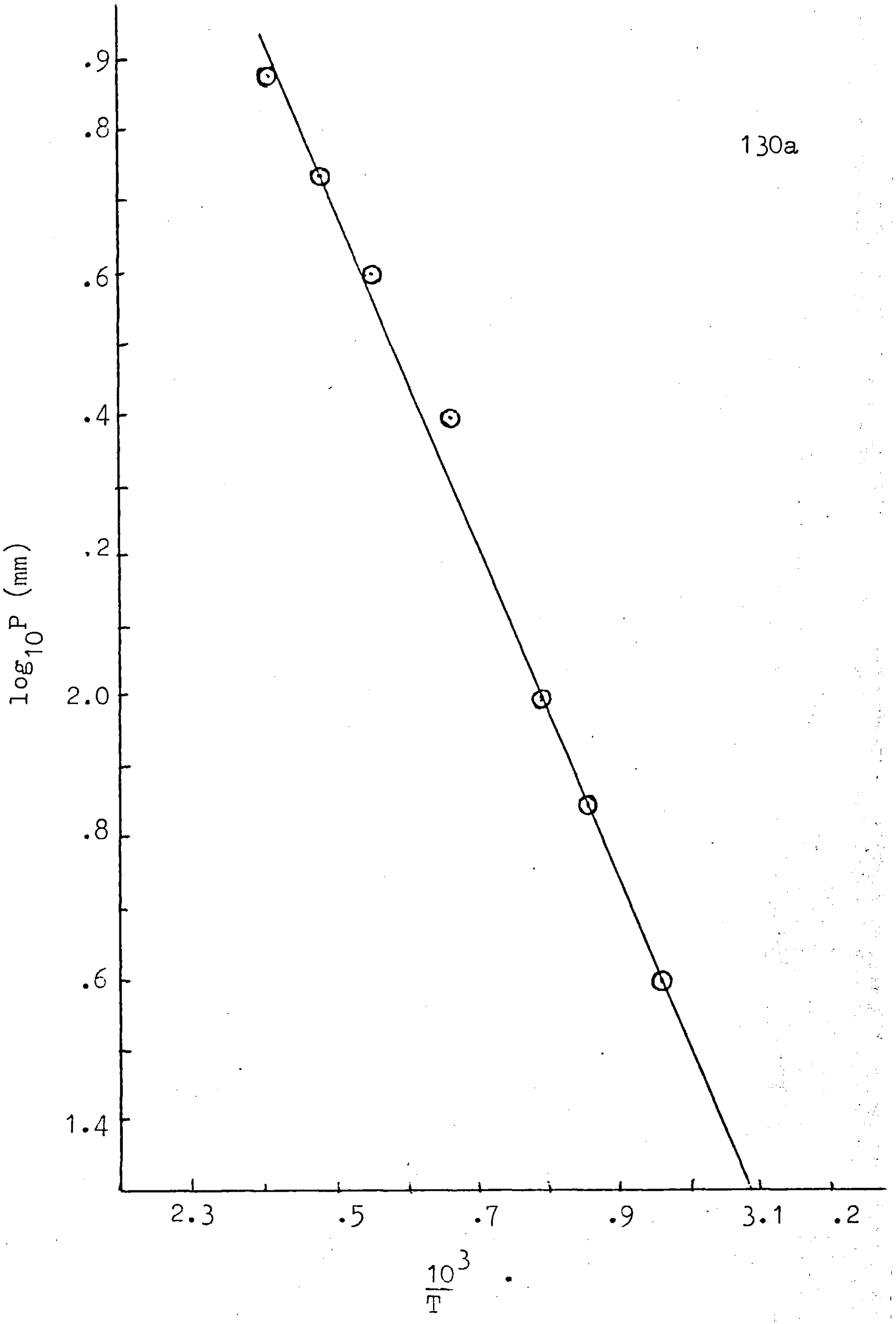


FIG. 13(b), Plot of $\log_{10}$ vs $\frac{10^3}{T}$ for PROPIONIC ACID OVER THE RANGE, 338K - 414K

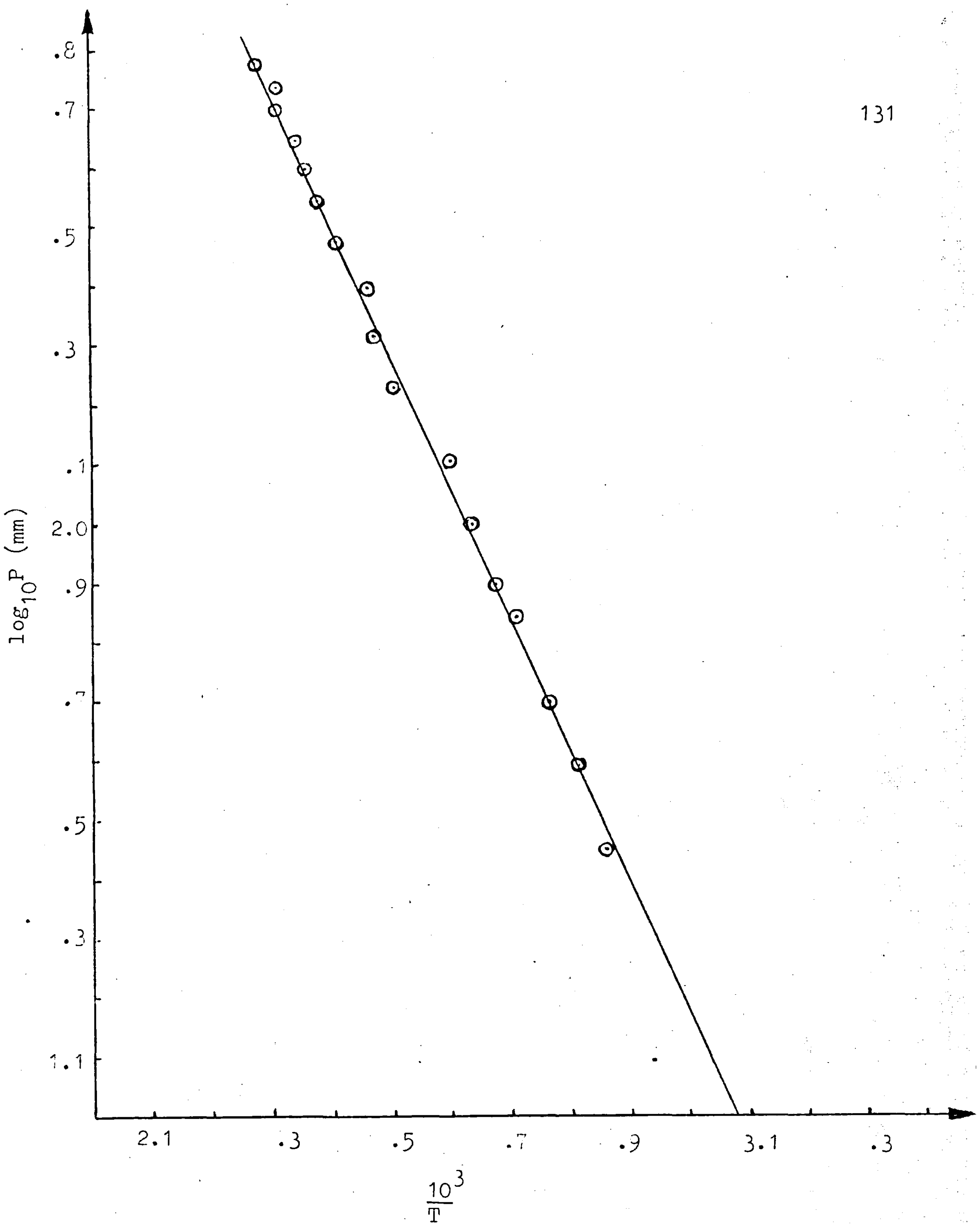


FIG. 13(c), Plot of Log$_{10}$P vs $\frac{10^3}{T}$ for PHENYLDICHLOROBORANE

OVER THE RANGE, 350K – 439K

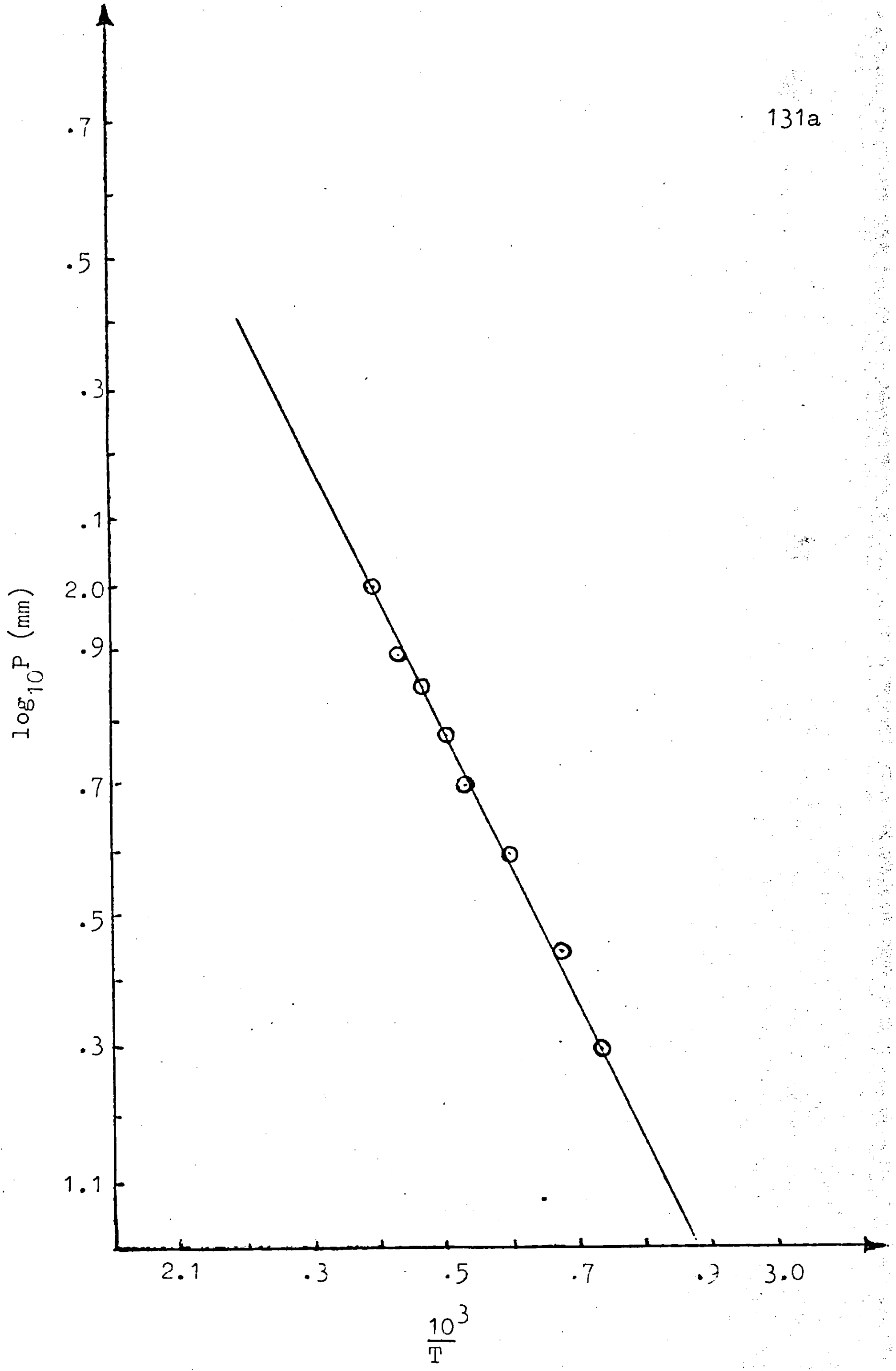


FIG. 13(d) Plot of $\text{Log}_{10}P$ vs $\frac{10^3}{T}$ for p-TOLYLDICHLOROBORANE OVER THE RANGE, 364K - 418K

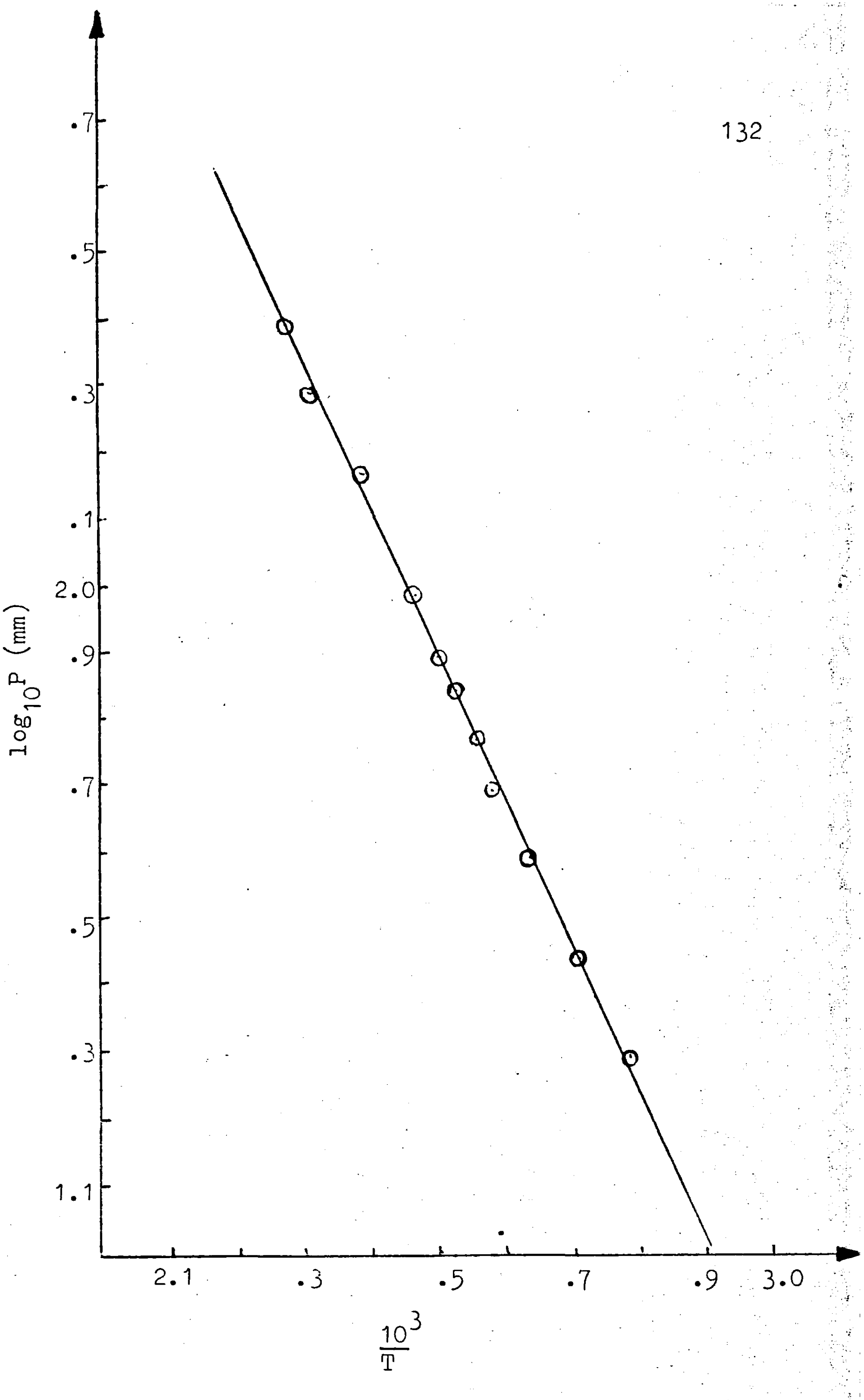


FIG. 13(e), Plot of $\text{Log}_{10}P$ vs $\frac{10^3}{T}$ for o-TOLYLDICHLOROBORANE

