Combustion- and Solution-Calorimetric Studies on Organophosphorus Compounds

by

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A thesis submitted in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Royal Holloway College
University of London
1974

ABSTRACT

The standard enthalpies of formation of phenylphosphonic, phenylphosphinic, and diphenylphosphinic acids have been determined by oxygen static bomb calorimetry to be:

$$\Delta H_f^\circ[\mathrm{PhPO_3H_2,c,298.15\ K}] = -(212.6 \pm 2.8)\ \mathrm{kcal_{th}\ mol^{-1}}$$

$$\Delta H_f^\circ[\mathrm{PhPO_2H_2,c,298.15\ K}] = -(133.3 \pm 4.9)\ \mathrm{kcal_{th}\ mol^{-1}}$$

$$\Delta H_f^\circ[\mathrm{Ph_2PO_2H,c,298.15\ K}] = -(124.2 \pm 5.8)\ \mathrm{kcal_{th}\ mol^{-1}}$$

These values were compared and combined with the results of solution reaction calorimetry on related compounds and the standard enthalpy of formation of dibromophenylphosphine derived, $\Delta H_f^\circ[\mathrm{PhPBr_2,1,298.15\ K}] = -(16.24 \pm 2.81)\ \mathrm{kcal_{th}\ mol^{-1}}$. The existing literature on these compounds has been critically reviewed and the significance of dπ-pπ bonding in halophenylphosphines briefly discussed.

The standard enthalpy of formation of tri(p-tolyl) methanol has been determined from the enthalpy of combustion measured by oxygen static bomb calorimetry, $\Delta H_f^\circ[\mathrm{C_{22}H_{22}O,c,298.15\ K}] = -(13.5 \pm 5.8)\ \mathrm{kcal_{th}\ mol^{-1}}$ and a value, $-(4.3 \pm 1.9)\ \mathrm{kcal_{th}\ mol^{-1}}$, derived for the gas-phase enthalpy of formation increment per p-methyl group.

ACKNOWLEDGMENTS

I would like to express my gratitude to Dr. Arthur Finch and Dr. P. J. Gardner for their supervision and encouragement throughout this project.

My thanks are also due to my co-workers in this laboratory, C. P. McDermott, N. Hill, M. Stevens, Miss V. Eaton and Miss E. Gosling for their friendship and help, and to all the staff of the Department of Chemistry, Royal Holloway College for many kindnesses too numerous to detail.

To my parents for their understanding and encouragement, I wish to express my most sincere gratitude.

Financial support for this project was provided by the Government of Northern Ireland, Ministry of Education.

CONTENTS

CHAPTER I

GENERAL INTRODUCTION

Nearly all chemical processes are accompanied by changes of energy and structure. These two basic and interrelated properties of matter are of essential interest to the chemist. The present work is concerned with their relationship in the series of compounds Ph_3P, Ph_2PX, $PhPX_2$, PX_3, where Ph is the phenyl radical and X represents the halogens Cl and Br, and specifically with the variation of the carbon-phosphorus bond energy with the conformation of the benzene ring.

The two intermediate members of this series have been extensively used in the synthesis of organophosphorus compounds but little work has been done on the thermochemistry of these halophenylphosphines, in keeping with the general neglect of the thermochemistry of organophosphorus compounds. Some combustion and solution calorimetry has been carried out on these and related compounds but the values obtained by these different techniques do not agree. This investigation seeks to resolve this disagreement.

Previous workers[1,2,3] sought to determine the standard enthalpies of formation of Ph_2PX and $PhPX_2$ by a combination of solution and combustion calorimetry.

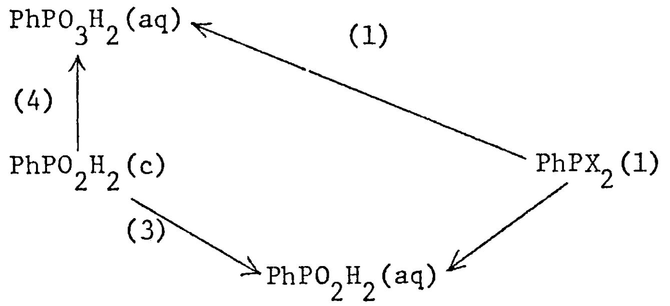
The standard heat of formation of Ph_2PX was to be determined from a combination of the heats of the following reactions:

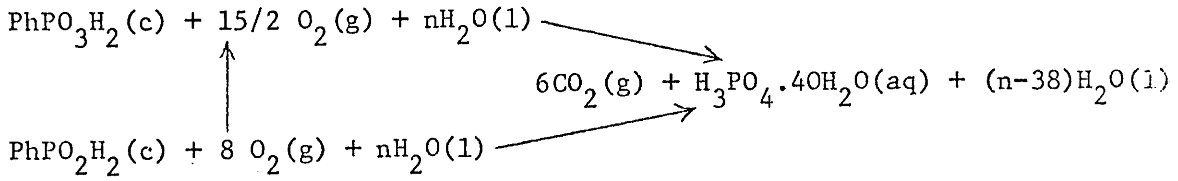
$$Ph_2PX(1) + H_2O_2(aq) \rightarrow Ph_2PO_2H(c) + HX(aq) \qquad [1]$$

$$PhPO_2H(c) + 15O_2(c) + nH_2O(1) \rightarrow 12CO_2(g) + H_3PO_4.40H_2O + (n-36)H_2O(1)$$

The only unknowns, the standard enthalpies of formation of Ph_2PX and Ph_2PO_2H, may be readily derived.

The determination of the standard enthalpy of formation of $PhPX_2$ involved two interlinked cycles of reactions which are given below:





Cycle of solution reactions:

(1) $PhPBr_2(liq.) + [Br_2 + 3H_2O](aq.) \rightarrow [PhPO_3H_2 + 4HBr](aq.)$

(2) $PhPBr_2(liq.) + 2H_2O(liq.) \rightarrow [PhPO_2H_2 + 2HBr](aq.)$

(3) $PhPO_2H_2(c) + nH_2O(liq.) \rightarrow PhPO_2H_2.nH_2O\ (aq)$

(4) $PhPO_2H_2(c) + [Br_2 + H_2O](aq.) \rightarrow [PhPO_3H_2 + 2HBr](aq.)$

From a consideration of the stoichiometries it is obvious that the following relation holds:

$$\Delta H_1 = \Delta H_2 - \Delta H_3 + \Delta H_4$$

provided that in (3) n is chosen to correspond with the extent of dilution of phenylphosphinic acid, $PhPO_2H_2$, in equation (2), that the extents of dilution of HBr and $PhPO_3H_2$ correspond in all equations, and that the enthalpies of these reactions should sum to zero. Hameed[2] reports enthalpies for reactions (1) and (4) which on combination with Sen Gupta's[1] enthalpies for reactions (2) and (3) give a value for the cycle equal to zero within experimental error.

Both equation (4) and the cycle from combustion calorimetry yield a value for the difference in the standard enthalpies of formation of phenylphosphinic acid and phenylphosphonic acid, $PhPO_3H_2$. Hussain[3] has reported values for the enthalpies of combustion of these compounds which give a value for the difference in the standard enthalpies of formation at variance with that obtained by solution calorimetry.

Since the cycle of solution reactions was over-determined and found to be internally consistent and because of the difficulties inherent in the oxygen combustion calorimetry of phosphorus compounds evident in the range of values obtained by Hussain for the enthalpies of combustion, it was thought likely that the source of the discrepancy lay in the combustion calorimetry. Accurate values for the standard enthalpies of formation of phenylphosphinic and phenylphosphonic acids were required for the calculation of the standard enthalpies of formation of the halophenyl-phosphines so it was decided to re-determine the enthalpies of combustion of the acids after some improvements had been made to the bomb calorimeter.

The results of the combustion calorimetric measurements made necessary a reinvestigation of the solution reactions given above.

CHAPTER II

BOMB CALORIMETRY

Introduction

According to Partington[4] the first bomb calorimeter was constructed by Thomas Andrews of Belfast in 1845 and used by him to determine the heat of combustion of hydrogen by exploding a mixture of hydrogen and oxygen with an electrically heated fine platinum wire. Andrews' calorimeter was a thin copper vessel and his results were unusually accurate for the times.

The bomb calorimeter as it is known today was first introduced by Berthelot in 1881[5] and has since been used, with various degrees of success, for over half of the elements in the Periodic Table. The technique has enjoyed particular success in the combustion of organic compounds containing carbon, hydrogen, oxygen and nitrogen. During the early decades of the present century the bomb calorimeter was developed into an instrument capable of measurements of high precision. The more recent developments of the rotating[6], fluorine[7], and micro-bomb[8] calorimeters have greatly enlarged the scope of this technique.

The problems encountered during the combustion of organophosphorus compounds are similar to those attendant on the combustion of sulphur-containing compounds[9]. As in the case of sulphur-containing materials the inhomogeneity of the combustion products of phosphorus compounds may be eliminated by using a rotating bomb calorimeter. However, with one notable exception[10], the combustion calorimetry of phosphorus compounds has been carried out using static bomb calorimeters. Most workers in this field have made use of a technique, described below, due to Long and Sackman[11] to mitigate the problem of inhomogeneity. Although this procedure reduces the problem of inhomogeneity it does not eliminate it and the accuracy and precision of phosphorus combustion results (>0.1%) falls far short of the standard of the best measurements on carbon compounds (<0.01%).

The experimental difficulties associated with the application of the bomb calorimetric technique to phosphorus-containing compounds are due to the corrosive nature of the products, the determination of the state of hydration of the phosphorus oxides formed during combustion, and the non-uniformity of distribution of phosphorus acids within the bomb. When burned in the presence of an auxiliary material such as Nujol or benzoic acid organophosphorus compounds have been shown to give orthophosphoric acid as the sole product of combustion[12]. The problem of the non-uniform distribution of this acid inside the bomb may be reduced by placing 3ml. of water, instead of the customary 1ml., within the bomb prior to combustion and causing it to condense, in part, onto the walls and roof of the bomb cylinder. However, the remaining concentration gradients together with the high enthalpy of dilution of orthophosphoric acid make the final thermodynamic state irreproducible. Notwithstanding these difficulties results of an acceptable precision may be obtained.

EXPERIMENTAL

COMBUSTION CALORIMETER

This was a Gallenkamp Automatic Adiabatic Bomb Calorimeter (Model CB-110) modified as follows:

(a) The mercury-in-glass thermometer was replaced by a platinum resistance thermometer (PRT, type P_4, R(273 K) = 100 Ω, Degussa Zweigniederlassung Hanau) in one arm of a d.c. Wheatstone bridge from which the out-of-balance potential was displayed on a 1 mV chart recorder (Bryans 27000). The resistance (R_d) of the PRT at any pen displacement (d) was obtained from the equation $R_d = E(p + qd)/(r - sd)$ where p,q,r, and s are known functions of the bridge arms and the resistance in series with the driving potential (a lead-acid accumulator, E volts). The initial and final resistances so obtained were converted into temperatures (T) using a mean temperature coefficient, $(dR_d/dT)(T = \langle T \rangle)$, obtained from a table of (a + 2bT) at 0.1 K intervals (a and b are the PRT temperature coefficient constants). This table is given in Appendix A. This non-linearity correction in the resistance-temperature characteristic of the PRT was necessary to adjust for the differences in the mean temperature rises in each series of experiments.

(b) The Gallenkamp bomb was replaced with a twin-valve Parr No. 1101 bomb (internal volume 360 cm^3, Parr Instrument Company, Moline, Illinois).

(c) The Gallenkamp calorimeter can and lid, fabricated in stainless steel, has been criticised[13] because of its sluggish thermal equilibration and hence have been replaced by units made from copper (1mm. thick).

MATERIALS

British Chemical Standards No. 190j Thermochemical Benzoic Acid having a certified energy of combustion under standard bomb conditions of -(26.456 ± 0.005) kJ g^{-1} (weighed in air) was used to calibrate the bomb.

Succinic acid (B.D.H. Laboratory Reagent Grade) was recrystallised four times from distilled water and the crystals rinsed with cold, deionised, distilled water. The crystals were dried at 388 K for one hour then finely ground using a glass mortar and pestle. They were further dried for 24 hours at 388 K, 3 hours at 410 K and 3 hours at 418 K. The crystals were then stored in a desiccator over Drierite for one week. The purity of the succinic acid was shown to be 99.9 mol per cent by differential scanning calorimetry. (See Appendix B).

Phenylphosphonic acid (Aldrich Chemical Co., Inc.) was recrystallised three times from distilled water (m.p. = 431.7 K, lit. m.p. = 431.2 to 432.2 K). The crystals were dried for 70 hours at 383 K, finely ground using a glass mortar and pestle, then dried for 3 hours at 404 K and 20 hours at 418 K. The crystals were stored in a desiccator over Drierite.

The purity was determined by potentiometric titration against standard alkali (0.1 M NaOH) and was 99.85 percent.

Phenylphosphinic acid (Aldrich Chemical Co., Inc.) was recrystallised nine times from benzene (Pure Recrystallisable Grade, B.D.H.). The crystals were finely ground using a glass mortar and pestle and dried for two days at 338 K. The purity was determined by titration against standard alkali, 0. 1 M NaOH, and was 99.9 per cent. Attempts to determine the purity by potentiometric titration were unsuccessful as the derivative plot showed a split peak rather than the expected single peak. The same phenomenon was observed when the same glass electrode was used for the potentiometric titration of hydrochloric and sulphuric acids. This indicated that the split peak effect was caused by a poisoning of the glass electrode and not by the presence of an acidic impurity in the phenylphosphinic acid.

Diphenylphosphinic acid, prepared by Sen Gupta[1], was recrystallised twice from ethanol (B.D.H., AnalaR), finely ground using a glass mortar and pestle and dried for 3 hours at 428 K, then stored over Drierite. The purity was determined by titration against standard alkali, 0.1 M NaOH, to a phenolphthalein end point and was 100.0 per cent.

The densities at 298 K of phenylphosphonic, phenylphosphinic and diphenylphosphinic acids were determined pyknometrically as 1.42, 1.38 and 1.34 g cm^{-3} respectively.

PROCEDURE

1. The circulation of the cooling water was begun and the temperature of the calorimeter jacket was brought to nearly 25°C. The mercury-in-glass thermometer supplied with the instrument has been left in place and was used to make this adjustment.

2. A platinum wire fuse of length 10 cm. and a cotton fuse of the same length were weighed. The material to be combusted was pelleted. In the pelleting process the cotton fuse is imbedded in the pellet. The platinum crucible was weighed, the pellet and attached fuse were placed in the crucible and all three items were weighed together.

3. For combustions of phosphorus compounds 3 ml. of distilled water was pipetted into the bomb and the water was caused to condense in part on the bomb cylinder walls and lid by standing the bomb on a water-bath. The bomb was then allowed to cool to room temperature (the room was thermostated at 25 ± 1 °C).

4. The platinum wire was tied to the bomb electrodes, the crucible placed in its support ring and the cotton fuse tied to the platinum wire. The firing circuit was then tested. For those compounds containing only C, H and O the customary 1 ml. of water was pipetted into the bomb.

5. The bomb was closed by screwing the cap down finger-tight and charged with oxygen to a pressure of 30 atmospheres. During

charging the bomb head is automatically sealed to the cylinder. The lifting knob was then screwed into position.

6. The calorimeter can was filled with water and the weight of the can plus water adjusted to 3000.0 g.

7. The bomb was placed in the can and the temperature of the water brought to nearly 25 °C by heating on a water-bath. They were then placed within the calorimeter and the temperature adjusted to 25.00 ± 0.01 °C. This adjustment was made using the 24 to 30 °C mercury-in-glass thermometer supplied by Gallenkamp. This thermometer was calibrated at the National Physical Laboratory, Teddington.

8. When the temperature had settled down, generally after about 20 min., this being monitored on the chart recorder, the initial period was begun. The initial period continued for at least 10 min. after which the bomb was fired. The main period lasted less than 10 min. and the final period for at least 10 min.

9. The bomb was removed from the calorimeter and the pressure gently released. After combustions of phosphorus containing compounds the crucible invariably contained a small quantity of a pale yellow liquid which was carefully washed into the bomb cylinder so that no soot was removed from the crucible. The crucible was transferred to a desiccator. The bomb lid and cylinder were washed with distilled water, the washings

collected and made up to 250 ml. prior to analysis. After several hours of desiccation the crucible was weighed to determine the amount of soot. It was then cleaned by boiling in concentrated nitric acid, 4M sodium hydroxide and distilled water. The extent of reaction was obtained from the mass of combustant and soot.

ANALYSIS OF THE PRODUCTS OF COMBUSTION

1. C,H,O-containing compounds:

The products of combustion of these compounds were analysed only for nitric acid. This was accomplished by titration against 0.1M NaOH using methyl-orange as indicator.