OVER THE RANGE, 346K - 439K

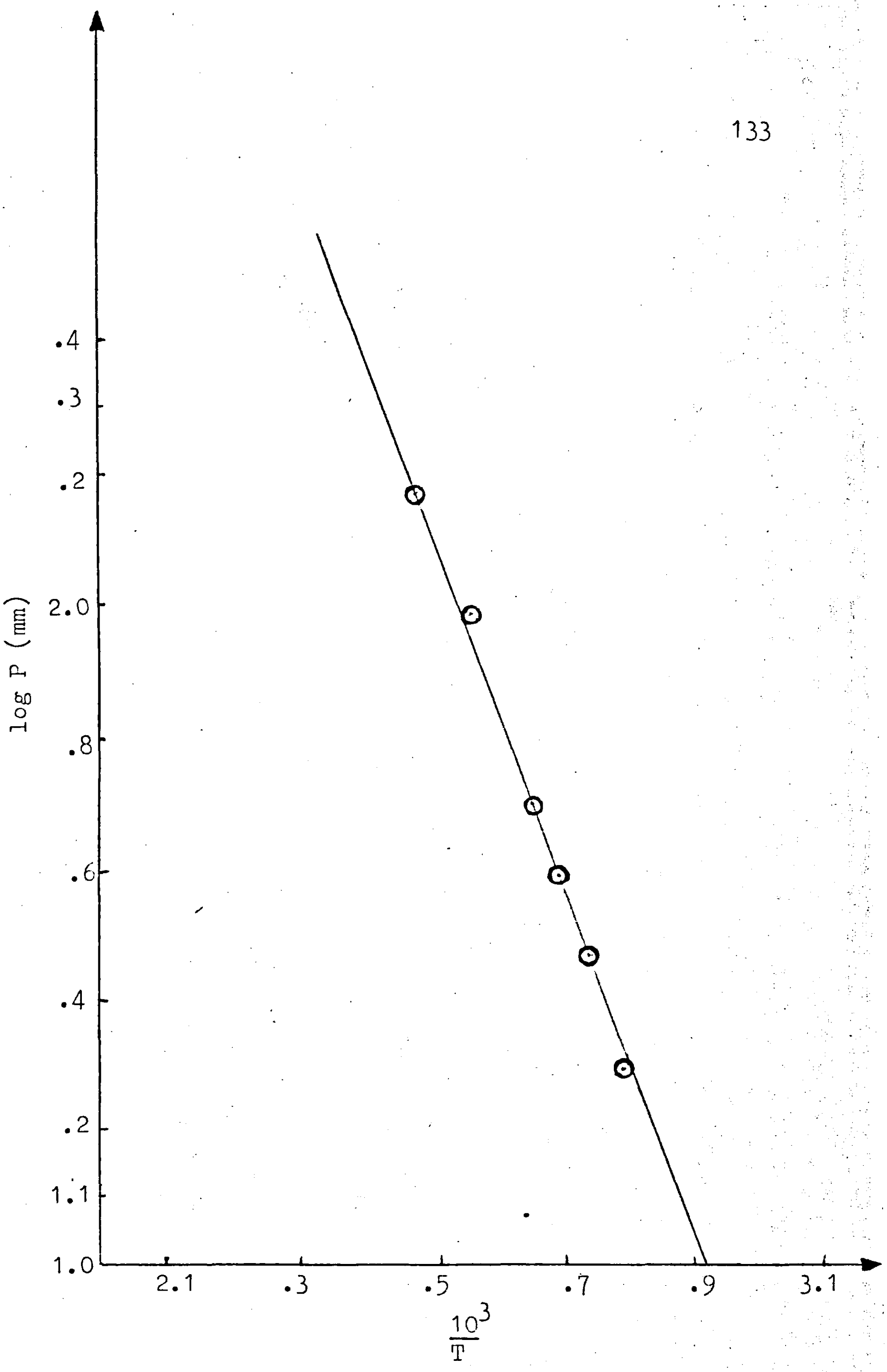


FIG. 13(f) Plot of Log_{10} P VS$\frac{10^3}{T}$for MESITYLDICHLOROBORANE

OVER THE RANGE 358 K - 427K

PART 2

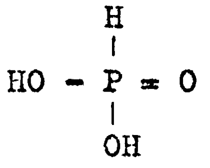
Section 1.

Thermochemistry of some phosphorus compounds and some diols.

Introduction

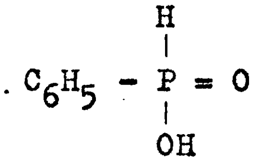
(a) Phosphorus Compounds

The nomenclature for organo phosphorus compounds described in this thesis follows the system adopted by the American Chemical Society's committee on the nomenclature of organic phosphorus compounds.[152] The following compounds were therefore named as,



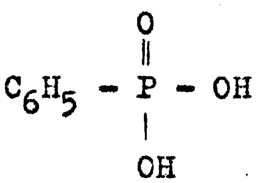
$HO-\overset{H}{\underset{OH}{P}}=O$

Phosphorous acid



$C_6H_5-\overset{H}{\underset{OH}{P}}=O$

Phenylphosphonous acid



$C_6H_5-\overset{O}{\underset{OH}{P}}-OH$

Phenylphosphonic acid.

Phosphonous acids and their derivatives have been excellently reviewed by Frank,[153] while the preparation and properties of phosphonic acids have been reviewed by Fredman et al.[154] Thermochemical properties of a number of phosphorus compounds have been extensively reviewed by Hartley and Holmes.[155] However, for the majority of phosphorus compounds accurate thermodynamic data are unavailable.

Most of the physical, chemical and structural properties of phosphorus compounds are described in monographs by Kosolapoff[156] and van Wazer.[157]

Organophosphorus compounds have acquired a unique importance in the fields of biochemistry[158] (nucleic acids, coenzymes), insecticidal chemistry, and polymer chemistry.[160] Phenylphosphonous acid and phenylphosphoric acids are commercially important compounds, because they are used to produce fire- and temperature-resistant products.[161]

The heats of formation of phosphorus halides have been determined via thermochemical investigations of their hydrolysis,[162,163] or oxidative hydrolysis.[164] The main products in these reactions were the lower acids of phosphorus, e.g. phosphorous acid. The heats of formation of these lower acids were sketchy and divergent. The heats of formation of crystalline[165] and aqueous phosphoric acid[166] are now available from various sources and are in agreement. It was, therefore, useful to carry out the oxidative hydrolysis of the phosphorous acid to determine accurately its heat of formation.

The hydrolysis of phenylphosphorousdihalides has been, for the first time, attempted in our laboratory.[167] The process had been thought, earlier, as ambiguous, and the hydrolysis was not supposed to proceed to completion.[153] The hydrolysis, carried out with a wide range of concentration and varying conditions, did not lead to any significant difference in the observed heat of hydrolysis. The reaction, therefore, was used to determine an approximate heat of formation of phenylphosphonous dihalides.[167]

In order to determine an accurate heat of formation of phenylphosphonous dihalides, an accurate heat of formation of phenyl phosphonous acid is needed, since

$$C_6H_5PX_2 + 2H_2O \longrightarrow C_6H_5PO_2H_2 + 2HCl$$

The thermodynamic data on phenylphosphonous acid is unavailable and so an attempt is made in this research to determine the heat of formation of this compound by combustion calorimetry.

An alternate method for the determination of the heats of formation of phenylphosphonous dihalides can be that of oxidative hydrolysis:

$$C_6H_5PX_2 + 3Br + 3H_2O \longrightarrow C_6H_5PO_3H_2 + 6HBr$$

The reaction product in this case will be phenylphosphonic acid. This reaction is under careful investigation in our laboratory. In order to determine the heat of formation of this compound, combustion calorimetry on $C_6H_5PO_3H_2$ was carried out. Moreover, the aqueous oxidation of phenylphosphonous to phenylphosphonic acid is also under investigation in our laboratory.

The combustion of organophosphorus compounds has been studied by several workers,[168] particularly by Mortimer et al.[169] These workers combusted the phosphorus compounds in the presence of excess oxygen; the products were mainly phosphoric acid, carbon dioxide and water. Thus:

$$Ph_3P_{(c)} + 23O_2(g) \longrightarrow H_3PO_4(c) + 1800_2g + 6H_2O_{(1)}$$

$$Ph_3PO_{(c)} + 22\tfrac{1}{2}O_2(g) \longrightarrow H_3PO_4(c) + 1800_2(g) + 6H_2O_{(1)}$$

$$(C_2H_5O)_3PO_{(c)} + 9O_2(g) \longrightarrow H_3PO_4(c) + 600_2(g) + 6H_2O(1)$$

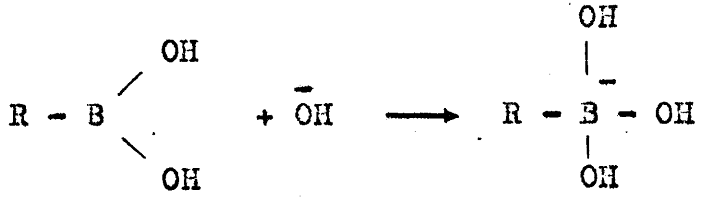
The process was applied to various types of phosphorus compounds (aliphatic, aromatic, cyclic) and the heat of formation was obtained. From these thermochemical values, several bond energies were estimated and compared with other available data. These are now fully discussed in an excellent monograph by Mortimer.[170]

(b) <u>Simple Aliphatic Diols</u>

Diols are commercially important compounds because they are used in the manufacture of lubricating products, etc. In addition they form complex, condensation polymeric products with phosphorus[171] and with boron compounds.[28]

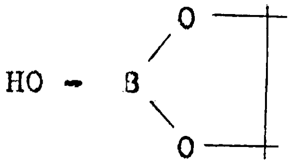
Most of the diols react with dihydroxyboranes, (boronic acids) boric acid, boron esters, boron halides and boranes etc., to give cyclic boron compounds. These cyclic compounds consist of five, six-and seven- (or more) membered rings and are obtained easily from the respective diols. The percentage yield depends upon the sterochemistry of the diols and its ring formation. Thus the six-membered esters of phenyldihydroxyborane (phenylboronic acid) and 2,3-butane diol are obtained in higher yeild than the five- and seven-membered rings from other diols.[173] That the six-membered esters of boric acid are more easily formed and are more stable than the five membered esters has been confirmed by competitive esterifications between boric acid and ethylene and 1,3 propane diols. The difference in stability is due to the greater strain present in five-membered rings by comparison with the six-membered rings, leading to a considerable distortion of the bond angles in the former with subsequent decrease of the stabilizing -O-B back-coordination.

Boric acid and boronic acids are Lewis acids, and add hydroxide ion in solution to form a very stable tetrahedral configuration of boron:

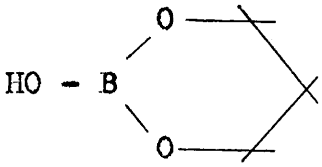


$$R-B\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} \quad + \overset{-}{O}H \longrightarrow R-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{B^{-}}}-OH$$

The difference in acidity between hydroxydioxaborolan (I) and dioxaborinan (II) was confirmed by the relative heats of formation of



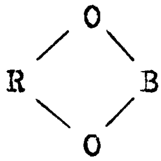
I



II

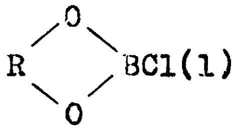
complexes with benzylamine and pyrolidine.[174]

Recently, thermochemical investigations on several five- and six-membered cyclic compounds of boron trichloride and the diols were carried out according to the following equations:[175]



$$R(O)_2BCl(l)+(n+3)(H_2O,l) \longrightarrow H_3BO_3+[R(CH)_2+HCl]_nH_2O$$

or



$$\Delta H_f^o\ R(O)_2BCl(l) = \Delta H_f^o\ H_3BO_3(aq) + \Delta H_f^o[R(OH)_2aq]+\Delta\ H_f^o(HCl,aq]-\Delta H_{obs.}$$

$$\Delta H_{obs.} = \Delta H_h^o - \ \Delta H_s^o \text{ (reaction products)}$$

where ΔH_s^o = heat of solution at 25°C and mole ratio N.

In order to estimate different parameters, i.e. strain energy in the rings etc., accurate heats of formation of diols were needed.

The thermochemical properties of diols were least investigated.[7] The heats of formation of some of the diols reported were old, and corresponded to different temperatures[176] (17°C) than that of the standard temperature (25°C). This is the reason that the combustion calorimetry of various diols were carried out, in order to re-check the available data, to provide some new data and to produce necessary thermodynamic data for various present problems.

The diols studied in this investigation are as follows:

1)	Ethane diol	$CH_2(OH).CH_2(OH)$
2)	Propane, 1,2-Diol	$CH_3.CH(OH).CH_2(OH)$
3)	2,2,Dimethylpropane diol	$CH_2(OH).C(CH_3)_2.CH_2(OH)$
4)	Butane-1,4-Diol	$CH_2(OH).CH_2.CH_2.CH_2(OH)$
5)	Butane-1,3-Diol	$CH_3.CH(OH).CH_2.CH_2(OH)$
6)	Pentane 1,5-Diol	$CH_2(OH).(CH_2)_3.CH_2(OH)$
7)	Hexane-1,6-Diol	$CH_2(OH).(CH_2)_4.CH_2(OH)$

Latent heats of vaporization of these diols are currently being determined in our laboratory.

EXPERIMENTAL

Section 2

GENERAL TECHNIQUES

Many of the handling techniques for these compounds are covered in Part 1, page . Phosphorous acid was stored in vacuo and was transferred in ampoules for calorimetric determinations, in a dry, inert atmosphere of nitrogen, using a glove bag. Phenylphosphonous acid and phenylphosphonic acid are stable compounds and were stored in stoppered bottles. They were powdered, in a glove bag, before use. Diols were moisture-sensitive compounds. They were stored in ground-glass containers, and for calorimetric procedures were filled in polyethylene bags in an atmosphere of dry, oxygen-free nitrogen. The nitrogen was further dried over anhydrous calcium chloride.

Preparation of pure samples

[Most of the samples were already purified and were supplied by the courtesy of Dr. P.J. Gardner, Royal Holloway College].

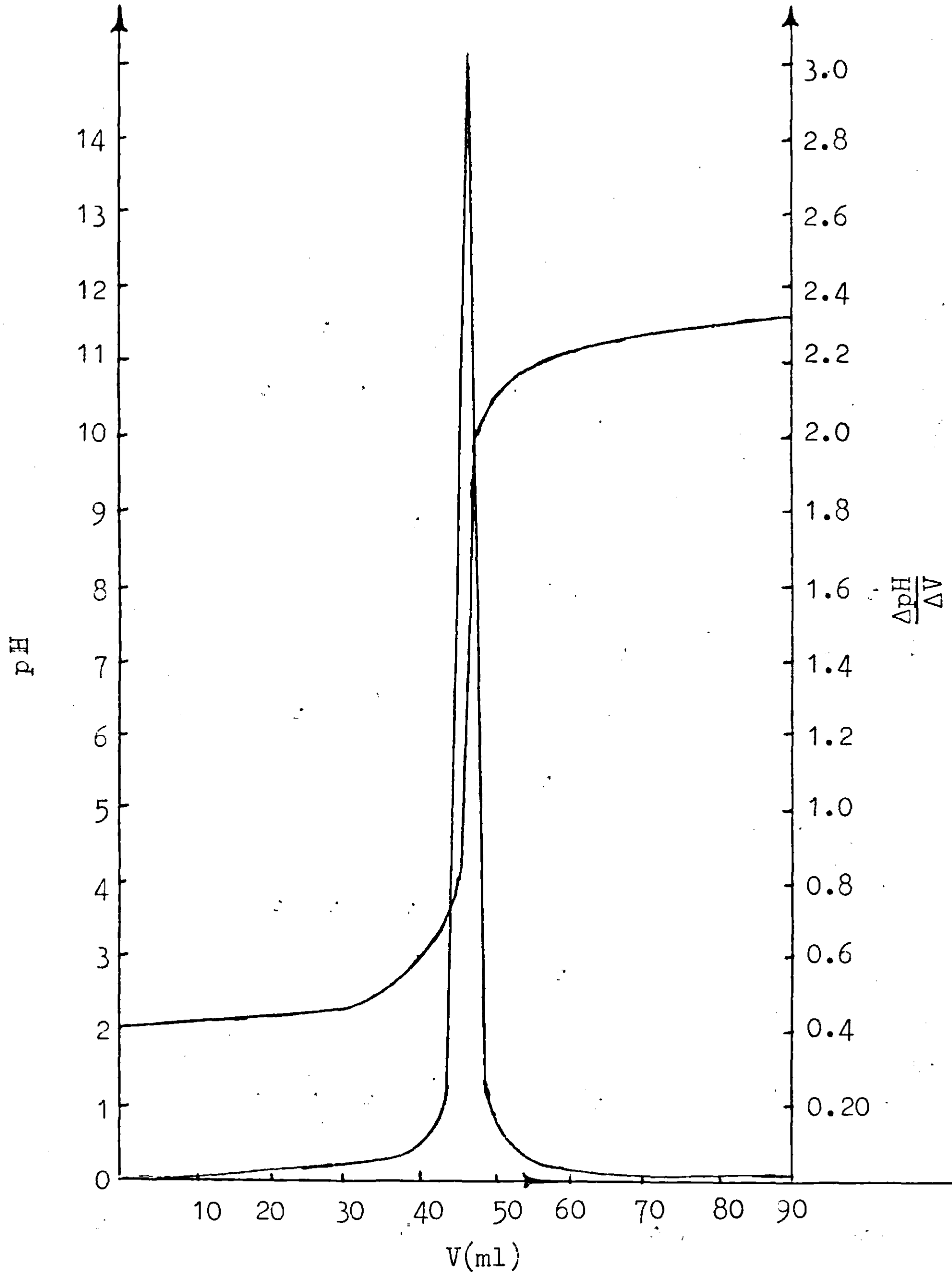
(i) Phosphorous acid was supplied by Dr. P.J. Gardner. This was a pure compound, crystallized several times from water and shown by analysis to be 99.8% pure. It was dried and stored under vacuum.