2. P-containing compounds:

The procedure followed was that of Bedford and Mortimer[12]. Four aliquots of the bomb washings were analyzed: one was titrated against 0.1N-sodium hydroxide, with thymolphthalein as indicator, to give the total phosphorus acids and nitric acid; a second was treated with acetic acid, hydrochloric acid, and mercury(II) chloride, but in no case was mercury(I) chloride precipitated, showing the absence of phosphorus(III) acids; a third was analysed by the quinoline phosphomolydate method[14]; a fourth was boiled with nitric acid to convert any condensed phosphorus(V) acids into the orthophosphoric acid, and the total phosphorus(V) acids found, but in no case were any condensed acids detected. The quantity of phosphate recovered corresponded closely to the theoretical amount.

The Quinoline Phosphomolybdate Method

This method depends on the equation:

$$(C_9H_7N)_3H_3[PO_4.12MoO_3] + 26NaOH = Na_2HPO_4 + 12Na_2MoO_4 + 3C_9H_7N + 14H_2O$$

A 50ml. aliquot of the bomb washings was taken, placed in a conical flask and concentrated hydrochloric acid (20ml.) and sodium molybdate solution (30ml.) were added. The temperature of the solution was raised to boiling and a few drops of quinoline hydrochloride solution were added from a burette. The solution was swirled, again heated to boiling, more quinoline hydrochloride added dropwise with constant swirling until a few ml. had been added. The solution was again boiled and to the gently boiling solution the quinoline hydrochloride reagent was added a few millilitres at a time, with swirling, until 60ml. had been added. The slow addition with constant swirling was intended to produce a coarsely crystalline precipitate with good filtering properties. The solution was allowed to stand on a water-bath for 15min. and then cooled to room temperature.

A paper-pulp filter was prepared in a funnel fitted with a porcelain cone and well tamped down. The clear solution was decanted through the filter and the precipitate washed twice with about 20ml. of hydrochloric acid (1+9) by decantion. The precipitate was transferred to the pad with cold water, the flask thoroughly washed, the filter and precipitate washed with cold water using small washes allowing each wash to run through before applying the next. This was continued until the washings were acid-free. The washings were tested for acid with litmus paper and silver nitrate solution. The pad was then transferred together with precipate back into the original flask (now acid-free). The funnel was inserted in the flask and washed to ensure that all the precipitate was transferred to the flask. The flask was well shaken to break up the filter paper and precipitate.

From a 50ml. pipette exactly 50ml. of 0.5M sodium hydroxide was added and the flask swirled during the addition. A few drops of indicator solution, a mixture of two volumes of 0.1% phenolphthalein solution and three volumes of 0.1% thymol blue solution (both in alcohol), were added and the excess sodium hydroxide solution was titrated against 0.5M hydrochloric acid.

The quinoline phosphomolybdate analysis was tested on potassium dihydrogen phosphate (B.D.H. Analar Grade) and the results obtained were in excellent agreement with the actual lot analysis provided by B.D.H. The analysis of the products of combustion presented a difficulty not encountered in the experiments with potassium dihydrogen phosphate, viz., prolonged washing was required in order to obtain an acid-free precipitate.

Wilson[14] tested for the presence of acid in the precipitate washings by using litmus-paper. This method was found to be unsatisfactory as washings which the litmus-paper test showed to "acid-free" were indeed significantly acidic as they formed a precipitate of silver chloride when added to a 1M silver nitrate solution, the source of the chloride ions being hydrochloric acid, and required several ml. of standard base, 0.1 N NaOH, to bring them to the mixed-indicator end point.

Nikolaev et al,[15] have suggested that the quinoline phosphomolybdate method does not permit the detection of pyrophosphoric acid as this method involves boiling with nitric acid which would oxidise any pyrophosphoric acid present to orthophosphoric acid and thus give the total phosphorus present in the products of combustion. However, they fail to realise that this is only one part of a four part analysis procedure and that another part of the analysis is the application of the quinoline phosphomolybdate method without the use of nitric acid. Subtraction of the titres obtained in these two analyses gives the quantity of phosphorus originally present as pyrophosphoric acid. This criticism of the quinoline phosphomolybdate method was invoked by Nikolaev et al in an attempt to explain the disagreement between their value for the standard heat of formation of triethyl phosphate (ΔH_f° = -312.4 ± 11.6 $\mathrm{kcal_{th}}$ $\mathrm{mol^{-1}}$) and that of Bedford and Mortimer (ΔH_f° = -297.5 ± 1.3 $\mathrm{kcal_{th}}$ $\mathrm{mol^{-1}}$). This discrepancy could better be explained by the failure of Nikolaev et al to make use of an auxilliary material to promote combustion, resulting in the formation of large quantities of soot (0.009 g, cf. Bedford and Mortimer's 0.003 g.) and pyrophosphoric acid, and by their neglecting to exploit the technique of Long and Sackman for reducing the inhomogeneity in the products of combustion.

The result of Bedford and Mortimer is in excellent agreement with that obtained by Chernick and Skinner[16] from solution calorimetry ($\Delta H_f^\circ = -297.8 \pm 3.0$ kcal_{th} mol^{-1}). This agreement shows that systematic errors in the oxygen combustion calorimetry of phosphorus compounds can be reduced to acceptable levels through the use of an auxilliary material to promote combustion and the evaporation technique of Long and Sackman.

THE CALCULATION OF THE ENERGY OF COMBUSTION

The energies of combustion were calculated from the following equation:

$$E_{sf} = [m_s(-\Delta U_c^\circ) + q_i + q_n + q_b + q_p + q_v - q_c]/\Delta T - E_{cf}$$

where the symbols have the following significance:

E_{sf}/kJK^{-1} = the energy equivalent of the final calorimeter system which consists of the calorimeter can plus water, weighing 3000.0g., and the empty bomb (including the electrodes).

E_{cf}/kJK^{-1} = the energy equivalent of the products of combustion and is calculated from the heat capacities of the crucible, oxygen, carbon dioxide, water when the combusted compound contains C,H,O, and aqueous orthophosphoric acid when it also contains phosphorus.

The heat capacities of aqueous orthophosphoric acid solutions were taken from the work of Egan, et al.[17]

m_s/g = mass of sample.

$-\Delta U^\circ_c/kJg^{-1}$ = energy of combustion of the sample.

q_i/kJ = ignition energy.

q_n/kJ = correction for the formation of nitric acid.

q_b/kJ = energy released on combustion of the benzoic acid promoter.

q_p/kJ = energy of dilution of orthophosphoric acid, taken from ref.[18], to convert the actual bomb process to the standard thermodynamic reaction in which the aqueous orthophosphoric acid appears as $H_3PO_4.40H_2O$.

q_w/kJ = Washburn Reduction.

q_c/kJ = energy which would have been released by the combustion in the bomb of any soot found in the crucible on completion of the experiment.

$\Delta T/K$ = corrected temperature rise during combustion. The thermal leakage correction was made using the method of Dickinson[19]. This correction is very small and in many cases is negligible as the calorimeter was run in a near adiabatic mode.

Ancilliary data were taken from Ref. [6] p.57.

THE WASHBURN REDUCTION

The energy evolved upon the combustion of substance in a bomb calorimeter may differ significantly from the decrease in internal energy which would accompany the combustion were it possible to carry out the reaction under standard conditions. It is thus necessary to correct the internal energy change for the isothermal bomb process so as to obtain the internal energy change for the idealised combustion process. The bomb process may be represented by the following equation, in which all the reactants are at a pressure P_1 (water vapour at P_w) and temperature 25°C, and all the products at a pressure P_2 (water vapour at P'_w) and temperature 25°C:

$$n_1C_aH_bO_cP_d(\text{liq. or c}) + n_1'C_{a'}H_{b'}O_{c'}(\text{liq. or c}) + r_1O_2(\text{g}) + m_1H_2O(\text{g}) + m_1'H_2O(\text{liq.}) =$$

$$(r_2O_2 + q_2CO_2)(\text{g}) + m_2H_2O(\text{g}) + (q_2''CO_2 + m_2''H_2O)(\text{liq.}) + mH_3PO_4.40H_2O(\text{liq.}) \ldots\ldots\ldots\ldots (1)$$

The thermodynamic standard reaction is given in the following equation:

$$n_1[C_aH_bO_cP_d(\text{liq. or c}) + (a + 2d + (b - 3d)/4 - c/2)O_2(\text{g}) =$$

$$dH_3PO_4.40H_2O(\text{liq.}) + aCO_2(\text{g}) + ((b - 3d)/2)H_2O(\text{liq.})] \ldots\ldots\ldots\ldots (2)$$

The thermodynamic standard reaction for the auxiliary material may be represented by the following equation:

$$n_1'[C_{a'}H_{b'}O_{c'}(\text{liq. or c}) + (a' + b'/4 - c')O_2(g) =$$

$$a'CO_2(g) + (b'/2)H_2O(\text{liq.})] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The Washburn Reduction, q_w, is the difference in internal energy between the thermodynamic standard reactions and the actual bomb process and is given by:

$$q_w = \Delta U_2 + \Delta U_3 - \Delta U_1$$

The procedure followed in evaluating the Washburn Reduction was a simplified version of the rigorous calculation, based on Prosen's procedure for compounds containing carbon, hydrogen, oxygen and nitrogen.[20] Prosen's procedure was modified to take account of the presence of the auxiliary material and that the substance being combusted contained phosphorus rather than nitrogen. This shortened form of the Reduction corrects only for the following processes:

(i) The energy change of a mixture of r_2 moles of oxygen when the pressure changes from zero to P_1 atmospheres:

$$\Delta u_1 = -6.59\ P_1 r_1$$

(ii) The energy change of a mixture of r_2 moles of oxygen and q_2 moles of carbon dioxide when the pressure changes from P_2 to zero atmospheres:

$$\Delta u_2 = [6.589\ R_2 + 28.875\ Q_2 - 11.15 Q_2 R_2] P_2 (r_2 + q_2)$$

where $R_2 = r_2/(r_2 + q_2)$ is the mole fraction of oxygen in the mixture and Q_2 that of carbon dioxide.

(iii) The energy change accompanying the condensation of $(m_2 - m_1)$ moles of water:

$$\Delta u_3 = -41530(m_2 - m_1)$$

(iv) The energy of vaporisation of q''_2 moles of carbon dioxide from m''_2 moles of water:

$$\Delta u_4 = 17100\ q''_2$$

The quantities of each substance taking part in the bomb process were calculated from the following equations:

$V = 0.36\ \mathrm{dm}^3$ = internal volume of the bomb, containing no water or sample.

$T = 298.15$ K = temperature to which ΔU_1 was referred, the initial temperature of the experiments.

$n_1 = m_s/M$, where m_s is the mass of substance and M is its molecular weight.

$P_1 = 30$ atmospheres, the initial pressure of oxygen at temperature T.

$m''_1 = 0.166$ = moles of water placed in the bomb.

m_b = mass of benzoic acid, the auxiliary substance.

$M_b = 122.1238$ = molecular weight of benzoic acid.

$n'_1 = m_b/M_b$ = moles of benzoic acid.

d_s = density of substance.

$d_b = 1.32\ \mathrm{g\ cm}^{-3}$ = density of benzoic acid.

$V_1 = V - 0.018m'_1 - m_s/1000d_s - m_b/1000d_b$

$r_1 = P_1V_1/[RT(1 - 0.000609P_1)]$ where R is the gas constant

$r_2 = r_1 - n_1[a + b/4 - c/2 - 5d/4] - n'_1[a' + b'/4 - c'/2] - 7/4(\text{moles of } HNO_3)$

$$m''_2 = m''_1 + n_1[b/2 - 3d/2] + n'_1[b'/2]$$

$$x = (an_1 + a'n'_1)/(r_2 + an_1 + a'n'_1)$$

$$u_2 = 0.000609[1 + 3.21x(1 + 1.33x)]$$

$$V_2 = V - 0.018m''_2$$

$$P^a_2 = \text{approx. final pressure} = [(r_2 + an_1 + a'n'_1)RT(1 - u_2P_1)]/V_2$$

$$m_1 = [13.0375 + 0.04125P_1]10^{-4}V_1$$

$$m_2 = [12.45 + (0.04125 + 0.21625x)P^a_2]10^{-4}V_2$$

$$q''_2 = 5.53m''_2.10^{-4}P^a_2.x$$

$$q_2 = an_1 + a'n'_1 - q''_2$$

$$P_2 = [(r_2 + q_2)RT(1 - u_2P^a_2)]/V_2$$

The value for the vapour pressure of aqueous orthophosphoric acid solutions was taken from reference [21].

RESULTS

These are presented in Tables I, II, III, IV, V.

TABLE I

COMBUSTION DATA FOR BENZOIC ACID

Ref. No.	m*(B.A.)/g	m(Fuse)/g	m(Crucible)/g	m(Pt wire)/g	m(Soot)/g
12	0.97362	0.00331	3.62514	0.00955	0.00000
14	1.06317	0.00338	3.62499	0.01088	0.00000
15	0.98044	0.00355	3.62488	0.00920	0.00078
16	1.02253	0.00377	3.62507	0.00814	0.00002
17	1.02632	0.00295	3.62495	0.00901	0.00000
20	1.12851	0.00292	3.62494	0.00909	0.00107
21	1.21216	0.00262	3.62471	0.00770	0.00010
22	0.95918	0.00312	3.62472	0.00957	0.00000
23	0.97991	0.00435	3.62453	0.00918	0.00017
24	1.05827	0.00282	3.62458	0.00913	0.00014
25	0.95039	0.00378	3.62458	0.00903	0.00011
26	1.14148	0.00308	3.62455	0.01014	0.00124

m* = in vacuo mass   m = weight in air

B.A. = benzoic acid

COMBUSTION DATA FOR BENZOIC ACID (continued)

Ref.No.	$\Delta R/\Omega$	$f/\Omega\ K^{-1}$	q_i/kJ	q_n/kJ	q_c/kJ	E_{cf}/kJK^{-1}
12	1.00784	0.387680	0.05964	0.00236	0.00000	0.016277
14	1.10685	0.387668	0.06096	0.00354	0.00000	0.016479
15	1.01586	0.387677	0.06393	0.00472	0.02574	0.016292
16	1.05832	0.387664	0.06769	0.00472	0.00050	0.016387
17	1.06541	0.387664	0.05344	0.00354	0.00000	0.016396
20	1.17126	0.387650	0.05291	0.00472	0.03531	0.016626
21	1.25399	0.387638	0.04766	0.00472	0.00330	0.016815
22	0.99306	0.387670	0.05641	0.00472	0.00000	0.016244
23	1.01564	0.387678	0.07792	0.00354	0.00561	0.016291
24	1.09106	0.387664	0.05116	0.00354	0.00462	0.016468
25	0.98593	0.387673	0.06795	0.00354	0.00363	0.016224
26	1.18688	0.387654	0.05571	0.00354	0.04076	0.016656

COMBUSTION DATA FOR BENZOIC ACID (continued)

Ref. No.	E_{sf}/kJK^{-1}
12	9.9080
14	9.8499
15	9.8911
16	9.9114
17	9.8763
20	9.8645
21	9.9041
22	9.9060
23	9.9005
24	9.9414
25	9.8892
26	9.8453

Mean = $9.891 \pm 0.016\ kJK^{-1}$

The quoted error is twice the standard deviation of the mean.

TABLE II

COMBUSTION DATA FOR SUCCINIC ACID

Ref.No.	m*(S.A.)/g	m(Fuse)/g	m(Cruc.)/g	m(Pt wire)/g	m(Soot)/g
27	1.16248	0.00291	3.62592	0.00973	0.00022
28	1.60223	0.00330	3.62338	0.01002	0.00027
29	1.18417	0.00339	3.62294	0.00950	0.00052
30	1.33473	0.00267	3.62280	0.00930	0.00056
31	1.31623	0.00334	3.62275	0.00759	0.00045
32	1.25230	0.00312	3.62265	0.00876	0.00050
33	1.39320	0.00326	3.62264	0.00901	0.00035
34	1.09980	0.00296	3.62250	0.00867	0.00040
35	1.26311	0.00387	3.62268	0.00925	0.00001
36	1.32658	0.00309	3.62272	0.00777	0.00088
37	1.08381	0.00314	3.62245	0.00762	0.00025
38	1.31656	0.00267	3.62233	0.00729	0.00031

m* = in vacuo mass   m = weight in air

S.A. = succinic acid

COMBUSTION DATA FOR SUCCINIC ACID (continued)

Ref.No.	$\Delta R/\Omega$	$f/\Omega K^{-1}$	q_i/kJ	q_n/kJ	q_c/kJ	E_{cf}/kJK^{-1}
27	0.57629	0.387741	0.05274	0.00118	0.00726	0.016731
28	0.79360	0.387707	0.05956	0.00236	0.00891	0.017734
29	0.58696	0.387730	0.06113	0.00354	0.01716	0.016780
30	0.66064	0.387728	0.04854	0.00000	0.01865	0.017123
31	0.65199	0.387730	0.06026	0.00071	0.01485	0.017081
32	0.62161	0.387736	0.05641	0.00118	0.01650	0.016935
33	0.68959	0.387724	0.05877	0.00118	0.01139	0.017257
34	0.54223	0.387746	0.05361	0.00000	0.01320	0.016587
35	0.62666	0.387732	0.06953	0.00000	0.00033	0.016960
36	0.65917	0.387728	0.05588	0.00000	0.02888	0.017104
37	0.54197	0.387745	0.05676	0.00000	0.00825	0.016551
38	0.65606	0.387729	0.04854	0.00236	0.01023	0.017081