(ii) Phenyl phosphonous acid was prepared according to the method of Kosolapoff[177] as follows:

Phenyldichlorophosphine (50.0 ml.) was added, without external cooling, dropwise and with stirring into ethanol (absolute, 250 ml.) and the hot solution was diluted with distilled (100.0 ml.) water. The solution was boiled for five to ten minutes and then evaporated, on a water bath to give white crystals. The crystals were separated and recrystallized, several times, from 100-150 ml. of benzene. The resultant product was a white, shining plate, m.pt. 82°C (lit. 86°C, 70°).[153,177,178] Potentiometric (acidimetric) titrations showed 100% purity. It was monobasic and did not show any sign of dibasic impurity, (see graph Fig. 14a pK_a = 2.29 (lit. 1.75).[179]

(iii) Phenylphosphonic Acid. A pure commercial sample was recrystallized several times from water, to give pure white crystals, m.pt. 159°C (lit. 163,[180] 158°C.[178]) Potentiometric titration in water indicated a 100% pure sample, (see graph Fig. 14b) pKa_1 2.45 pKa_{II} 7.1; (lit. pKa_I 1.84, pKa_{II} 7.07).[181]

(iv) Diols were supplied by Dr. P.J. Gardner, in their pure, analysed forms. They were purified by several fractional distillations and the water contents were determined by Karl-Fischer titrations.[182] The water contents were always less than 0.08% w/w. The purity of the compounds were assayed by G.L.C., except for 1,3 propane and 1,4-butane diols, which decomposed on the column. Refractive index and



Normality of NaOH = 0.0493; Molarity of Acid = 0.0114

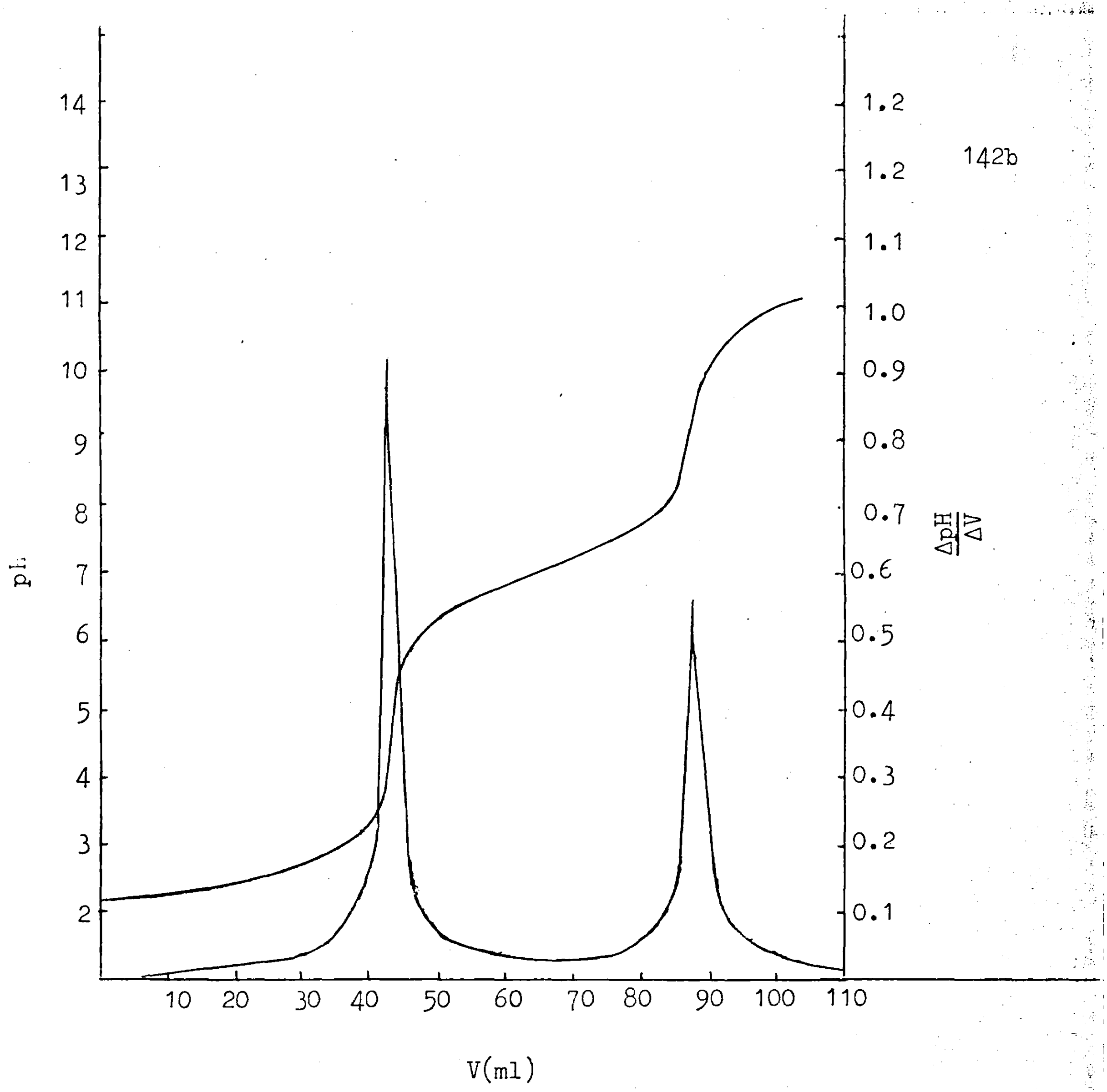
pH at half neutralization = 2.29; K(classical) = 5.13×10^{-3}

Ionic Strength (μ) = 0.005 Activity Coeff.($f^{\pm}$ = 0.927

K (Thermodynamic) = 4.8×10^{-3}

FIG. 14(a), POTENTIOMETRIC TITRATION OF PHENYLPHOSPHONOUS ACID,

PLOT OF pH AND $\frac{\Delta pH}{\Delta V}$ AGAINST VOLUME OF ALKALI (V)



Normality of NaOH = 0.0493, Molarity of Acid = 0.011

pH at half neutralization, (I) 2.45; (II) 7.1

K_I (Classical) = 3.55×10^{-3}; K_{II} (Classical) 7.94×10^{-8}

Ionic Strength (μ) = 0.125;

Acticity Coeff. (I), 0.925, (II), 0.7413

K_I (Therm.) = 3.28×10^{-3}, K_{II} (Therm.) = 5.86×10^{-8}

FIG. 14(b). POTENTIOMETRIC TITRATION OF PHENYLPHOSPHONIC ACID

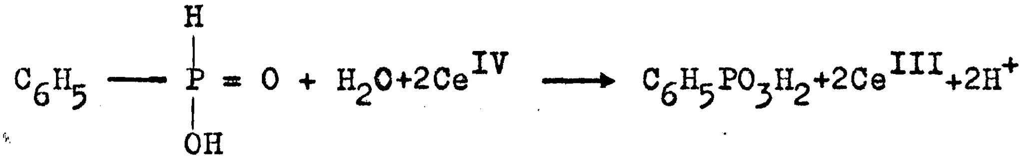
PLOT OF pH AND $\frac{\Delta pH}{\Delta V}$ AGAINST VOLUME OF ALKALI (V)

density determinations were used as purity criteria for these two diols.

Analytical procedures:

Determination of phenylphosphonous acid was attempted by a standard oxidative method,[183] which consisted in reaction with a ceric^{IV} solution and then titration with 0.1N ferrous ammonium sulphate using ferroin as the indicator.

The reaction can be represented as:



$$C_6H_5 - \overset{\displaystyle H}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{P}}}} = O + H_2O + 2Ce^{IV} \longrightarrow C_6H_5PO_3H_2 + 2Ce^{III} + 2H^+$$

The procedure was not found useful even when performed at higher temperatures.

Determination of phosphoric acid in the combustion products The ortho-phosphoric acid in the combustion products of phosphorus compounds was analysed according to the quinoline phospho-molybdate method,[184] which is as follows:

Reagents:

Sodium molybdate solution = 15% solution of A.R.$Na_2MoO_4.2H_2O$. The solution was stored in polythene bottles.

Quinoline hydrochloride solution. To a 800 ml. of hot, acidified water (25 ml. of pure conc. HCl) was added, with stirring, 20 ml. of quinoline. The mixture was allowed to cool to room temperature. A little paper pulp (made from filter paper No.1) was then added, again stirred well and then filtered, with suction, through a paper pulp-pad (without washing). The solution was made up to one litre with distilled water.

Indicator (Thymolphthalein) = 0.1 g. in 100 ml. alcohol.

Procedure.

The solution, containing 60-70 mg. of H_3PO_4, was taken in a conical flask (250 ml.). 30 ml. of sodium molybdate solution, and 20 ml. of conc. hydrochloric acid (A.R.) were added, and the mixture heated to boiling. 60 ml. of quinoline - hydrochloride solution was then added dropwise, to the flask. 1-2 ml. of solution was first added, the solution boiled and stirred, and then 1-2 ml. quinoline solution similarly added, boiled and stirred, and the procedure repeated till the whole of the solution (60 ml.) was added. A yellow, coarsely crystalline, precipitate was produced. It was boiled for fifteen minutes on a water bath and then cooled to room temperature. The precipitate was transferred to a porcelain funnel on a pad of paper-pulp and the liquid filtered. The precipitate was washed, first with 20 ml. 11% aq HCl solution and then cold distilled water, till acid-free (no ppt. with $AgNO_3$ soln.). It was quantitatively transferred to a conical flask (250 ml.) together with paper pulp. The funnel was washed with a minimum amount of distilled water (50 ml.) and the washings were added to the conical flask. The conical flask was shaken well and 50 ml. of standard sodium hydroxide (0.5N, carbonate free) added with stirring, till the precipitate completely dissolved. A few drops of indicator were added and titration with standard hydrochloric acid (0.5N) was carried out to a colourless end-point (9-10 pH).

THERMOCHEMISTRY

The thermochemistry of phosphorous acid was studied by solution calorimetry using a constant-temperature-environment calorimeter, which is described in detail in section 4, part 2.

The thermochemical studies of phenylphosphonous acid, phenylphosphonic acid and the diols were carried out using a static adiabatic bomb calorimeter, described in detail in section 5, part 2.

Thermochemistry of Phosphorous acid (H_3PO_3).

The available data for the standard heat of formation of H_3PO_3 have been reported in a recent review by Hartley et al.[155] These were in disagreement with each other; i.e. -232.2, -227.1,[164] -226.0,[155] -227.5[76]. These values were obtained either by the oxidation of aqueous phosphorous acid to phosphoric acid[185] or by a study of the hydrolysis of phosphorus trichloride to aqueous phosphorous acid.[155] The oxidation of H_3PO_3 (crystal) to phosphoric acid (aq.) has been carried out in this laboratory by excess aqueous bromine. The thermal effect of the equilibria,

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

and

$$Br_3^- + Br_2 \rightleftharpoons Br_5^-$$

were included, since bromine in aqueous solution produces Br_3^- and Br_5^- but not higher polybromides.[187] The heats of formation of Br_3^- [140] and Br_5^- [140] and the equilibrium constants for the above equilibria are available. The contribution of the above thermodynamic equilibria was therefore calculated as approx. 1 kcal.mole^{-1} H_3PO_4. The course of the reaction is represented as follows:

$$H_3PO_3(\text{cryst.})+(n+1)Br_2+(m+1)H_2O \longrightarrow [H_3PO_4+2HBr]_n Br_2 mH_2O; \quad \Delta H_{obs.}$$

The standard enthalpy of formation of H_3PO_3 was therefore calculated from the following equations:

$$\Delta H_f^o H_3PO_3(\text{cryst.})=\Delta H_f^o[H_3PO_4,aq]+2\Delta H_f^o[HBr,aq]-\Delta H_f^o[Br,aq]-\Delta H_f^o[H_2O,l] \quad \Delta H_{obs.}$$

$$[Br_2,aq] + [Br^-,aq] \rightleftharpoons [Br_3^- aq] \;;\; \Delta HB$$

$$[Br_3^- aq] + [Br_2,aq] \rightleftharpoons [Br_5^-,aq]; \; \Delta HC$$

$$\Delta H_{obs.} = \Delta HA + \Delta HB \; \Delta HC$$

The observed heats of oxidation of phosphorous acid at 25.0± 0.1°C are given as follows:

TABLE 28

N	$\Delta H_{obs.}$ kcal.mole^{-1}
2467	-70.8
2429	-70.2
3373	-71.1
3470	-71.4
3895	-70.9

/contd.

TABLE 28 (continued)

N	$\Delta H_{obs.}$ kcal.mole
4608	-71.2
2898	-72.0
2725	-71.1
3221	-71.5
2876	-70.4
2832	-71.1
3739	-69.8
mean 3211	-71.0±0.2

where

N = mole ratio of water to that of H_3PO_3.

The concentration of Br_2 was 0.22 moles litre^{-1} (a saturated soln.).

Thermochemistry of Phenylphosphonous and Phenylphosphonic Acids

The heats of formation of these compounds were determined by combustion calorimetry in the presence of excess O_2 (30 atm.). The reactions can be represented as

$$C_6H_5PO_2H_2+8O_2 \longrightarrow 6CO_2+H_3PO_4+2H_2O$$

$$C_6H_5PO_3H_2+\frac{15}{2}O_2 \longrightarrow 6CO_2+H_3PO_4+2H_2O.$$

The compounds were combusted in a platinum crucible and gave the quantitative amount of H_3PO_4. The analytical procedures for the combustion products are given in section 5 part 2. There was no sign of lower phosphorus acids and polyphosphorus acids. Standard state corrections were evaluated using a computer programme. The experimental results are tabulated as follows:

TABLE 29

$$C_6H_5PO_3H_2 + 7\tfrac{1}{2}O_2 \longrightarrow 6CO_2+H_3PO_4+2H_2O$$

S.NO.	Code No.	Wt. of Compd.(g)	Wt. of benzoic acid(g)	soot (g)	loss in pt. (g)	N	$-\Delta U_c^o$ Kj g^{-1}
1	p- 3	0.4996	0.4983	0.0002	0.000	58.6	20.847
2	p- 4	0.4909	0.4976	0.0005	"	59.6	21.007
3	p- 5	0.4955	0.4978	0.0005	0.0010	59.0	20.864
4	p- 9	0.4961	0.4968	"	"	"	20.934
5	p-16	0.4604	0.4983	0.0004	"	63.4	21.018
6	p-16A	0.3856	0.4606	0.0009	"	75.0	20.921
7	p-17	0.4291	0.4425	"	"	67.0	20.762
8	p-21	0.5412	0.5434	0.0012	0.0002	54.5	21.043
9	p-22	0.4590	0.4810	0.0010	0.0000	63.0	20.863
10	p-24	0.4635	0.4855	0.0012	0.0009	63.0	20.829
11	p-25	0.5058	0.4822	0.0010	0.0000	61.0	20.922
12	p-27	0.4928	0.4902	0.0014	0.0000	69.0	20.939
13	p-28	0.5000	0.4659	0.0010	0.0000	58.0	21.095
mean							20.9341 ±.025

TABLE 30

$$C_6H_5PO_2H_2 + 8O_2 \longrightarrow 6CO_2+H_3PO_4+2H_2O$$

S.NO.	Code No.	Wt. of Compd.(g)	Wt. of benzoic acid(g)	soot (g)	loss in pt.(g)	N	$-\Delta U^o$ Kj g^{-1}
1	P_2- 1	0.4817	0.5163	0.0009	0.0000	54.87	25.795
2	P_2- 2	0.4655	0.4607	0.0010	0.0001	56.29	25.580
3	P_2- 3	0.4609	0.4605	0.0016	0.0006	56.83	25.630
4	P_2- 4	0.4638	0.4478	0.0013	0.0000	56.39	25.728
5	P_2- 6	0.4598	0.4301	0.0014	0.0010	56.73	25.595
6	P_2- 8	0.4616	0.4297	0.0018	0.0009	56.52	25.780
7	P_2-11	0.4559	0.4826	0.0016	0.0008	57.60	25.791
8	P_2-12	0.4549	0.4901	0.0016	0.0000	57.78	25.621
9	P_2-13	0.4563	0.4714	0.0025	0.0004	57.47	25.657
10	P_2-14	0.4566	0.4584	0.0010	0.0005	57.33	25.655
mean							25.683 ± .026

Thermochemistry of Diols

These compounds were combusted by the usual procedure described in section 5, page 176; because they were hygroscopic, they were first filled in polyethylene bags. There was no loss of weight in sealing a polyethylene bag. The loss of weight of diols by evaporation, while sealing a polyethylene bag filled with the compound, was also nil.