COMBUSTION DATA FOR SUCCINIC ACID (continued)

Ref.No.	q_w/kJ	$-\Delta U_c^\circ$/kJ g^{-1}
27	0.016843	12.612
28	0.024148	12.610
29	0.025966	12.603
30	0.019651	12.611
31	0.013961	12.612
32	0.018385	12.636
33	0.020555	12.599
34	0.015825	12.546
35	0.018342	12.608
36	0.019386	12.662
37	0.015483	12.718
38	0.019184	12.688

Mean = 12.625 ± 0.026 kJ g^{-1}

TABLE III

COMBUSTION DATA FOR PHENYLPHOSPHONIC ACID

$$40H_2O(l) + C_6H_5PO_3H_2(c) + 15/2\ O_2(g) \rightarrow 6CO_2(g) + 2H_2O(l) + H_3PO_4.40H_2O(aq)$$

Ref.No.	m*(PPOA)/g	m*(B.A.)/g	m(Fuses)/g	m(Cruc.)/g	m(Pt wire)/g
50	0.81937	0.30507	0.00690	3.60006	0.00763
51	0.90750	0.24434	0.00715	5.59704	0.00763
52	0.75132	0.36532	0.00772	3.59592	0.00873
54	0.97256	0.32016	0.00680	3.59061	0.00756
55	0.53741	0.64661	0.00707	3.59065	0.00824
56	0.46198	0.69414	0.00716	3.58623	0.00829
58	0.77833	0.54172	0.00715	3.57785	0.00776
59	0.60524	0.48701	0.00693	3.57753	0.00681
61	0.60285	0.52349	0.00726	3.57446	0.00751
62	0.64180	0.68997	0.00823	3.57054	0.00683
63	0.54154	0.58466	0.00740	3.56532	0.00874

m* = in vacuo mass m = weight in air

PPOA = phenylphosphonic acid B.A. = benzoic acid

COMBUSTION DATA FOR PHENYLPHOSPHONIC ACID (continued)

Ref.No.	m(Soot)/g	$\Delta R/\Omega$	$f/\Omega\ K^{-1}$	q_i/kJ	q_n/kJ
50	0.00000	0.99248	0.387676	0.12243	0.01977
51	0.00310	1.00485	0.387672	0.12681	0.00000
52	0.00186	0.99672	0.387672	0.13686	0.00861
54	0.00196	1.13747	0.387653	0.12077	0.00000
55	0.00442	1.11394	0.387658	0.12549	0.00000
56	0.00396	1.09886	0.387660	0.12698	0.00000
58	0.00133	1.20586	0.387643	0.12681	0.00000
59	0.00008	1.00868	0.387674	0.12296	0.00000
61	0.00000	1.04969	0.387669	0.12873	0.10207
62	0.00289	1.24982	0.387637	0.14578	0.00000
63	0.00054	1.05294	0.387667	0.13118	0.00000

COMBUSTION DATA FOR PHENYLPHOSPHONIC ACID (continued)

Ref.No.	q_b/kJ	q_c/kJ	q_p/kJ	q_w/kJ	E_{cf}/kJK^{-1}
50	8.06453	0.00000	0.000735	0.023925	0.024400
51	6.45913	0.10230	0.001446	0.024074	0.024416
52	9.65723	0.06138	0.000175	0.024077	0.024416
54	8.46343	0.06452	0.001879	0.027573	0.024697
55	17.09314	0.14586	-0.000749	0.027020	0.024681
56	18.34959	0.13068	-0.000961	0.026682	0.024661
58	14.32037	0.04389	-0.000705	0.029381	0.024783
59	12.87411	0.00264	-0.000504	0.024206	0.024433
61	13.83846	0.00000	-0.000527	0.012684	0.024511
62	18.23936	0.09521	-0.000444	0.030470	0.024950
63	15.45549	0.01782	-0.000530	0.025447	0.024545

COMBUSTION DATA FOR PHENYLPHOSPHONIC ACID (continued)

Ref.No.	$-\Delta U^\circ_c/\mathrm{kJ\ g^{-1}}$
50	20.934
51	21.149
52	20.931
54	21.128
55	21.195
56	21.065
58	21.084
59	21.112
61	21.173
62	21.266
63	20.931

$$-\Delta U^\circ_c = 21.088 \pm 0.068 \mathrm{\ kJ\ g^{-1}}$$

$$= 3333.9 \pm 10.8 \mathrm{\ kJ\ mol^{-1}}$$

$$\Delta nRT = -3.718 \mathrm{\ kJ\ mol^{-1}}$$

$$H = U + PV$$

$$-\Delta H^\circ_c = 3337.6 \pm 10.8 \mathrm{\ kJ\ mol^{-1}}$$

$$= 797.71 \pm 2.57 \mathrm{\ kcal_{th}\ mol^{-1}}$$

Throughout this thesis $1 \mathrm{\ cal_{th}} = 4.184 \mathrm{\ J}$

TABLE IV

COMBUSTION DATA FOR PHENYLPHOSPHINIC ACID

$$40H_2O(l) + C_6H_5PO_2H_2(c) + 8\,O_2(g) \rightarrow 6CO_2(g) + 2H_2O(l) + H_3PO_4.40H_2O(aq)$$

Ref.No.	m*(PPIA)/g	m*(B.A.)/g	m(Fuses)/g	m(Cruc.)/g	m(Pt wire)/g
64	0.69219	0.56839	0.00795	3.56502	0.00905
65	0.62608	0.42941	0.00569	3.56390	0.00998
66	0.60813	0.65522	0.00799	3.56529	0.00993
67	0.65548	0.60152	0.00680	3.56292	0.00890
68	0.50527	0.59236	0.00750	3.55936	0.00934
69	0.41123	0.42643	0.00622	3.55652	0.00928
70	0.39112	0.47351	0.00667	3.55482	0.01038
71	0.29747	0.36875	0.00760	3.55347	0.00918
72	0.33182	0.43720	0.00699	3.55310	0.00894
73	0.49150	0.57118	0.00659	3.55269	0.00818
74	0.48321	0.53648	0.00680	3.55147	0.00896
75	0.44380	0.57953	0.00657	3.54962	0.00913
76	0.51367	0.52801	0.00696	3.54827	0.00844

m* = in vacuo mass m = weight in air

PPIA = phenylphosphinic acid B.A. = benzoic acid

COMBUSTION DATA FOR PHENYLPHOSPHINIC ACID (continued)

Ref. No.	m(Soot)/g	$\Delta R/\Omega$	$f/\Omega K^{-1}$	q_i/kJ	q_n/kJ
64	0.00088	1.28472	0.387627	0.14089	0.00000
65	0.00118	1.08244	0.387664	0.10136	0.00000
66	0.00000	1.30662	0.387630	0.14159	0.00000
67	0.00199	1.29243	0.387630	0.12068	0.00000
68	0.00202	1.21685	0.387657	0.13302	0.00531
69	0.00157	0.85589	0.387694	0.11063	0.00684
70	0.00074	0.88585	0.387689	0.11850	0.00000
71	0.00020	0.68500	0.387723	0.13476	0.00118
72	0.00000	0.78718	0.387706	0.12401	0.00195
73	0.00002	1.09326	0.387658	0.11710	0.00236
74	0.00048	1.05377	0.387665	0.12077	0.00000
75	0.00100	1.04577	0.387665	0.11675	0.00047
76	0.00151	1.06840	0.387660	0.12357	0.00301

COMBUSTION DATA FOR PHENYLPHOSPHINIC ACID (continued)

Ref.No.	q_b/kJ	q_c/kJ	q_p/kJ	q_w/kJ	E_{cf}/kJK^{-1}
64	15.025389	0.02888	-0.000161	0.028901	0.02485
65	11.351453	0.03894	0.000142	0.023695	0.02442
66	17.320740	0.00000	0.000302	0.029368	0.02489
67	15.901181	0.06567	0.000085	0.028973	0.02486
68	15.659036	0.06666	0.001724	0.025282	0.02456
69	11.272677	0.05181	0.000895	0.018889	0.02402
70	12.517236	0.02442	0.000967	0.019746	0.02409
71	9.747906	0.00660	0.001088	0.015126	0.02369
72	11.557382	0.00000	0.001095	0.017540	0.02390
73	15.099143	0.00066	0.000702	0.024450	0.02449
74	14.181848	0.00048	0.000716	0.023379	0.02439
75	15.319875	0.03300	0.000844	0.023642	0.02442
76	13.957944	0.04983	0.000625	0.023787	0.02443

COMBUSTION DATA FOR PHENYLPHOSPHINIC ACID (continued)

Ref. No.	$-\Delta U_c^\circ$/kJ g^{-1}
64	25.565
65	25.950
66	26.196
67	26.048
68	25.854
69	25.605
70	25.624
71	25.623
72	25.398
73	25.877
74	26.158
75	25.502
76	25.827

$-\Delta U_c^\circ = 25.787 \pm 0.142$ kJ g^{-1}

$= 3664.2 \pm 20.2$ kJ mol^{-1}

$\Delta nRT = -4.9578$ kJ mol^{-1}

$H = U + PV$

$-\Delta H_c^\circ = 3669.2 \pm 20.2$ kJ mol^{-1}

$= 876.96 \pm 4.83$ $kcal_{th}$ mol^{-1}

TABLE V

COMBUSTION DATA FOR DIPHENYLPHOSPHINIC ACID

$40H_2O(l) + (C_6H_5)_2PO_2H(c) + 15\ O_2(g) \rightarrow 12CO_2(g) + 4H_2O(l) + H_3PO_4.40H_2O(aq)$

Ref.No.	m*(DPPA)/g	m*(B.A.)/g	m(Fuses)/g	m(Cruc.)/g	m(Pt wire)/g
P1	0.43987	0.35514	0.00788	3.54734	0.01087
P2	0.39556	0.30046	0.00688	3.54844	0.01129
P3	0.40495	0.42265	0.00823	3.54788	0.01015
P4	0.39463	0.42988	0.00726	3.54984	0.01152
P5	0.41676	0.38425	0.00794	3.54861	0.01564
P7	0.41532	0.43410	0.00738	3.54985	0.01243
P8	0.42261	0.40967	0.00802	3.54840	0.01108
P9	0.41996	0.40860	0.01008	3.54706	0.01182
P10	0.41838	0.39703	0.00778	13.37547	0.01113
P11	0.39887	0.44739	0.00877	13.37492	0.01106

m* = in vacuo mass m = weight in air

DPPA = diphenylphosphinic acid B.A. = benzoic acid

COMBUSTION DATA FOR DIPHENYLPHOSPHINIC ACID

Ref.No.	m(Soot)/g	$\Delta R/\Omega$	$f/\Omega K^{-1}$	q_i/kJ	q_n/kJ
P1	0.00210	0.89302	0.387717	0.13966	0.00000
P2	0.00032	0.78581	0.387719	0.12217	0.00000
P3	0.00339	0.91888	0.387677	0.14578	0.00000
P4	0.00025	0.91623	0.387690	0.12698	0.00000
P5	0.00043	0.89240	0.387700	0.14071	0.00000
P7	0.00100	0.94795	0.387682	0.13092	0.00000
P8	0.00152	0.93370	0.387691	0.14211	0.00000
P9	0.00114	0.92966	0.387691	0.17814	0.00000
P10	0.00089	0.91589	0.387689	0.13791	0.00000
P11	0.00073	0.94421	0.387700	0.15339	0.00000

COMBUSTION DATA FOR DIPHENYLPHOSPHINIC ACID (continued)

Ref.No.	q_c/kJ	q_b/kJ	q_p/kJ	q_w/kJ	E_{cf}/kJK^{-1}
P1	0.06930	9.38813	0.001112	0.019378	0.024000
P2	0.01056	7.94266	0.001103	0.016890	0.023748
P3	0.11187	11.17275	0.001123	0.020235	0.024082
P4	0.00825	11.36388	0.001120	0.020161	0.024079
P5	0.01419	10.15765	0.001117	0.019544	0.024022
P7	0.03300	11.47543	0.001124	0.020794	0.024129
P8	0.05016	10.82963	0.001121	0.020346	0.024089
P9	0.03762	10.80134	0.001120	0.020251	0.024081
P10	0.02937	10.49549	0.001119	0.019913	0.025389
P11	0.02409	11.82675	0.001125	0.020728	0.025464

COMBUSTION DATA FOR DIPHENYLPHOSPHINIC ACID (continued)

Ref. No.	$-\Delta U_c^\circ$/kJ g^{-1}
P1	30.365
P2	30.390
P3	30.304
P4	30.223
P5	30.032
P7	30.452
P8	30.607
P9	30.506
P10	30.595
P11	30.492

$$-\Delta U_c^\circ = 30.397 \pm 0.112 \text{ kJ g}^{-1}$$

$$= 6632.4 \pm 24.4 \text{ kJ mol}^{-1}$$

$$\Delta nRT = -7.437 \text{ kJ mol}^{-1}$$

$$H = U + PV$$

$$-\Delta H_c^\circ = 6639.9 \pm 24.4 \text{ kJ mol}^{-1}$$

$$= 1586.97 \pm 5.83 \text{ kcal}_{th} \text{ mol}^{-1}$$

DISCUSSION

The combustion of the recommended secondary standard substance, succinic acid, provides a check on the accuracy of the calorimeter. Vanderzee, et al;[22] have shown that the energy of combustion of succinic acid is significantly dependent on the drying procedure adopted, the more thorough the drying the higher is the energy of combustion obtained. The drying procedure used in this work was similar to that of Wong and Westrum[23] and the value obtained for $-\Delta U_c^\circ = 12.625 \pm 0.026$ kJ g^{-1} is in good agreement with their value $-\Delta U_c^\circ = 12.635 \pm 0.002$ kJ g^{-1} which, according to Vanderzee, is in good accord with other samples handled in a similar manner. The value found in this work is 0.08% lower than that of Wong and Westrum and is representative of the level of accuracy attainable with this calorimeter. Wilhoit[24] reports that the Gallenkamp calorimeter with a thermometer capable of measuring the initial and final temperatures with an accuracy of 1.5×10^{-3} deg. C has a level of accuracy of 0.5 to 0.1%.

The enthalpies of combustion of phenylphosphonic, phenylphosphinic, and diphenylphosphinic acids are given at the bottoms of Tables III, IV and V respectively. These values together with the ancillary data $\Delta H_f^\circ[CO_2,g,298.15\ K] = -(94.051 \pm 0.031)$[25], $\Delta H_f^\circ[H_2O,1,298.15\ K] = -(68.315 \pm 0.010)$[25], and $\Delta H_f^\circ[H_3PO_4 40H_2O,298.15\ K] = -(309.34 \pm 0.38)$ $kcal_{th}\ mol^{-1}$ [10], yield the following standard enthalpies of formation:

$$\Delta H_f^\circ[\mathrm{PhPO_3H_2},c,298.15\ \mathrm{K}] = -(212.6 \pm 2.8)\ \mathrm{kcal_{th}\ mol^{-1}}$$

$$\Delta H_f^\circ[\mathrm{PhPO_2H_2},c,298.15\ \mathrm{K}] = -(133.3 \pm 4.9)\ \mathrm{kcal_{th}\ mol^{-1}}$$

$$\Delta H_f^\circ[\mathrm{Ph_2PO_2H},c,298.15\ \mathrm{K}] = -(124.2 \pm 5.8)\ \mathrm{kcal_{th}\ mol^{-1}}.$$

The standard enthalpies of formation of phenylphosphonic and phenylphosphinic acids derived from the present combustion calorimetry are shown together with the corresponding values obtained by Hussain[3] in the following table:

	A	B	C
	$-\Delta H_f^\circ/\mathrm{kcal_{th}mol^{-1}}$	$-\Delta H_f^\circ/\mathrm{kcal_{th}mol^{-1}}$	$-\Delta H_f^\circ/\mathrm{kcal_{th}mol^{-1}}$
Phenylphosphonic acid	212.6 ± 2.8(11)	256.4 ± 9.1(29)	219.3 ± 1.8(13)
Phenylphosphinic acid	133.3 ± 4.9(13)	143.5 ± 6.5(14)	136.9 ± 2.0(11)
$\Delta(\Delta H_f^\circ)$	79.3 ± 5.9	112.9 ±11.2	82.4 ± 2.6

Column A contains the results of the present work.

Column B gives Hussain's original data.