The amount of soot left after combustion was always very small ($<$ 0.0004 g). The analysis of the combustion products was done in a simplified way, described in detail in section 5. The standard-state reductions ("Washburn corrections") were calculated using a computer programme. The results representing the following general equation are given as:

$$C_aH_bO_c + [a+\frac{b}{4} - C]O_2 \xrightarrow{\quad} aCO_2 + \frac{b}{2} H_2O; \quad \Delta U^o_c$$

TABLE 31

Compound	S.NO.	Code No.	Wt. of Compound	Wt. of poly-ethylene	Wt. of soot	$-\Delta U^o_c$ KJ.g^{-1}
ETHANE DIOL	1	1.01	1.1229		0.0001	19.2812
	2	1.04	1.1965		"	19.2393
	3	1.06	1.3317		"	19.2895
	4	1.07	1.2877		"	19.2575
	5	1.09	1.3098		"	19.2174
	6	1.10	1.2965		"	19.2749
	7	1.11	1.2487		"	19.2421
	8	1.12	1.3214		"	19.3124
	9	1.13	1.1494		"	19.2054
					mean	19.258±012
	1	1.14	0.8695	0.1887	0.0002	19.2143
	2	1.15	0.7487	0.2043	"	19.2776
	3	1.16	1.1490	0.2468	0.0001	19.2073
	4	1.18	0.7954	0.2154	0.0002	19.3014
	5	1.20	0.39[illegible]0	0.2186	0.0001	19.3027
	6	1.21	0.9330	0.1800	0.0002	19.2660

/contd.

TABLE 31 (continued)

Compound	S.NO.	Code No.	Wt. of Compound	Wt. of poly-ethylene	Wt. of soot	$-\Delta U_c^0$ $K_J g^{-1}$
ETHANE DIOL (contd.)	7	1.22	0.9872	0.2043	0.0002	19.2203
	8	1.23	0.8245	0.2413	"	19.2523
					mean	19.255± 0.014
Propane 1,2-Diol	1	2.01	0.6500	0.1752	0.0002	24.1616
	2	2.02	0.6601	0.1612	"	24.1970
	3	2.03	0.5909	0.1528	"	24.1976
	4	2.04	0.5684	0.1756	0.0001	24.1143
	5	2.05	0.6714	0.1936	"	24.1526
	6	2.06	0.5316	0.1508	"	24.1644
	7	2.07	0.5699	0.1748	0.0002	24.1273
	8	2.08	0.6210	0.1816	0.0001	24.1397
					mean	24.157± .014
Butane 1,3-Diol	1	3.01	0.4044	0.1872	0.0003	27.7668
	2	3.02	0.6414	0.2065	0.0002	27.7681
	3	3.03	0.5835	0.1812	"	27.7460
	4	3.04	0.6238	0.1779	"	27.7063
	5	3.05	0.6187	0.2131	"	27.7502
	6	3.06	0.6565	0.1798	"	27.7341
					mean	27.745± 0.015

/contd.

TABLE 31 (continued)

Compound	S.NO.	Code No.	Wt. of Compound	Wt. of poly-ethylene	Wt. of soot	$-\Delta U_c^o$ Kjg^{-1}
BUTANE-1,4-Diol	1	4.01	0.5873	0.1844	0.0002	27.7434
	2	4.02	0.6921	0.1586	"	27.8091
	3	4.04	0.6620	0.1490	0.0001	27.6960
	4	4.05	0.6097	0.1566	"	27.7418
	5	4.06	0.6576	0.1652	"	27.6995
	6	4.07	0.6502	0.1549	"	27.7015
	7	4.08	0.5896	0.1574	"	27.7084
	8	4.09	0.6628	0.1635	"	27.8022
	9	4.10	0.6605	0.1720	"	27.7940
					mean	27.744 ± .016
2,2-Dimethyl propane 1,3-diol.	1	5.01	0.8678		0.0003	30.0368
	2	5.02	0.7671		0.0002	30.0503
	3	5.03	0.8142		"	30.0989
	4	5.04	0.8005		0.0003	29.9822
	5	5.05	0.8228		"	30.0401
	6	5.07	0.7773		"	30.0988
	7	5.09	0.8046		"	30.0314
					mean	30.047 ± 0.018

TABLE 31 (continued)

Compound	S.NO.	Code No.	Wt. of compound	Wt. of poly-ethylene	Wt. of soot	$-\Delta U_c^o$ $K_j g^{-1}$
PENTANE 1,5-Diol	1	6.03	0.4402	0.2002	0.0002	30.2573
	2	6.05	0.5321	0.2397	"	30.3514
	3	6.07	0.5879	0.1703	"	30.3327
	4	6.09	0.5288	0.1638	"	30.2766
	5	6.10	0.5345	0.1829	"	30.3204
	6	6.11	0.5138	0.1662	"	30.2938
	7	6.13	0.5486	0.1654	"	30.2712
					mean	30.305 ±0.013
HEXANE 1,6-Diol	1	7.04	0.4729	0.1560	0.0002	32.1114
	2	7.06	0.5079	0.1750	"	32.0819
	3	7.07	0.4527	0.1622	"	32.1111
	4	7.08	0.5740	0.1724	"	32.1468
	5	7.10	0.6640	0.1695	"	32.0835
					mean	32.107 ± 0.015

RESULTS and DISCUSSION

For thermodynamic calculations the difference in heat contents of the reactants and the products are required. The process of combustion in a bomb of constant volume gives the energy of combustion ΔU_c^o. The enthalpy of combustion ΔH_c^o, therefore, is given by the equation,

$$\Delta H_c^o = \Delta U_c^o + \Delta n\ RT.$$

where Δn = change in the number of moles of the gaseous reactants and the products. Since the usual products of combustion are CO_2 and O_2, they are assumed to behave as ideal gases under one atmosphere pressure. Thus for a reaction such as

$$C_aH_bO_c\ (s.s.) + [a + \frac{b}{4} - \frac{c}{2}]O_2(g) \longrightarrow aCO_2(g) + \frac{b}{2}\ H_2O\ (liq)$$

and $\Delta n = a - [a + \frac{b}{4} - \frac{c}{2}]$

From the ΔH_c^o of the compound and the ΔH_f^o of the reactants and products, the ΔH_f^o of the compound is calculated. Thus for the above reaction,

$$\Delta H_f^o C_aH_bO_c(s.s.) = a\Delta H_f^o[CO_2,g] + \frac{b}{2}\ \Delta H_f^o[H_2O(l)] - \Delta H_c^o$$

because ΔH_f^o of $O_2 = 0$ by thermodynamic convention.

Calculation of standard enthalpies of formation

(a) ΔH_f^o of Phosphorous Acid

The thermodynamic ancillary data used were taken from ref. 140. The heat of formation of aqueous phosphoric acid was taken as -310.5 ± 0.5 kcal.mole^{-1} [166] therefore

$$\Delta H_f^o[H_3PO_3,\text{cryst.}]-\Delta H_f^o[H_3PO_4,\text{aq}]+2\Delta H_f^o[HBr,\text{aq}]-\Delta H_f^o[Br,\text{aq}]-\Delta H_f^o H_2O(l)$$
$$-\Delta H_{obs.}$$

or

$$\Delta H_f^o[H_3PO_3,\text{cryst.}]-\Delta H_f^o[H_3PO_4 3000H_2O]=81.37 \text{ kcal.mole}^{-1} \pm 0.2$$

and

$$\Delta H_f^o[H_3PO_3,\text{cryst.}] = -229.1 \pm 0.6 \text{ kcal.mole}^{-1}.$$

(b) ΔH_f^o of Phenylphosphorous acid ($C_6H_5PO_2H_2$)

$$[C_6H_5PO_2H_2,\text{cryst.}]+8[O_2(g)] \longrightarrow 6[CO_2(g)]+2[H_2O(l)]+[H_3PO_4 50H_2O\text{aq}] \quad ; \quad \Delta H_c^o$$

$$\Delta H_f^o[C_6H_5PO_2H_2,\text{cryst.}]=6\Delta H_f^o CO_2+2\Delta H_f^o[H_2O,l]+\Delta H_f^o[H_3PO_4,\text{aq}]-\Delta H_c^o.$$

$\Delta U_c^o = -25.683 \pm 0.026$ kcal.mole^{-1}

$\Delta n = -2$

$\Delta nRT = -[2 \times 1.987 \times 298.2] \times 10^{-3}$

$= -1.185$ kcal.mole^{-1}

$\Delta U_c^o = -25.68 \times \frac{142.096}{4.184} = -872.23$ kcal.mole^{-1}

$\Delta H_c^o = -872.23 - 1.19 = -873.42 \pm 0.89$ kcal.mole^{-1}

$\Delta H_f^o[C_6H_5PO_2H_2\text{cryst.}] = 6[-94.051]+2[-68.315]+[-309.72]-[-873.42]$

$= -137.2 \pm 1.0$ kcal.mole^{-1}

The $\Delta H_f^o[H_3PO_4,50H_2O]$ was taken as [-309.72], the mean of the two values reported recently by Irving et al.[166] and Skinner et al.[165] respectively.

The latent heat of sublimation (ΔH^osub) of this compound is unavailable and probably could not be obtained due to thermal instability. However, the value of ΔH^o sub was estimated by comparison with ΔH sub of benzoic acid (Mol. wt. 122) so

$$\Delta H^o\text{sub. } C_6H_5PO_2H_2 = \frac{21}{122} \times 142 = 24.4 \text{ kcal.mole}^{-1}$$

therefore

$$\Delta H_f^o[C_6H_5PO_2H_2,g] = -137.2 + 24.4$$
$$= -112.8 \text{ kcal.mole}^{-1}$$

(c) <u>ΔH_f^o of Phenylphosphoric acid $C_6H_5PO_3H_2$</u>

$$\Delta H_f^o\ [C_6H_5PO_3H_2 \text{ cryst.}] = 6\Delta H_f^o[CO,g] + 2\Delta H_f^o[H_2O,l] + \Delta H_f^o[H_3PO_4;\ 50H_2O] - \Delta H_c^o.$$

we have $\Delta nRT = -1.5 \times 1.987 \times 298.15 \times 10^{-3} = 0.89$ kcal.mole^{-1}

$$\Delta U_c^o = -20.934 \pm 0.025 \ K_jg^{-1}$$
$$= -[20.934 \times \frac{158.095}{4.184} = 791.004 \text{ kcal.mole}^{-1} \pm 0.94$$

and thus using the above mentioned data we get

$$\Delta H_f^o[C_6H_7PO_3, \text{ cryst.}] = 6[94.051]+2[-68,315]+[-309.72]-791.00$$
$$= -218.8 \pm 1.0 \text{ kcal.mole}^{-1}.$$

The heat of sublimation of this compound is also unavailable, so it was also estimated as detailed above.

ΔH^{o}sub. of $C_6H_5PO_3H_2 = \frac{21}{122} \times 158 = 27.2$ kcal.mole^{-1}

and so

$\Delta H^{o}_{f}[C_6H_5PO_3H_2,g] = -218.8 + 27.2 = -191.6 \pm 1.0$ kcal.mole^{-1}.

(d) ΔH^{o}_{f} of Diols

(i) Ethane diol $[C_2H_6O_2]$.

$\Delta H^{o}_{f}[C_2H_6O_2,l] = 2\Delta H^{o}_{f}[CO_2,g] + 3\ \Delta H^{o}_{f}[H_2O]-\Delta H^{o}_{c}$.

$\Delta nRT = -0.30$ kcal.mole

$$\Delta U^{o}_{c} = -19.256 \pm 0.014\ K_jg^{-1}$$

$$= -19.256 \times \frac{62.069}{4.184} = -285.69\ \text{kcal.mole}^{-1} \pm 0.2$$

$$\Delta H^{o}_{c} = (-285.69)+[-0.30]$$

$$= -286.0 \pm 0.2\ \text{kcal.mole}^{-1}$$

therefore

$$\Delta H^{o}_{f}[C_2H_6O_2,l] = 2(-94.051) + 3(-68.315)-(-286.0)$$

$$= -107.06 \pm 0.2\ \text{kcal.mole}^{-1}$$ (lit. -108.74)

$\Delta H^{o}_{vap.} = 13.6$ kcal.mole^{-1}

$\Delta H^{o}_{f}\ [C_2H_6O_2,g] = -93.46$ kcal.mole^{-1}

(ii) Propane 1,2 Diol $[C_3H_8O_2,l)$

$\Delta H^{o}_{f}[C_3H_8O_2,l]_{1,2} = 3\ H^{o}_{f}[CO_2,g]+4\Delta H^{o}_{f}[H_2O,l]-\Delta H^{o}_{c}$.

$\Delta U^{o}_{c} = -24.157 \pm 0.014\ K_jg^{-1}$ $\Delta nRT = -0.5963$ kcal.mole^{-1}

$= -[24.157 \times \frac{79.096}{4.184} = -439.35 \pm 0.25$ kcal.mole^{-1}

$\Delta H^o_c = [-439.35] + [-0.60]$

$= -439.95 \pm 0.25$ kcal.mole^{-1}

$\Delta H^o_f[C_3H_8O_2,l]_{1,2} = 3[-94.051]+4[-68.315]-[-439.95]$

$= -115.42 \pm 0.20$ kcal.mole^{-1}

$\Delta H_{vap.}$(est) $[13.6 + 1.2]^*$ = 14.8 kcal.mole^{-1}

* The latent heat of vaporization of most of the diols is unavailable. The mean contribution of $\Delta H_{vap.}$ per methylene $[-(CH_2)-]$ group was calculated from the $\Delta H_{vap.}$ of aliphatic alcohols.[144] It is 1.2 kcal./methylene group. This contribution was added to the $\Delta H_{vap.}$ of a known diol to get the approximate $\Delta H_{vap.}$ of a known diol to get the approximate $\Delta H_{vap.}$ of various aliphatic diols.

Thus $\Delta H^o_f[C_3H_8O_2,g] = -100.62$ kcal.mole^{-1}

(iii) ΔH^o_f of Butane 1,3-Diol $[C_4H_{10}O_2,l]$

$\Delta nRT = -0.90$ kcal.mole^{-1}

$\Delta H^o_f[C_4H_{10}O_2,l]_{1,3} = 4\ \Delta H^o_f[CO_2,g] + 5\Delta H^o_f[H_2O,l] - \Delta H^o_c.$

$\Delta U^o_c = -27.72 \pm 0.015\ K_jg^{-1}$

$= -[27.72 \times \frac{90.123}{4.184} = -597.62 \pm 0.33$ kcal.mole^{-1}

$\Delta H^o_c = [-597.62] + [0.90]$

$= -598.52 \pm 0.33$ kcal.mole^{-1}

$\Delta H_f^o[C_4H_{10}O_2,l]_{1,3} = 4[-94.051)+5(-68.315)-(-598.52)$

$= -119.26\pm0.33$ kcal.mole^{-1}

$\Delta H_{vap.}$(est) = 16.0 kcal.mole^{-1}

$\Delta H_f^o[C_4H_{10}O_2,g]_{1,3} = 103.26$ kcal.mole^{-1}

(iv) ΔH_f^o of Butane, 1,4 Diol $[C_4H_{10}O_2,l]_{1,4}$

$\Delta H_f^o[C_4H_{10}O_2,l]_{1,4} = 4\Delta H_f^o[CO_2,g]+5\Delta H_f^o[H_2O,l]-\Delta H_c^o$

$\Delta U_c^o = -27.744 \pm 0.016$ K_Jg^{-1} $\Delta nRT = -0.90$

$= -[27.744 \times \frac{90.123}{4.184} = -597.60$ kcal.mole^{-1}

$\Delta H_c^o = [-597.50] + [-0.90]$

$= -598.50 \pm 0.33$ kcal.mole^{-1}

$\Delta H_f^o[C_4H_{10}O_2,l]_{1,4} = -119.28$ kcal.mole^{-1}

$\Delta H_{vap.}^o$ (est) = 16.0 kcal.mole^{-1}

$\Delta H_f^o[C_4H_{10}O_2,g] = [-119.28 + 16.0] = -113.28$ kcal.mole^{-1}

(v) ΔH_f^o of Pentane, 1,5 Diol $[C_5H_{12}O_2,l]_{1,5}$

$\Delta H_f^o[C_5H_{12}O_2,l]_{1,5} = 5\Delta H_f^o[CO_2,\bar{\ }g] + 6\Delta H_f^o[H_2O,l] - \Delta H_c^o$

$\Delta U_c^o = -30.305 \pm 0.013$ K_Jg^{-1} $\Delta nRT = -1.19$ kcal.mole^{-1}

$$= -[30.305 \times \frac{104.1502}{4.184} = -754.36 \pm 0.35\ \mathrm{kcal.mole^{-1}}$$

$$\Delta H^o_c = [-754.36]+[-1.19]$$

$$= -75.55 \pm 0.35\ \mathrm{kcal.mole^{-1}}$$

$$\Delta H^o_f[C_5H_{12}O_2,l]_{1,5} = 5(-94.051)+6[68.315]-[-755.55]$$

$$= -124.5 \pm 0.35\ \mathrm{kcal.mole^{-1}}$$

$$\Delta H_{vap.}(est) = 17.2\ \mathrm{kcal.mole^{-1}}$$

$$\Delta H^o_f[C_5H_{12}O_2,g]_{1,5} = -107.3\ \mathrm{kcal.mole^{-1}}$$

(vi) ΔH^o_f of 2,2,Dimethylpropane 1,3 Diol $[C_5H_{12}O_2,c]_{1,3}$

$$\Delta H^o_f[C_5H_{12}O_2,cryst.]_{1,3} = 5\Delta H^o_f[CO_2,g]+6\Delta H^o_f[H_2O,l]-\Delta H^o_c.$$

$$\Delta nRT = -1.19\ \mathrm{kcal.mole^{-1}}$$

$$\Delta U^o_c = -30.047 \pm 0.016\ K_J g^{-1}$$

$$= -[30.047 \times \frac{104.1502}{4.184} = -747.94\ \mathrm{kcal.mole^{-1}}$$

$$\Delta H^o_c = [-747.94]+[-1.19]$$

$$= -749.13 \pm 0.40\ \mathrm{kcal.mole^{-1}}$$

$$\Delta H^o_f[C_5H_{12}O_2,cryst.]_{1,3} = -131.02 \pm 0.4\ \mathrm{kcal.mole^{-1}}$$

$$\Delta H\ sub\ (est) = [17.2 + 4.8]^{114}$$

$$= 22.0\ \mathrm{kcal.mole^{-1}}$$

here 4.8 kcal. is the heat of fusion, taken as equivalent to succinic anhydride[114] $[C_4H_4O_3$ mol. wt. 100, m.pt. 119°C $[(C_5H_{12}O_2,cryst.)_{1,3}$, m.pt. 127°C mol. wt. 104.15].