Column C gives Hussain's reported results which were obtained from those presented in Column B by rejection of data on statistical grounds. This involved a three-fold application of a procedure whereby those results falling outside the limits $(\bar{x} \pm 2s)$, $(\bar{x}$ = mean of n observations and $s = [\Sigma_i(\bar{x} - x_i)^2/(n - 1)]^{1/2})$, were rejected. Hussain's procedure eliminated 16 of 29 results for phenylphosphonic acid and 3 of 14 results for phenylphosphinic acid. The values in parenthesis in the above table are the number of experimental results used in the calculation of the means and uncertainty intervals. In the present work experiments were rejected in which soot was found outside the crucible, none were eliminated on statistical grounds.

The agreement between the present work and that of Hussain is extremely poor even in the case of his statistically treated results. No differences in procedure were discovered which might account for the poor precision of Hussain's results.

The value obtained for $\Delta H_f^\circ[\mathrm{PhPO_2H_2,c,298.15\ K}] = -133.3 \pm 4.9\ \mathrm{kcal_{th}\,mol^{-1}}$ is in good agreement with the estimated value of Sen Gupta[1] $\Delta H_f^\circ[\mathrm{PhPO_2H_2,c,298.15\ K}] = -130 \pm 10\ \mathrm{kcal_{th}\ mol^{-1}}$ derived from a consideration of the bond energy changes in the following reaction:

$$\mathrm{PhH(g) + H_3PO_3(g) \rightarrow PhPO_2H_2(g) + H_2O(g)}$$

The results of the combustion calorimetry may also be compared with solution calorimetric measurements. Hameed[2] has reported the enthalpy change for the reaction

$$\mathrm{PhPO_2H_2(c) + [Br_2 + H_2O](aq) \rightarrow [PhPO_3H_2 + 2HBr](aq)}$$

which gives

$$\Delta H_f^\circ[\mathrm{PhPO_3H_2,c,298.15\ K}] - \Delta H_f^\circ[\mathrm{PhPO_2H_2,c,298.15\ K}] = 72.2 \pm 0.7\ \mathrm{kcal_{th}\,mol^{-1}}.$$

This value is not in accord with the same function derived from combustion calorimetry and this disagreement prompted a reinvestigation of the solution calorimetry the results of which are reported in the following chapter.

The standard enthalpy of combustion of diphenylphosphinic acid yields a standard enthalpy of formation, $\Delta H_f^\circ[\mathrm{PhPO_2H_2,c,298.15\ K}] = -124.2 \pm 5.8\ \mathrm{kcal_{th}\ mol^{-1}}$. This is the first reported value of the standard enthalpy of formation for diphenylphosphinic acid. A rough estimate of $\Delta H_f^\circ[\mathrm{Ph_2PO_2H}]$ can be made from $\Delta H_f^\circ[\mathrm{PhPO_2H_2}]$. These molecules differ only in that a Ph group has replaced a H atom.

$$
\begin{aligned}
\Delta H_f^\circ[\mathrm{PhPO_2H_2,g}] - \Delta H_f^\circ[\mathrm{Ph_2PO_2H,g}] &= (\Delta H_f^\circ[\mathrm{H,g}] - \Delta H_f^\circ[\mathrm{Ph,g}]) - (\bar{E}[\mathrm{P{-}H}] - \bar{E}[\mathrm{P{-}Ph}]) \\
&= (52.1) - (77.7) - (77) + (77) \\
&= -25.6\ \mathrm{kcal_{th}\ mol^{-1}}
\end{aligned}
$$

Ignoring differences in the enthalpies of sublimation the following equation may be written:

$$
\begin{aligned}
\Delta H_f^\circ[\mathrm{Ph_2PO_2H,c}] &= \Delta H_f^\circ[\mathrm{PhPO_2H_2,c}] + 25.6 \\
&= -133.3 + 25.6 \\
&= -107.7\ \mathrm{kcal_{th}\ mol^{-1}}
\end{aligned}
$$

$$\text{cf. experimental } \Delta H_f^\circ = -124.2 \pm 5.8\ \mathrm{kcal_{th}\ mol^{-1}}$$

The agreement between the experimental and calculated values is as good as can be expected considering the assumptions made and is sufficiently good to have relevance in the following discussion of some reported solution calorimetry.

Sen Gupta[1] has reported

$$\Delta H_f^\circ[\mathrm{Ph_2PBr,l}] - \Delta H_f^\circ[\mathrm{Ph_2PO_2H,c}] = 37.4 \pm 0.8\ \mathrm{kcal_{th}\ mol^{-1}}.$$

This combined with $\Delta H_f^\circ[Ph_2PO_2H,c]$ obtained from combustion calorimetry gives

$$\begin{aligned}\Delta H_f^\circ[Ph_2PBr,l] &= -124.2 + 37.4 \\ &= -86.8\ kcal_{th}\ mol^{-1}\end{aligned}$$

The standard enthalpy of formation of $Ph_2PBr(g)$ may also be estimated from the energies of the bonds broken in the reaction

$$Ph_2PBr(g) \rightarrow 2Ph(g) + P(g) + Br(g)$$

$$\begin{aligned}\Delta H_R &= 2\Delta H_f^\circ[Ph,g] + \Delta H_f^\circ[P,g] + \Delta H_f^\circ[Br,g] - \Delta H_f^\circ[Ph_2PBr,g] \\ &= 2 \times 77.7 + 75.584 + 26.735 - \Delta H_f^\circ[Ph_2PBr,g] \\ &= 257.7 - \Delta H_f^\circ[Ph_2PBr,g] \\ &= 2\bar{E}[Ph\text{-}P] + \bar{E}[P\text{-}Br] \\ &= 2 \times 77 + 63 \\ &= 217\ kcal_{th}\ mol^{-1}\end{aligned}$$

Thus $\Delta H_f^\circ[Ph_2PBr,g] = 257.7 - 217 = 41\ kcal_{th}\ mol^{-1}$.

An approximate value for the enthalpy of vaporisation, $\Delta H^\circ_{vap} = 28\ kcal_{th}\ mol^{-1}$, was obtained by fitting $\log_{10} p = A + B/T$ (where p is the vapour pressure, A and B are constants, and T is the boiling point temperature) to some boiling point/vapour pressure data.[25]

$$\begin{aligned}\Delta H_f^\circ[Ph_2PBr,l] &= \Delta H_f^\circ[Ph_2PBr,g] - \Delta H^\circ_{vap} \\ &= 41 - 28 \\ &= 13\ kcal_{th}\ mol^{-1}.\end{aligned}$$

This differs from the experimental value by $-99.8\ kcal_{th}\ mol^{-1}$ and suggests that the solution reaction does not proceed according to the equation

$$Ph_2PBr(l) + H_2O_2(aq) \rightarrow Ph_2PO_2H(c) + HBr(aq)$$

To be in accord with the estimated $\Delta H_f^\circ[Ph_2PBr,l]$ and the experimental $\Delta H_f^\circ[Ph_2PO_2H,c]$ the enthalpy change for this reaction, ΔH_R, should be

$$\Delta H_R = \Delta H_f^\circ[Ph_2PO_2H,c] + \Delta H_f^\circ[HBr,aq] - \Delta H_f^\circ[Ph_2PBr,l] - \Delta H_f^\circ[H_2O_2,aq]$$
$$= -121.2 \text{ kcal}_{th} \text{ mol}^{-1}.$$

In order to rationalise this huge discrepancy of -99.8 kcal_{th} mol^{-1} it is necessary to consider the chemistry of the solution reaction in more detail. According to Sen Gupta dihalophenylphosphines hydrolyse to give initially hydrogen halides and $Ph_2P\text{-}OH$, which being unstable easily disproportionates to diphenylphosphinic acid and diphenylphosphine according to the equation

$$2Ph_2P\text{-}OH \rightarrow Ph_2PO_2H + Ph_2PH$$

Hydrogen peroxide was used to avoid the contamination of the hydrolysate by diphenylphosphine. Sen Gupta reports, "post-hydrolysis analysis of the reaction indicated 99.7% recovery of diphenylphosphinic acid."

Kosolapoff writes, "Hydrolysis of secondary monohalophosphines, however, yields the expected phosphinous acids, R_2POH, only on very rare occasions. Specifically in the aromatic series the p-dialkylamino derivatives are capable of such reaction. Usually, however, the products undergo the oxidation reduction spontaneously, essentially at room temperature, and yield a mixture of the secondary phosphine, R_2PH, and secondary phosphonic acid, $R_2P(O)OH$. The reaction is facilitated by the use of aqueous alkali."[26]

However, Ph_2POH does not exist as $Ph_2P\text{-}OH$ but as $PhP(H)O$ which is considerably more stable thermodynamically, their estimated enthalpies of formation being 1.1 and -42 $kcal_{th}mol^{-1}$ respectively. In view of this it seems possible that Sen Gupta measured the enthalpy of hydrolysis of diphenylbromophosphine to diphenylphosphinous acid, $Ph_2P(H)O$, which proceeded according to the equation

$$Ph_2PBr(1) + H_2O(1) \rightarrow Ph_2P(H)O(aq) + HBr(aq).$$

The enthalpy change for this reaction, ΔH_R, may be estimated as follows:

$$\Delta H_R = \Delta H_f^\circ[Ph_2P(H)O,aq] + \Delta H_f^\circ[HBr,aq] - \Delta H_f^\circ[H_2O,1] - \Delta H_f^\circ[Ph_2PBr,1]$$

$$= (-42) + (-28.98) - (-68.315) - (13)$$

$$= -16\ kcal_{th}mol^{-1}$$

This estimated enthalpy of reaction is quite close to the experimental value of -20.8 $kcal_{th}\ mol^{-1}$.