$\Delta H_f^o[C_5H_{12}O_2,g]_{1,3} = 109.02$ kcal.mole^{-1}

(vii) ΔH_f^o of Hexane 1,6-Diol $[C_6H_{14}O_2,l]$

$\Delta H_f^o[C_6H_{14}O_2,l]_{1,6} = 6\Delta H_f^o[CO_2,g]+7\Delta H_f^o[H_2O,l]-\Delta H_c^o$

$\Delta U_c^o = -32.107 \pm 0.015\ K_J g^{-1}$. $\Delta nRT = 1.49$ kcal.mole^{-1}

$$= -[32.107 \times \frac{118.177}{4.184}$$

$$= -906.86 \pm 0.45 \text{ kcal.mole}^{-1}$$

$\Delta H_c^o = [-906.86]_{1,6} + [-1.49]$

$$= -908.35 \pm 0.45 \text{ kcal.mole}^{-1}$$

$\Delta H_f^o[C_6H_{14}O_2,l] = 6(-94.051) + 7(-68.315)-(-908.35)$

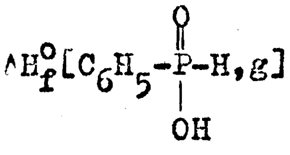
$$= -134.16 \pm 0.45 \text{ kcal.mole}^{-1}$$

$\Delta Hsub(est.) = [18.4 + 2.6]^{114} = 21.0$

2.6 is the latent heat of fusion of p.Cresol (Mol. wt. 108, m.pt. 36°C). $(CH_2)_6O_2H_2$ mol. wt. 116 m.pt. 42°C.

BOND ENERGIES CALCULATIONS

$E(C_{Ar}-P)$ was calculated from $\Delta H_f^o[C_6H_5PO_2H_2,g]$ and $\Delta H_f^o[C_6H_5O_3H_2g]$. Thus



$$\Delta H_f^o[C_6H_5-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-H,g] = \Delta H_f^o[C_6H_5,g]+\Delta H_f^o[P,g]+\Delta H_f^o[H,g]+\Delta H_f^o[OH,g]$$

$$+ \Delta H_f^o[O,g]-E(C_{Ar}-P)-E(P-H)-E(P-OH)-E(P{=}O.$$

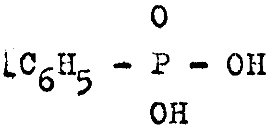
or $E(C_{Ar}-P) = \Delta H_f^o[C_6H_5,g]+\Delta H_f^o[P,g]+\Delta H_f^o[H,g]+\Delta H_f^o[OH,g]$

$+ \Delta H_f^o[O,g]-E[P-H]-E(P-OH)-E(P=O)-\Delta H_f^o[C_6H_5PO_2H_2h]$

$= [72]+[75.5]+[52.1]+[9.3]+[59.6]-[77]-[104]][128]-[-112.8]$

$= 268.5 - 309+112.8$

similarly, in



$[C_6H_5 - \overset{O}{P}(OH) - OH$

$E(C_{Ar}-p) = \Delta H_f^o[C_6H_5,g]+\Delta H_f^o[P,g]+\Delta H_f^o[O,g]+2\Delta H_f^o[OH,g]$

$-2E(P-OH)-E(P=O)-\Delta H_f^o[C_6H_5PO_3H_2,g]$

$= [72]+[75.5]+[59.6]+[18.6]-[208]-[128]-[-191.6]$

$= 225.7-328+191.6 = 89.3$ kcal.mole^{-1}

DISCUSSION

$E(C_{Ar}-P)$ in phenylphosphonic acid is about 17.0 kcal.mole^{-1} greater than in phenylphosphonous acid. This result indicates the thermal stability of phenylphosphonic acid and suggests some π-electronic contribution to E(Ar-P) in this compound. The $E(C_{Ar}-P)$ bond in triphenylphosphine (P_3P) is 71.0 kcal. mole^{-1}.[155]

The heats of formation of diols were experimentally determined in the liquid state and estimated for the gaseous state.

Two graphs are drawn, (i) ΔH_f^o of liquids against carbon atoms in the diols. (ii), ΔH_f^o of gaseous diols against carbon atoms comprising the molecule (Fig. 20). Propane 1,2 diol seems to be slightly more stable than its homologues in both the gaseous and liquid states. Enhanced stability of this compound cannot be explained in a simple way because of the uncertainties in the calculated heat of vaporization. In the liquid state this increase can be attributed to hydrogen-bonding (intermolecular and/or intramolecular) present in the compounds; the exact nature of this phenomenon is quite uncertain.

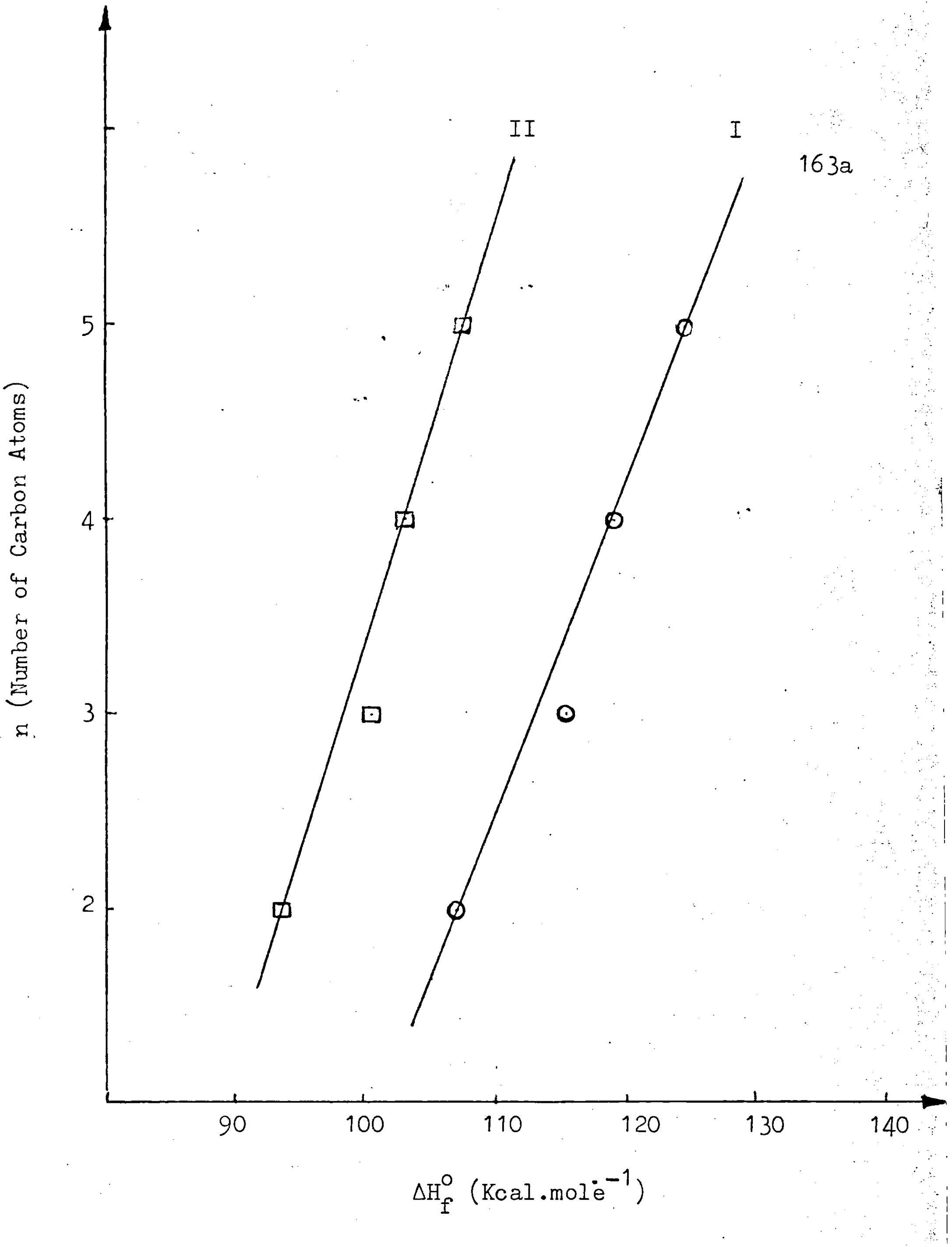


FIG. 20 PLOT OF NUMBER OF CARBON ATOMS (n) COMPRISING THE LIQUID DIOLS (I) AND THE GASEOUS DIOLS (II) AGAINST THEIR HEATS OF FORMATION (ΔH_f^o)

SOLUTION REACTION CALORIMETRY

Section 4

Reaction calorimetry has been classified as the technique for measuring heats of chemical reactions other than combustion. A number of important techniques have been developed in this area and are fully described by Skinner.[189]

Solution reaction calorimetry is also quite developed and has been frequently used for determining important thermodynamic data by exploiting simple chemical reactions. Thus most of the thermodynamic data on organometallic compounds were unavailable, and bomb calorimetry could not be applied to these compounds due to complexities in the nature of the combustion products. However, Skinner et al. developed reaction calorimetry and obtained valuable thermodynamic results on various organo-metallic compounds.[75]

Similar problems faced boron-oxygen compounds. Combustion calorimetry could not be applied, because combustion results in various products, (oxides and carbides, etc.) whose nature and standard states are uncertain. A simple and general reaction for many organoboron compounds is that of "oxidative hydrolysis".[83] This reaction has been exploited earlier in solution reaction calorimetry by Finch et al.,[83] who determined the heat of formation of various organo-boron compounds. In this investigation the same reaction was utilized to determine the heats of formation of various boroxines, dihydroxyboranes and dihaloboranes. The other reaction which is discussed in this section is the oxidation of phosphorous acid to phosphoric acid by excess aqueous bromine.

Principle

Generally, chemical reactions are accompanied by changes in heat-contents, which appear as the evolution or absorption of heat during the reaction. If such temperature changes are measured by any temperature-sensitive device, and the course of reaction and the enthalpies of formation of the known products are available, then the reaction can be utilized to determine the enthalpy of formation of the required reactant. However, certain conditions are adjusted to make the reaction a useful source of information. When a reaction is brought about in solution, dilution effects are prominent, and adequate adjustment is required. The temperature of the reaction medium is maintained at 25°C and the pressure should also be normal (1 Atm.); thus the reaction conforms to standard thermodynamic conventions (see Introduction, part 1).

The effect of surroundings on the temperature measurements is also significant and this effect is particularly considered in designing a solution reaction calorimeter. There are two important types of calorimeters (a) the adiabatic calorimeter (b) the constant-environment-calorimeter (C.T.E.) calorimeter.

In an adiabatic calorimeter the temperature of the surroundings is maintained equal to the temperature of the contents of the calorimeter. If the temperature of the contents changes during a chemical reaction, the temperature of the surroundings is automatically, by electronic devices, maintained at the new temperature. There is negligible loss of heat to the environment in this type of equipment and an accurate heat of reaction can be obtained. This type of apparatus is particularly useful for slow reactions.

In the C.T.E. reaction calorimeter, the temperature of the environment is maintained constant ($25.0 \pm 0.1^{\circ}C$) and there is always transfer of heat from the reaction vessel to the surroundings in an exothermic reaction. In this type of apparatus, therefore, heat loss during the reaction is computed and incorporated into the calculation. This type of calorimeter is simple to design and operate and is quite precise for fast reactions.

Since we used a C.T.E. reaction calorimeter, its construction is briefly described here.

Apparatus

It consisted of a flanged double walled, glass Dewar vessel approximately 2" internal diameter and a flanged lid, provided with several standard ground glass sockets [Fig. 15]. Through these sockets were mounted a stirrer, an ampoule holder,

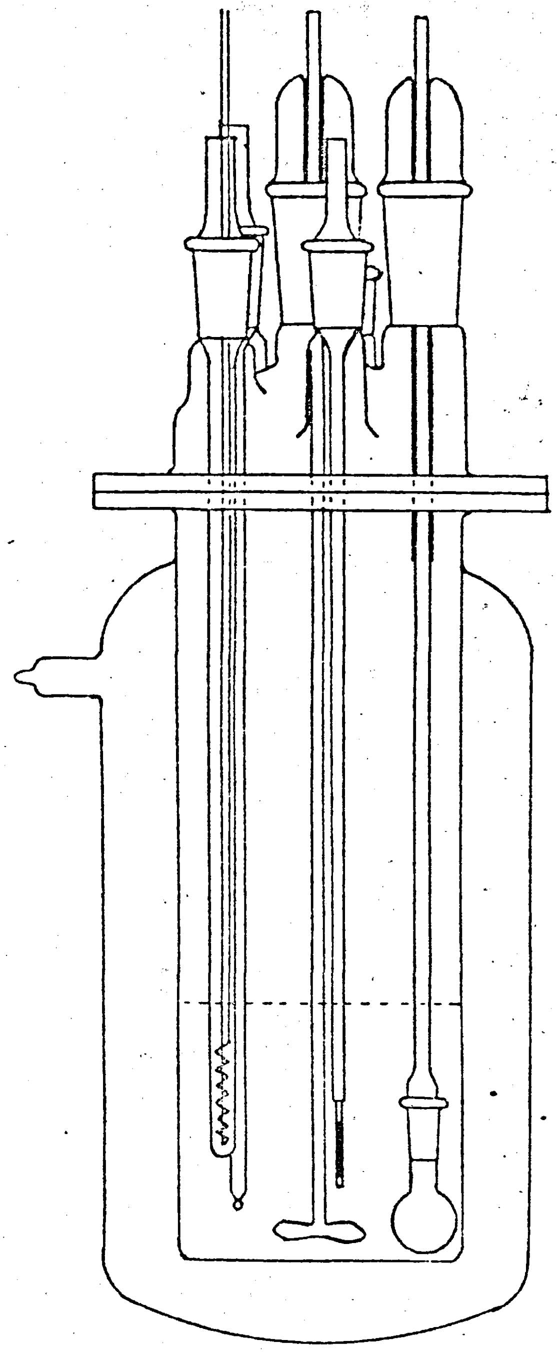


FIG. 15 Solution Reaction Calorimeter

a thermistor (temperature-sensitive device), a heater and a cooling tube. The stirrer and the ampoule-holder were made from a special precision diameter glass rod and were mounted in the calorimeter by the help of standard cones provided with precision bore glass tubing. The ampoule holder was provided with standard cone at the end, to fit in the standard socket of the glass ampoule which contained the substance. The ampoule, when placed in the solution in the calorimeter could be broken easily by striking it gently against the rotating stirrer.

The heater was constructed from "constantin" wire (47 gauge, 50 ohms/30 cm.) wound spirally on a glass former and soldered to the leads, made of copper wire (0.7 mm. diameter). Thermal conduction was improved by submerging the coil in transformer oil, the whole being encased in a thin glass sheath.

Temperature changes were measured with the thermistor [F-53, standard Telephone and Cables Ltd., 4400 Ω at ca. 25°C and thermal coefficient of 150 Ω /°C].

The Dewar vessel was completely immersed in a water-thermostat maintained at 25.00 ± 0.01°C.

Temperature measurements.

The thermistor was the usual temperature-measuring device in our solution reaction calorimetry.

The resistance (in ohms) of a thermistor is approximately related to the temperature (T^oK) by the expression,

$$R = A \exp.\left[\frac{B}{T}\right]$$

where A and B are the thermistor constants ($B > 0$). Knowledge of these constants can give the temperature directly from the equation. The constants were evaluated by calibrating the thermistor over the range 22-28°C, against a Beckman thermometer, which had been pre-calibrated against a standard N.P.L. Thermometer.

The thermistor formed one arm of a Wheatstone network, with fixed ratio arms of $4.3K\Omega$ and a variable arm measuring from 0 to $10^4\Omega$ (decade resistance box). The out-of-balance bridge current was detected on a galvanometer (Scalamp, 110Ω, 7902/s W.G. Pye and Co. Ltd.). The calorimeter was calibrated electrically. The electrical circuit for calibration is shown in Fig. 23. The current was supplied from a constant-voltage source (6 volts, Langham Thompson Ltd. with a stability of 1 part in 2000). All the potential changes were measured with a Tinsley potentiometer (type 3387B) used in conjunction with the Scalamp galvanometer (1400Ω, 7904/T, W.G. Pye

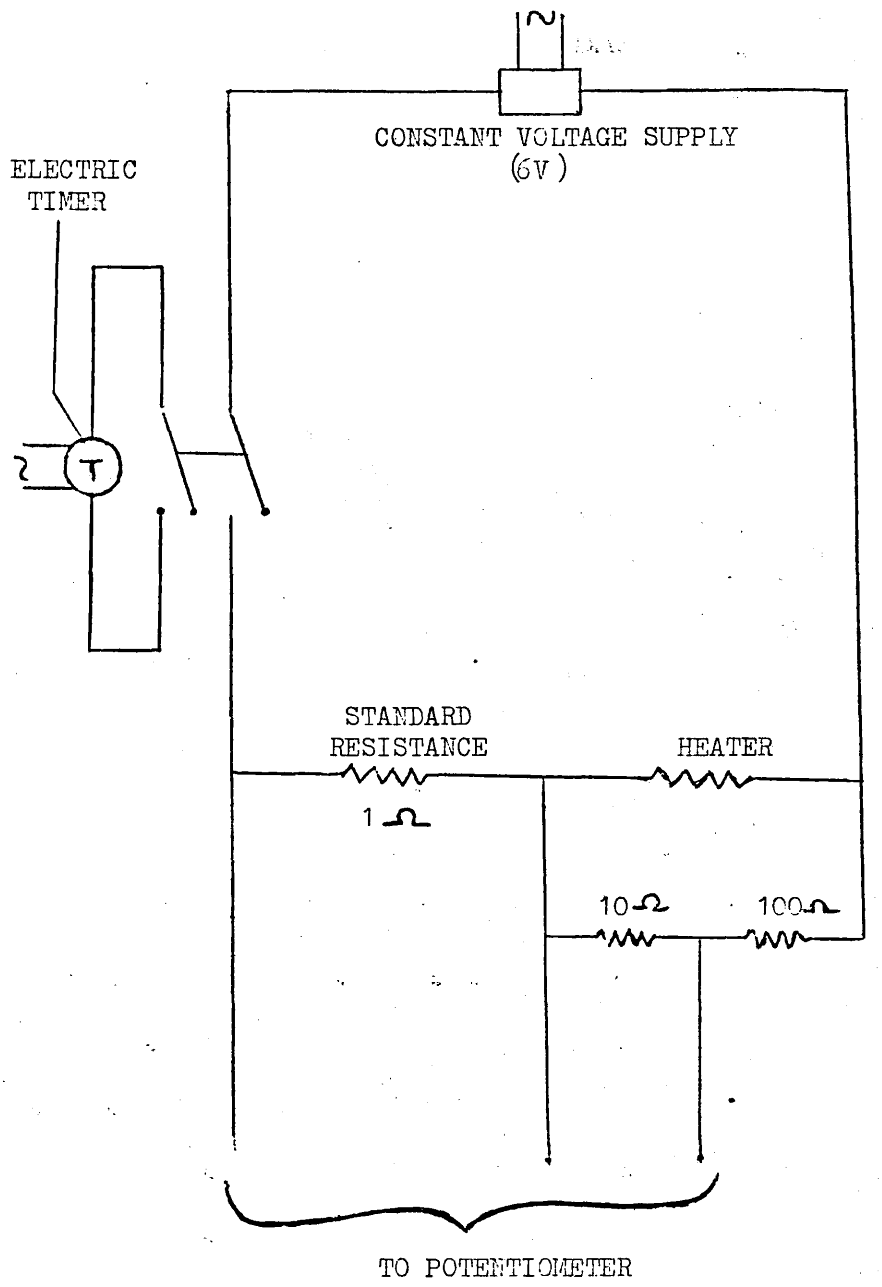


FIG. 23 HEATING CIRCUIT FOR CALORIMETER

and Co. Ltd.). Readings were accurate to ± 0.00005 volts. The potentiometer-standard cell was a Weston Standard cell (Cambridge Instrument Co. Ltd.). Calibration times were measured with an electric timer, (FO 43.4A, Hengstler & Co. G.B. Ltd.) which was accurate to ± .01 sec. Resistors for the potential divider circuit were supplied by Croydon Precision Resistors (tolerance to 0.25%). The circuit standard resistance (guaranteed 0.9996 Ω) was obtained from Cambridge Instrument Co. Ltd. All resistances had a temperature coefficient better than 20 ppm per degree centigrade.

Consider the case of a fast exothermic reaction. (Fig. 19). During the run two temperature changes were recorded. The reaction change is ΔT_R and the calibration temperature change is ΔT_c.

Since we are using a thermistor for temperature measurements then

$$\frac{\Delta TR}{\Delta T_c} = \frac{\log \frac{R_1}{R_2} . \log \frac{R_4}{A} . \log \frac{R_3}{A}}{\log \frac{R_3}{R_4} . \log \frac{R_2}{A} . \log \frac{R_2}{A}}$$

If, $T_1 \sim T_3$ and $T_2 \sim T_4$, then

$$\frac{\Delta TR}{\Delta T_c} = \frac{\log R_1 - \log R_2}{\log R_3 - \log R_4}$$

If Q is the heat change (in cal.), when a weight (w) of a compound reacts, then,

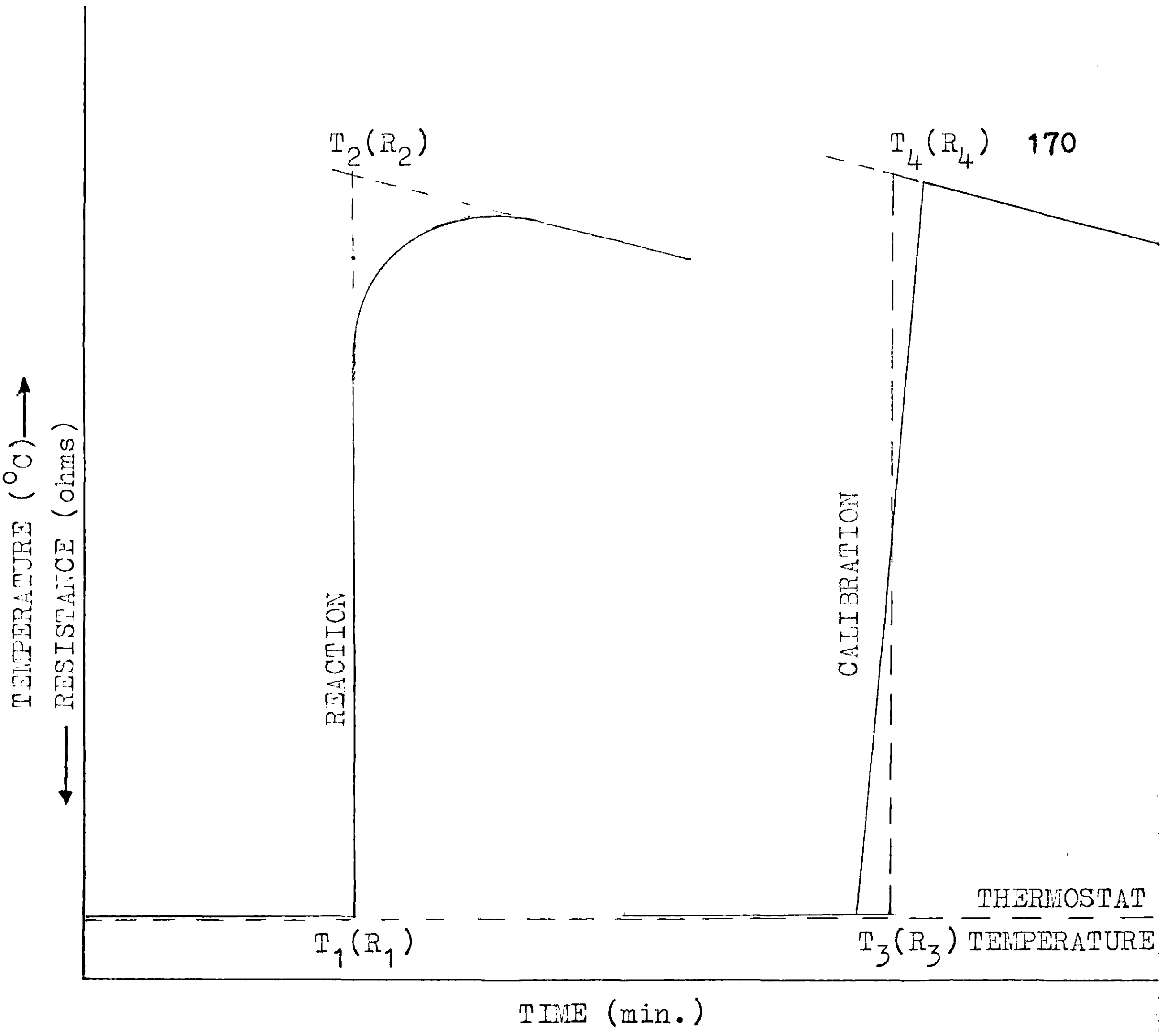


FIG. 19. AN ILLUSTRATIVE GRAPH OF A FAST EXOTHERMIC REACTION

$$\Delta T_R = T_2 - T_1 \text{ and } \Delta T_c = T_4 - T_3 \text{ and}$$

$$Q = \frac{\text{electrical energy}}{J\ w} \times \frac{\Delta TR}{\Delta T_c} \text{ cal. } g^{-1}$$

During the experiment two potential readings were recorded,

(i) V_s, across the standard resistance R_2 (ca. 1 ohm) and

(ii) V_1 across the resistance R_1 (10 ohms).

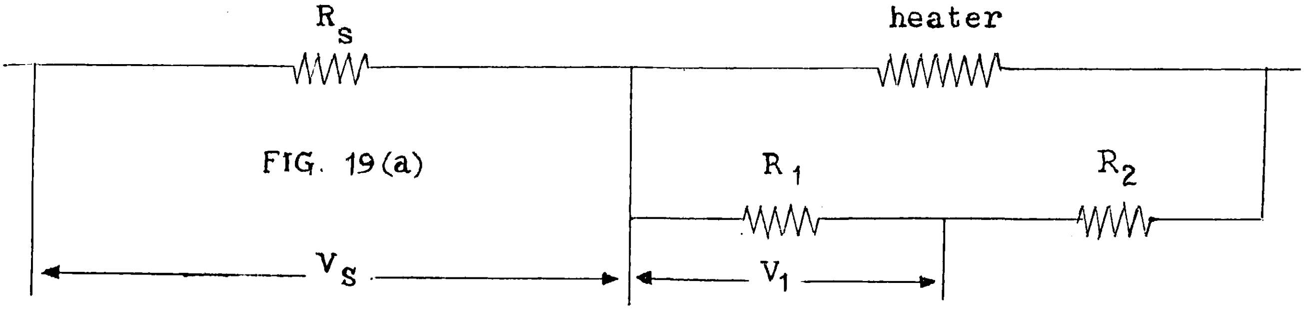


FIG. 19(a)

The power output (P) across the heater may be shown to be, (Fig. 19a)

$$P = V_1 \left[\frac{R_1+R_2}{R_1}\right] \left[\frac{V_s}{R_2} - \frac{V_1}{R_1}\right] \text{ watts.}$$

since $R_1 = 10\,\Omega$, $R_s = 1\,\Omega$ and $R_2 = 100\,\Omega$

we have $P = 11\ V_1 \left[V_s - \frac{V_1}{10}\right]$ watts.

and if t is the calibration time in seconds, then

P x t = total calibration energy supplied, and therefore, the complete equation for measuring the enthalpy change (ΔH_r) of the reaction becomes

$$\Delta H_r = \frac{f\ Pt\ M \log (R_1/R_2)}{J\ w \log (R_3/R_4)} \text{ cal. mole}^{-1}$$

where

ΔH_r = enthalpy change of the reaction.

P = power supplied, $11V_1[V_s - \frac{V_1}{10}]$ watts.

f = factor correcting the heater leads resistance

$$= \frac{R\ (\text{heater})}{R\ (\text{heater}) + R(\text{leads})}$$

M = Molecular weight of the reacting substance.

w = weight of reacting substance (g.).

t = time of heating (sec.)

J = 4.1840 Abs. Joules $cal.^{-1}$ (defined).

Thermal leakage correction. The temperature changes in our calorimetric determinations were obtained by plotting a change in resistance of the thermistor against time in seconds. However, in Fig. 16 temperature is plotted vs. time for clarity. The graph is for an exothermic reaction.

The method used for correction depends upon the type of reaction, i.e. slow or fast. A fast reaction is complete within a few minutes and since the majority of the reactions studied here were fast, the method outlined by Sturtevent[190] was used (the method was due to W.P. White,[191] i.e. the first Geophysical Laboratory method).

The curve ABCD represents a typical reaction taking place in the calorimeter. T_1 and T_2 are the temperatures corresponding to time t_1 and t_2. The observed rise in temperature of the calorimeter is the difference in temperature at the beginning T_1 and at the end T_2 of the reaction period. Let C be the correction term for the temperature difference ΔT of the calorimetric reaction.

$$\text{i.e. } \Delta T = T_2 - T_1 + C.$$

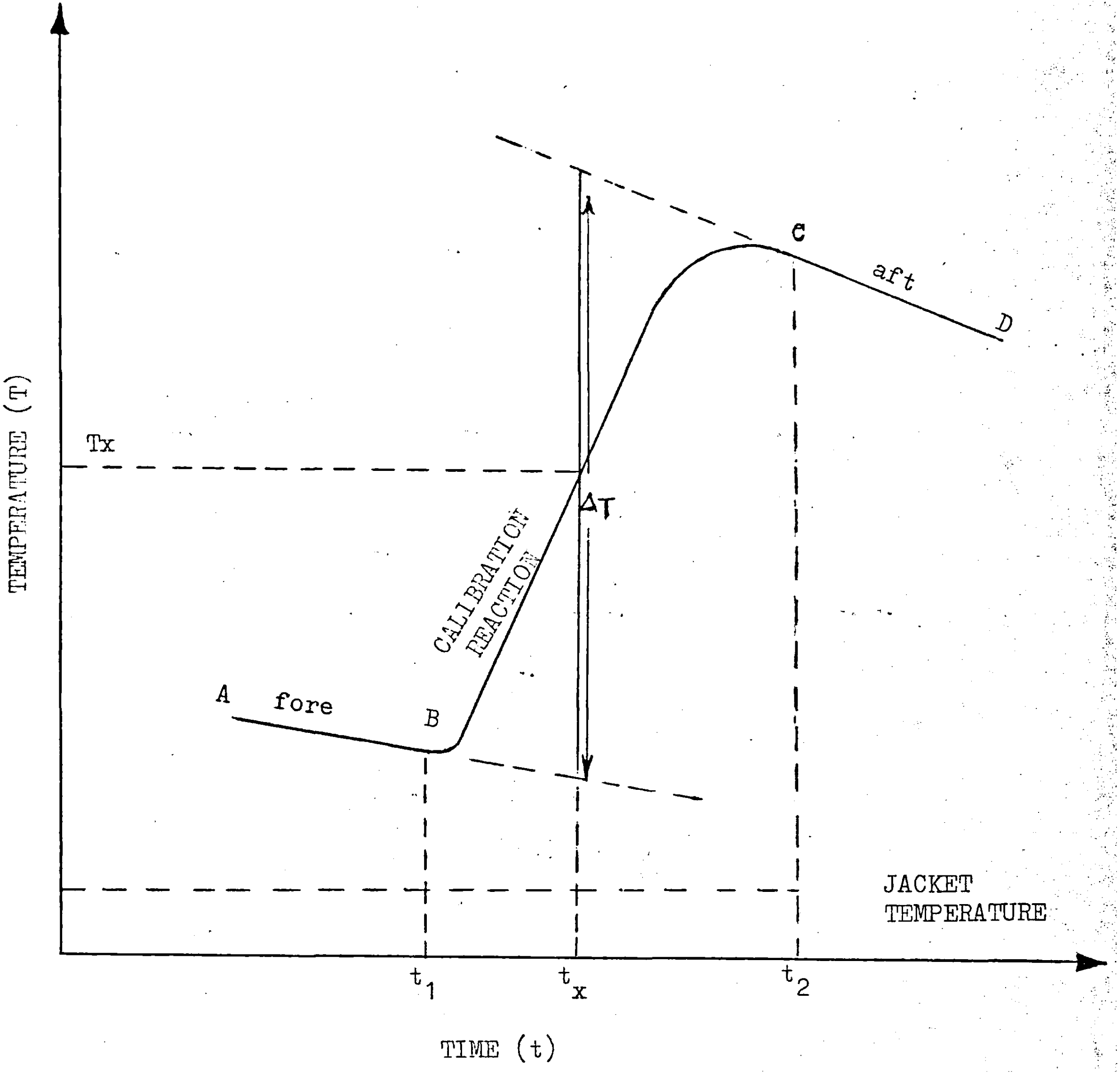


FIG. 16 THERMAL LEAKAGE CORRECTION

Assuming that the heat exchange is Newtonian, then the rate of temperature change during the reaction period due to heat exchange with the surroundings is given by

$$\frac{dT}{dt} = \alpha\ (T_k - T)$$

where T_k = Thermostat temperature.

α = cooling constant of the calorimeter.

Hence the heat correction factor C is given as,

$$C = \int_{t_1}^{t_2} \alpha\ (T_k - T)dT$$

The above integral was evaluated using Dickinson's method.

A line is drawn parallel to the temperature axis through a point t_x, such that the shaded areas A_1 and A_2 between the curve and the line AB and CD (suitably back extrapolated) are equal. Then

$$C = \int_{t_1}^{t_2} \alpha\ (T_k - T)dT$$

$$= -\alpha(T_1-T_k)(t_x-t_1)-\alpha(T_2-T_k)(t_2-t_x)$$

The position of t_x may then be determined by "counting squares" or numerical integration.

For reactions that are complete within ca. 60 sec., the corrected temperature change was obtained by back-extrapolation of the fore and aft-periods to $t = t_x$ where the position of t_x is gauged by eye.

Macleod[193] has recently compared several methods of temperature correction and has noted that Dickinson's method is satisfactory when the required precision is not greater than 0.2%.

The accuracy of the calorimeter

The principle source of error in evaluating ΔH occurs in the measurement of temperature (i.e. in back extrapolation procedure) rather than in measurement of electrical energy.

$$Q = \text{electrical energy} \times \frac{\Delta T_R}{\Delta T_c}$$

If in a calorimetric experiment $\Delta T_R = \Delta T_c$, then the errors can be reduced to minimum.

The accuracy of the calorimeter was checked using a standard chemical reaction. The neutralization of THAM [Tris(hydroxymethyl)aminomethane] in excess 0.1M hydrochloric acid is suitable for exothermic calibration. The enthalpy value of this reaction has been recently established as[194] -7.109 kcal.mole^{-1} [at 298.15°K and N =1200].

$$[(CH_2OH)_3C\ NH_2,\text{cryst.}]+[HCl,\text{aq.soln.}] \longrightarrow$$
$$[(CH_2OH)-C-\overset{+}{N}H_3\overset{-}{Cl},\text{aq.}]$$

Our experimental results are collected in Table 32.

TABLE 32

N^*	$\Delta H_{obs.}$ (298.15°K) kcal.mole^{-1}
609	7.115
863	7.114
851	7.187
866	7.129
909	7.086
724	7.070
710	7.160
817	7.070
794	7.120 ±0.02

* N is the mole ratio of H_2O to THAM

The procedure and the method of calculation have been fully described in a recent thesis.[175]

SECTION 5

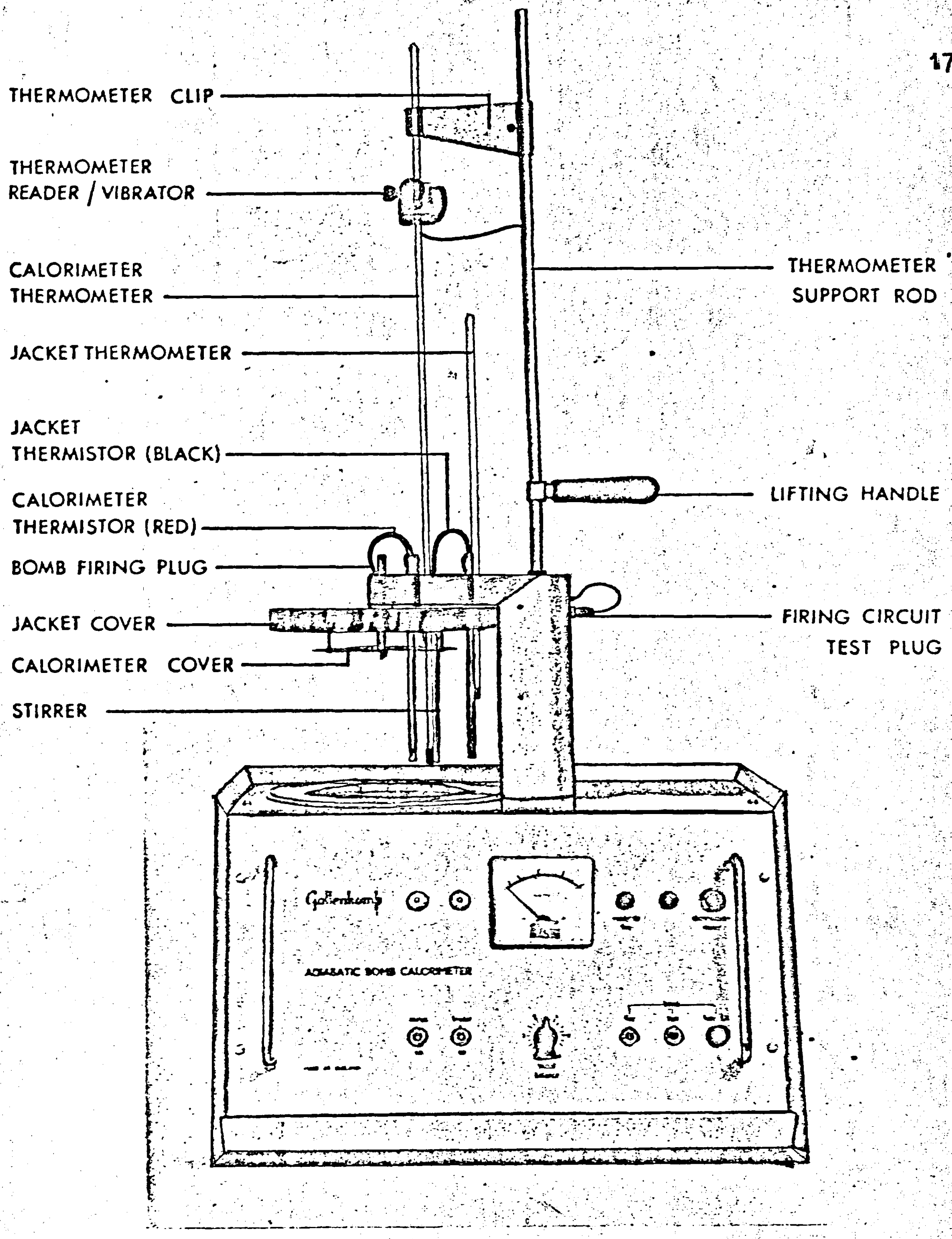
BOMB CALORIMETRY

The reaction which has been most widely studied in combustion calorimeters is oxidation and this is because many organic compounds can be burnt in an atmosphere of oxygen with comparative ease. The apparatus for combustion of solids and liquid compounds in oxygen under pressure was first introduced by Berthelot in 1869 and since then various improvements have been made with the purpose of achieving greater accuracy. These techniques and experimental details have been discussed by Rossini[195] and Skinner.[189]

However, the combustion of organometallic compounds presents great problems. The development of the rotating bomb calorimeter[196] and the technique of fluorine bomb calorimetry[197] have proved quite successful in solving many of these problems. However a conventional static-bomb calorimeter has been often used to give the results of quite satisfactory precision with comparative ease. The limitations of the static bomb calorimeter have been fully discussed by Good and Scott.[189] A brief description of the calorimeter follows:

Apparatus

The apparatus used in our combustion experiments was a static adiabatic bomb calorimeter, model CB-110 manufactured by Gallenkamp & Co., London (fig. 17).



GENERAL ASSEMBLY FIG. 17

It consisted of a bomb made of corrosion-resistant steel, of about 0.3L internal volume and a lid, which can be fixed tightly with the help of a locking ring to withstand great pressures (fig. 18). A gas-tight seal to 30 atmospheres internal pressure was ensured by the use of a rubber O-ring between the mating surfaces. The bomb was immersed in a stainless steel can (the calorimeter can), which was full of water. Both were placed in the adiabatic jacket of the apparatus. The cover of the jacket was provided with various holes to accommodate two thermistors, two mercury thermometers and a stirrer. The thermistors were precisely of equal resistance and were connected to an electrical circuit which amplified a small resistance difference between them to maintain an accurate uniform temperature of the outer jacket with the calorimeter can. The calorimeter thermometer was a special thermometer reading to 0.001°C and was provided with a reader-cum-vibrator, which eliminates hysteresis of the meniscus.

Procedure

The apparatus was first calibrated by the combustion of a standard substance (benzoic acid) and the effective heat capacity of the system was determined.

The apparatus was kept on for about half an hour with the outer jacket full of water. The cooling water circulation was started and electric connections checked. About 6 cm. of a

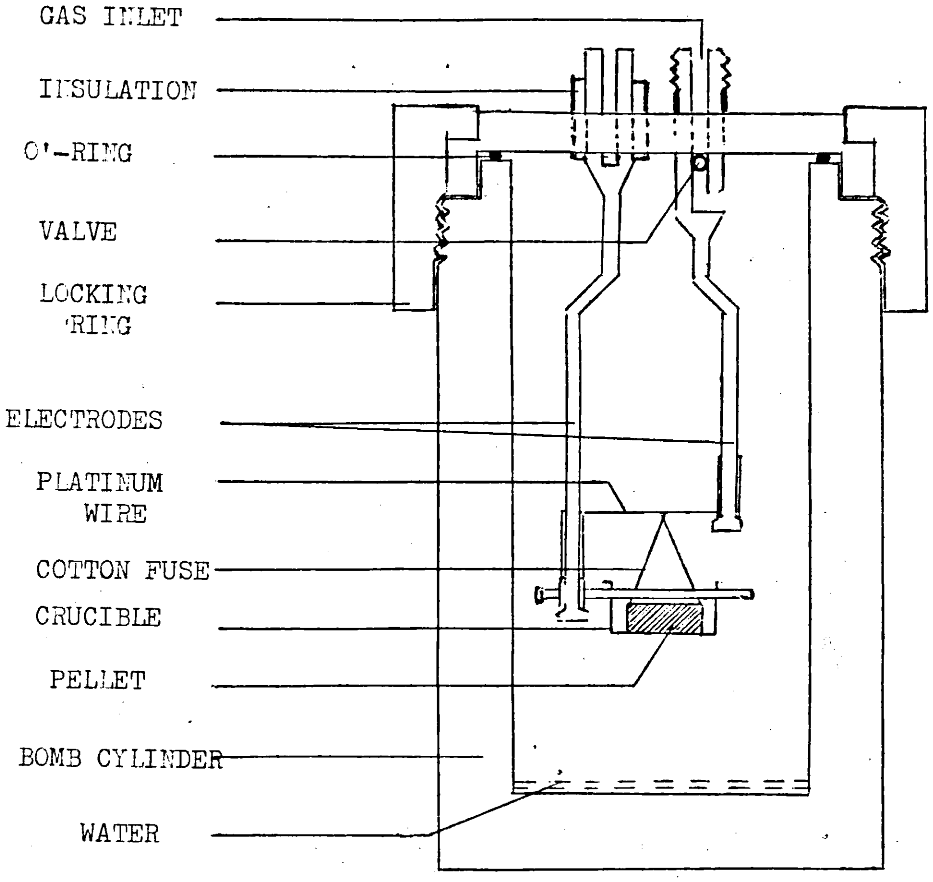


FIG. 18 COMBUSTION BOMB (LOADED)

cotton fuse and 9 cm. of the platinum wire (0.005 cm. gauge) and the crucible were weighed independently. A silica crucible was used for the combustion of organic compounds containing C, H and O only, while for the combustion of phosphorus compounds a platinum crucible was used. An appropriate amount of the benzoic acid, giving the desired temperature change (2^o - 3^oC) was made into a pellet together with the cotton fuse and weighed accurately in the above-mentioned crucible. The lid of the bomb was placed on the stand, the crucible was clamped in the ring and the platinum wire tied to the electrodes with the cotton fuse tied to the platinum wire. The requisite amount of distilled water (0.9 ml. for C, H & O compounds and 3.0 ml. for the phosphorus compounds) was placed in the bomb. The lid was placed over the bomb and the locking ring was screwed down tightly. The firing circuit of the bomb was checked, oxygen was passed in to 30 atmospheres and the firing circuit rechecked. The leakage of the bomb was checked by immersion in the diethyl ether. The lifting knob was screwed down and the complete bomb was weighed accurately. The calorimetric can was cleaned, filled with distilled water until the can plus water weighed 3Kg. The bomb was then placed in the calorimeter can and the temperature of the system was brought to 25.0 ± 0.1^oC by immersion in hot or cold water. The calorimeter can was then placed in the jacket of the apparatus and the lid was set down. The apparatus was left to equilibriate for about fifteen minutes. Then the reading of the thermometer was noted at every half minute. When the temperature was approximately constant for about ten minutes, the bomb was fired and the temperature readings continued. The temperature rose at once and then became steady after 10-20 min. Readings were continued for another fifteen minutes. The electrical circuit was then disconnected. The bomb was taken out and the valve was opened very gently to release the pressure. The crucible was transferred to a desiccator. The lid and the bomb were washed with distilled water and the washings collected in a conical flask and analysed.

The procedure for the combustion of the aliphatic diols and the phosphorus compounds was the same as described above, except for the following aspects:

(i) Diols, mostly liquids, were combusted in polyethylene bags, which were rectangular (15 mm x 30 mm) and were made from 0.05 mm thick polyethylene ("Layflat" tubing, British Visqueen Ltd.). The energy of combustion (ΔU_c^o) of this polyethylene was known $46427 \pm 9 \mathrm{jg}^{-1}$ [139]. The cotton fuse was tied round the twice-folded bag. The bags with their contents were combusted in fused silica crucible.

(ii) The phosphorus compounds were made into a pellet, together with the cotton fuse, and were combusted with the help of another pellet of benzoic acid, provided with another cotton fuse. In the actual combustion experiments the benzoic acid pellet was placed below the pellet of phosphorus compound (see Fig. 22) and they were tied together with a cotton fuse(Fig. 22). This arrangements helped to achieve complete combustion of the phosphorus compounds.

(iii) After combustion of phosphorus compounds, the contents of the platinum crucible were immediately transferred, by washing, into a conical flask. A delay in this procedure will decrease the phosphorus content of the bomb washings and increase the platinum loss, due to the attack of the strong acid solution on the platinum crucible. A brown or yellow colour was noted on the platinum crucible in these cases.

Analytical Procedure for the combustion products

Aliphatic Diols: Generally these compounds were completely combusted in presence of excess oxygen and if there was any carbon (soot) left, it was negligible (< 0.0003 g). Therefore, amount of CO_2 was supposed to be quantitative. The presence of uncombusted material was checked by extracting the products with ether and it was always nil. The presence of nitrogen-imputity in the bomb-atmosphere produced nitric acid, which was estimated by titration of the bomb washings against 0.1M sodium hydroxide using a methyl orange indicator.

Phosphorus compounds. The analytical procedure adopted for the post-combustion analysis of these compounds was that of Bedford and Mortimer.[198] The scheme is represented in the diagram (Fig. 21) and the details are as follows:

The phosphorus compounds were nearly completely combusted with the help of the auxillary substance, benzoic acid. The $CO_2(g)$ was not quantitatively determined and it was supposed, on the basis of other analyses, to be quantitatively produced. There was no sign of the unburnt compounds as shown by an extraction procedure with ether. The amount of orthophosphoric acid was quantitative and the lower-phosphorus acid and polyphosphorus acids were absent. The amount of soot was variable and was always low (< 0.002 g). The loss in platinum did not exceed 0.0010g, and was therefore thermally negligible. The nature of the process in loss of platinum were not identified.

The presence of HNO_3 was assumed to be negligible. This was checked in the benzoic acid experiments by twice flushing the bomb with oxygen. The titration with 0.1M NaOH indicated less than 0.001 mole HNO_3 each time.

Special procedures and precautions

1. The solid substances were first ground to a fine powder by a magnetic vibrator-powdering machine and then pelleted.

ANALYSIS
of
Combustion products of Organophosphorus Compounds

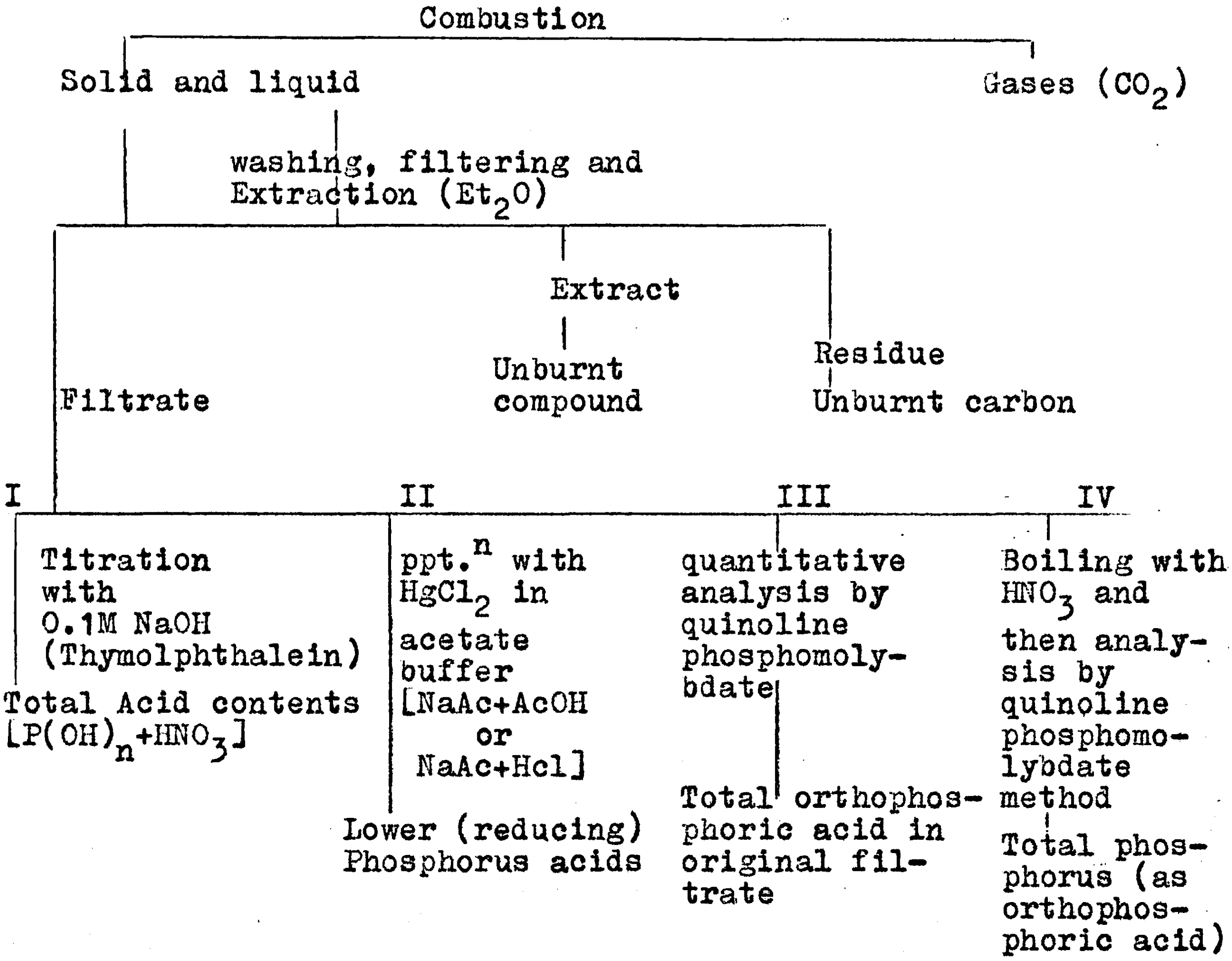


FIG. 21

2. The liquid diols were hygroscopic and were filled in leakproof polyethylene bags in a dry inert atmosphere of nitrogen before combustion.

3. The combustion of ethylene diol was performed both with polyethylene encapsulation and without it. The results were the same.

4. The phosphorus compounds were combusted with benzoic acid as auxillary substance. Two methods were used:

(a) Accurate weights of benzoic acid and the phosphorus compounds were powdered to homogeneous mass and then pelleted and the amount of the components were accordingly calculated.

(b) Two separate pellets were made from powdered benzoic acid and the powdered phosphorus compound and burnt by placing one over the other. The combustion with the pellet of phosphorus compound at the top gave quite good results. Fig. 22 illustrates arrangement.

5. Corrosion of the bomb was checked, frequently, by observation with the eye or by weighing the empty dried bomb.

6. Combustion of the phosphorus compounds was carried out in a platinum crucible, which was cleaned between determinations by boiling with conc. HNO_3 solution, conc. sodium hydroxide solution and followed by several washings with boiled distilled water.

7. The bomb was checked for leakage regularly and the gaskets were changed when necessary.

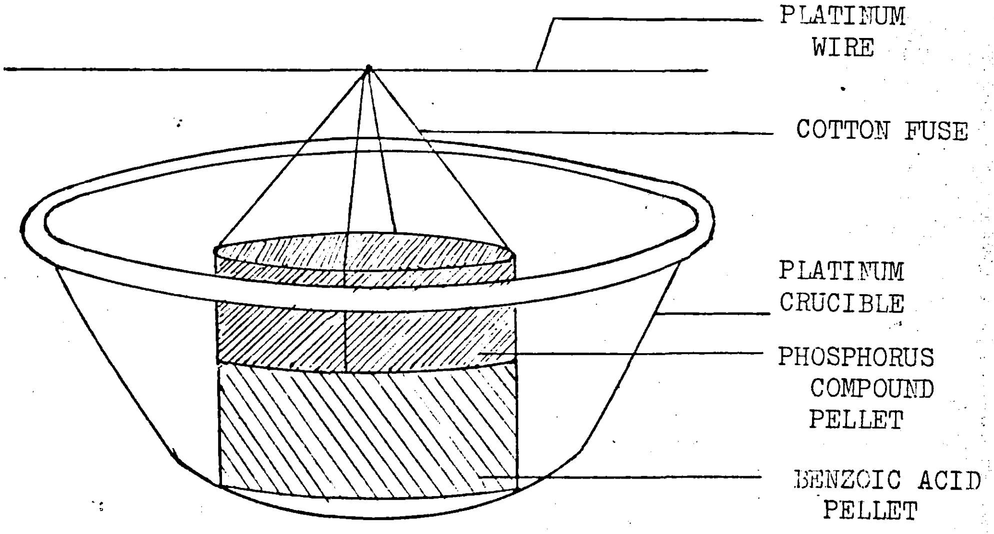


FIG. 22 ARRANGEMENT OF PELLETS IN PLATINUM CRUCIBLE

8. After every combustion the bomb and the lid were washed with methanol and water and cleaned thoroughly.

9. The pelleting apparatus was cleaned regularly with methanol.

10. The effective heat capacity of the apparatus was checked frequently with standard benzoic acid.

11. The benzoic acid used was always a pure, dry and standard sample obtained from B.D.H. or B.C.S., with a calibration traceable to N.P.L.

12. The weighings were carried out with standardized weights (N.P.L.) with an accuracy to ± 0.00005g.

Calculations

The calorimetric thermometer was calibrated against a standard (N.P.L.) thermometer, (Dr. P.J. Gardner) and the graph obtained was used to correct the experimental temperatures.

In an actual experiment the temperature (°C) was plotted against time (min.) and the exact temperature difference was obtained by back extrapolation.. The effective heat capacity of the system was calculated from the following equations, according to the method of Waddington.[195]

$$E_{fs} = E_f - E_{cf}$$

$$= \frac{[-\Delta U_c^o]m_s + q_i + q_w + q_n - q_c}{\Delta T} - E_{cf}.\ \text{Kjg}^{-1}\ \text{deg.}^{-1}$$

$$\text{and } E_{cf} = 10^{-3}\ [21.0 n_{O_2} + 4.18\ m_w + 2.28\ m_s + 0.136\ m_{Pt.}$$

$$+ 4.18\ m_w' - (\text{sp Cr})m_{Cr}]\ \text{Kjg}^{-1}\ \text{deg.}^{-1}$$

where

E_{fs} = energy of the standard final system.

E_f = energy of the actual combustion.

E_{cf} = energy deviations from standard calorimetric system in standard state conditions.

$-\Delta U_c^o$ = energy of combustion of benzoic acid.

m_s = mass of the (substance) benzoic acid.

q_i = energy of ignition.
[0.0042 (electrical) + 17.49 x mass of cotton].

q_w = standard state corrections (Washburn).

q_n = energy of formation of HNO_3.

q_c = energy due to unburnt carbon.

n = moles of oxygen in the bomb.

m_w = mass of water added to the bomb (1-3 ml.).

$m_{Pt.}$ = mass of platinum wire used.

m'_w = mass of excess water in calorimetric can.

m_{Cr} = mass of crucible.

(sp Cr) = specific heat of the crucible.

Washburn corrections (q_w) The method of calculating the Washburn correction is given in detail by Waddington.[195] Here we considered the following corrections only:-

(i) change in energy of r_1, moles of O_2 from zero pressure to P_1 Atm. (filling pressure).

(ii) change in energy of r_2 moles of O_2 and q_2 moles of CO_2 (gaseous products) from P_2 Atm. (post-reaction pressure).

(iii) energy of condensation of (m_2-m_1) moles of H_2O.

(iv) energy of vaporization of q_2 moles of CO_2 from m'_2 moles of H_2O.

The following points were ignored:

(a) The energy of solution of O_2 and water vapour in the samples.

(b) The energy of vaporization of the sample.

(c) Energy of solution of O_2(and N_2) in water in the initial and final systems.

(d) Compression energy of the substance; $\left(\frac{\partial U}{\partial P}\right)_T = 0$.

(e) Vapour pressure of H_2O unaffected by HNO_3 vapours and the effect of dilution of HNO_3.

The actual equation of combustion of a carbon, hydrogen and oxygen containing compound is,

$$n_1\ C_aH_bO_c + r_1O_2(g) + m_1H_2O(g) + m'_1H_2O(l) = (r_2O_2+q_2CO_2)(g) + m_2H_2O(g) + [q'_2CO_2 + m'_2\ H_2O](soln.).$$

and so if

$-\Delta U_B(298)$ = the bomb process for benzoic acid combustion.

and $-\Delta U^o_B(298)$ = the reduced bomb process for the same combustion

then $\Delta U^o_B - \Delta U_B = q^B_w$ (Washburn correction for benzoic acid).

The calculation of the above Washburn corrections has been given in simplified form by Prosen.[195]

In a similar way the heats of combustion of the diols and phosphorus compounds were calculated.

The Washburn corrections for various diols were calculated by a computer programme for different amounts of substance. The results were as follows:

TABLE 33

Compound	wt. of substance (g)	q_w(J)	Compound	wt. of substance	q_2(J)
Ethane Diol.	0.6	4.85	Butane 1,3-Diol.	0.5	4.56
	0.7	5.85		0.6	5.71
	0.8	6.88		0.7	6.95
	0.9	7.95		0.8	8.21
	1.0	9.06	Butane 1,4-Diol.	0.5	4.55
	1.1	10.21		0.6	5.72
	1.2	11.5		0.7	6.93
				0.8	8.21

/contd.

TABLE 33 (continued)

Compound	wt. of substance (g)	q_w(J)
Propane 1,2 Diol.	0.5	4.26
	0.6	5.34
	0.7	6.46
	0.8	7.65
Butane 1,4 Diol.	0.5	4.55
	0.6	5.72
	0.7	6.93
	0.8	8.21
Pentane 1,5 Diol.	0.3	2.48
	0.4	3.59
	0.5	4.76
	0.6	5.99
	0.7	7.30
	0.8	8.64
	0.9	10.07
	1.0	11.56
	1.1	13.11
Polyethylene	0.1	1.09
	0.15	1.66
	0.175	1.99
	0.20	2.31
	0.25	2.54
	0.30	3.66
2,2-Dimethyl propane 1,3 Diol.	0.3	2.48
	0.4	3.59
	0.5	4.75
	0.6	5.99
	0.7	7.29
	0.8	8.66
	0.9	10.10
Hexane 1,6 Diol.	0.3	2.57
	0.4	3.71
	0.5	4.92
	0.6	6.21
	0.7	7.56

The relevant Washburn correction was interpolated from the data.

Washburn corrections for phosphorus compounds

These were estimated according to the following equation

$$C_aH_bO_cP_d + r_1O_2(g) + m_1H_2O(g) + m'_1H_2O(b) =$$

$$[r_2O_2 + q_2CO_2](g) + m_2H_2O(g) + [q'_2CO_2 + dH_3PO_4 + m'_2H_2O]\ (liq)$$

The corrections were estimated as those for the nitrogen containing compounds described by Waddington.[195] The specific heats of H_3PO_4 at various concentrations were taken from the tabulation of Egan et al.[199]

Thus for 3 ml. H_2O in the bomb and assuming 1.1147 g. of the substance burnt, the Washburn corrections for phenylphosphoric acid (using Prosen's notation[195]) are,

$C_6H_5PO_3H_2$	Δu_1	Δu_2	Δu_3	Δu_4	$\sum_1^4 \Delta u$ Joules
1.1147g	-73.64	94.70	2.25	8.60	31.41
∴1g					28.63 joules

Similar corrections were applied in case of phenyl phosphonous acid.

Most of the experimental results have been tabulated earlier (vide pp 150 ff).

The results of effective heat capacity of the system are collected in Table 34.

TABLE 34

wt. of benzoic acid	Effective heat capacity E_{cf} K j deg.$^{-1}$
1.0402	10.787
0.9191	10.764
0.9183	10.755
0.9268	10.766
0.9196	10.787
0.9212	10.789
0.9124	10.808
0.9207	10.805
0.9014	10.770
0.9233	10.768
0.9119	10.791
0.9264	10.776
mean 0.9182	10.780 ± 0.03

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The Heat of Formation of Crystalline Phosphorous Acid

By ARTHUR FINCH, P. J. GARDNER,* K. S. HUSSAIN, and K. K. SEN GUPTA
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The Heat of Formation of Crystalline Phosphorous Acid

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THE heats of formation of the phosphorus trihalides (Hal = Cl, Br, I) have been determined *via* the thermochemical investigation of their hydrolyses[1,2] or oxidative hydrolyses.[3] Such experiments require, as ancillary data, accurate heats of formation for solutions of phosphorous and phosphoric acid, respectively. The available thermodynamic data for the lower acids of phosphorus, including phosphorous acid, are sketchy and divergent.[4]

Using a conventional constant-temperature-environment reaction calorimeter,[5] the oxidation of H_3PO_3 to H_3PO_4 in an excess of aqueous bromine was studied at 25°.

$$H_3PO_3(c) + [(n+1)Br_2 + (m+1)H_2O] \rightarrow [H_3PO_4 + 2HBr]nBr_2mH_2O$$

Equilibrium constants for $Br^- + Br_2 \leftrightharpoons Br_3^-$ and $Br_3^- + Br_2 \leftrightharpoons Br_5^-$ have been determined[6] under conditions approximating to the thermochemical conditions and the contribution of these equilibria to the final thermodynamic state has been included (*ca.* -1 kcal.mole^{-1} H_3PO_3). The concentration of higher polybromides is insignificant.[7]

In calculating the results (twelve experiments, *n* *ca.* 3500 and *m* *ca.* 15), heats of mixing were ignored and ancillary thermodynamic data were taken from ref. 8.

$$\Delta H_f^0[H_3PO_3,(c)] - \Delta H_f^0[H_3PO_4\ 3000\ H_2O] = 81{\cdot}37\ (\bar{S} = 0{\cdot}18)\ \text{kcal.mole}^{-1}$$

Using Irving's figure[9] for aqueous phosphoric acid ($-310{\cdot}5 \pm 0{\cdot}5$ kcal.mole^{-1}), $\Delta H_f^0[H_3PO_3,c] = -229{\cdot}1 \pm 0{\cdot}6$ kcal.mole^{-1} (lit., $-232{\cdot}2$,[10] $-232{\cdot}5$,[8] $-227{\cdot}5$,[11] and $-226{\cdot}0$[4] kcal.mole^{-1}). Preliminary experiments indicate that the integral heat of solution of H_3PO_3 in water is $<0{\cdot}3$ kcal.mole^{-1} at 25°.

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