Sen Gupta's post hydrolysis analysis results may be explained either by the fact that $Ph_2P(H)O$ is a weak acid or by the alkali used in the analysis catalysing the reaction

$$2Ph_2P(H)O \rightarrow Ph_2PO_2H + Ph_2PH$$

and the diphenylphosphine formed being oxidised to diphenylphosphinic acid, Ph_2PO_2H, by hydrogen peroxide.

CHAPTER III

SOLUTION CALORIMETRY

Introduction

The value for the function $\Delta H_f^\circ[PhPO_3H_2,c] - \Delta H_f^\circ[PhPO_2H_2,c]$ obtained from the combustion calorimetry detailed in the previous section is at variance with the value for the same function obtained by Hameed[2] from the enthalpy change for the reaction

$$PhPO_2H_2(c) + [Br_2 + 3H_2O](aq) \rightarrow [PhPO_3H_2 + 4HBr](aq)$$

This reaction has been reinvestigated and the results are shown in Table V. These results provide a value for the difference in the standard enthalpies of formation of phenylphosphonic acid, $PhPO_3H_2$, and phenylphosphinic acid, $PhPO_2H_2$, in good agreement with that given by the combustion experiments.

As the reaction shown above was part (4) of the cycle of reactions

$$\begin{tikzcd}
 & & PhPO_3H_2(aq) \\
PhPBr_2(l) \arrow[urr, "(1)"] \arrow[dr, "(2)"'] & & PhPO_2H_2(c) \arrow[u, "(4)"'] \arrow[dl, "(3)"] \\
 & PhPO_2H_2(aq) &
\end{tikzcd}$$

which had been reported by Hameed[2] to be internally consistent thermochemically and as the enthalpy change for either reaction (1) or (2) was required in order to determine $\Delta H_f^\circ[PhPBr_2,l]$ it became necessary to repeat the solution calorimetry for the entire cycle. The results are presented in Tables 7 and 8. The heat of solution of phenylphosphinic acid, reaction (3), and that of phenylphosphonic acid have been precisely measured by McDermott[27] using the LKB 8700 solution calorimeter.

THE SOLUTION CALORIMETER

This was an all glass Dewar vessel operated in the isoperibol mode at 298.15 ± 0.02 K and has been described previously[28]. The present calorimeter differs from the earlier one in the following respects:

(a) The Dewar vessel contained 200 ml. of calorimetric liquid and was of round-bottom design.

(b) The calibration heater was replaced by a nominal 100 Ω PTFE encapsulated resistor (Tronac Inc., Provo, Utah) of low thermal capacity. The resistor was aged to a near constant resistance prior to installation in the calorimeter.

(c) The platinum resistance thermometer for ancilliary temperature monitoring was abandoned.

(d) The out-of-balance bridge voltage was displayed on a pen recorder, a full scale deflection of approximately 2mV was used giving a sensitivity of 1 Ω cm^{-1} with a thermistor of 150 Ω K^{-1}.

(e) The ampoules had two fracture bulbs[29].

Errors in the experimental results derive from two sources. First, a constant proportional error due to uncertainties in electrical standards, thermal leakage corrections, etc., and second, a variable proportional error due to the limits imposed by thermometer sensitivity, variations in ampoule fracture energy, etc. The former error has been assessed[30] as ca. 0.1%. The latter error has been estimated to be ca. 0.3% ΔT, where ΔT is the temperature change[30]. The precision and accuracy of the system was checked before and after each series of experiments by a standard reaction, the neutralisation of tris(hydroxymethyl) aminomethane (THAM) in excess 0.1 M aqueous hydrochloric acid. The mean of 23 runs (Table VI) was ΔH (298.15°K, $1020<N<1547$) = $-(7.11 \pm 0.02)$ $\text{kcal}_{\text{th}}\text{mol}^{-1}$. Hill, et al[31] obtained ΔH (298.15 K, 1170 $N<1574$) = $-(7.109 \pm 0.003)$ $\text{kcal}_{\text{th}}\text{mol}^{-1}$, where N is the mole ratio of water to THAM. The National Bureau of Standards certified value for this reaction is $-(7.115 \pm 0.008)$ $\text{kcal}_{\text{th}}\text{mol}^{-1}$ [32]. The uncertainties in the solution calorimetric results are quoted as $\pm\ 2\bar{s}$, $\bar{s}$ being the standard deviation of the mean, $[\Sigma_i(x_i - \bar{x})^2/n(n-1)]^{1/2}$

CALCULATION DETAILS

Temperature measured with a thermistor is related to resistance by the equation $R = A.e^{B/T}$, where R is the resistance, T is the temperature in K, and A and B are constants. Differentiation gives $dR/dT = -RB/T^2$ or $\Delta R/\Delta T = -R_m B/T_m^2$, where m indicates a mean value. Thus $\Delta T \sim \Delta R.T_m^2/R_m$. In order to use this expression the thermistor bridge must be calibrated in degrees. However, during a series of calorimetric experiments T_m^2 is nearly constant which leads to the expression

$$\Delta T \sim \Delta R/R_m .$$

If R_m is very closely the same for all experiments involved one may simply use $\Delta T \sim \Delta R$. One may also derive useful expressions containing logarithmic R-values.

$$\Delta T = T_2 - T_1 = B(\log R_1 - \log R_2)/(\log \frac{R_1}{A} . \log \frac{R_2}{A})$$

The product $\log \frac{R_1}{A} . \log \frac{R_2}{A}$ is nearly constant during a series of calorimetric experiments and we can therefore use the simpler expression

$$\Delta T \sim \log R_1/R_2$$

The enthalpies of reaction were calculated using the equation

$$\Delta H = \frac{f.P}{4184} . \frac{M}{w} . t . \frac{\Delta T_r}{\Delta T_c} \text{ kcal mol}^{-1}$$

where $\Delta T_r = \log R_1/R_2$ and $\Delta T_c = \log R_3/R_4$, R_1 and R_2 are the initial and final resistances, respectively, in ohms, and R_3 and R_4 are those for the calibration, M = molecular weight in g mol^{-1}, w = weight of experimental sample in grams, P = power in watts, t = time in seconds, f = a factor which corrects for the resistance of the heater leads.

THE COOLING CORRECTION

The thermal leakage follows Newton's Law of Cooling, i.e., is proportional to the thermal head, the temperature difference between the calorimeter jacket and the reaction vessel, $T_j - T$. The rate of temperature change during the initial and final parts of the calorimetric curve can thus be written

$$dT/dt = u + k(T_j - T) \qquad \text{.............(1)}$$

where u is the constant rate of temperature change due to the heat of stirring and k is the cooling constant or leakage modulus of the calorimeter. When $T = T_\infty$, where T_∞ = convergence temperature, $dT/dt = 0$ and so we can eliminate u in equation (1) and obtain

$$g = dT/dt = k(T_\infty - T)$$

for the slopes of the linear portions of the calorimetric curve.

The temperature change during the main period of the calorimetric experiment, $T_c - T_b$, is caused by the process being studied but is also influenced by other factors. The observed temperature change, ΔT, may be considered as being made up of two terms

$$\Delta T = \theta + \Delta T_{corr}$$

where θ ("the corrected temperature change") is the temperature change which would be expected if the process being studied caused the observed temperature effects, ΔT_{corr} is the sum of contributions to the temperature change from other factors (heat leakage, heat of stirring, heat generated in the resistance thermometer). ΔT_{corr} may be obtained from equation (1) by integration between the time limits t_b and t_c

$$\Delta T_{corr} = \int_{t_b}^{t_c} k(T_\infty - T)dt$$

According to the mean value theorem this integral equals

$$\Delta T_{corr} = k(T_\infty - T_m)\Delta t$$

If the rate of heat evolution during a reaction is truly exponential, the mean temperature of the reaction period, T_m, will occur at the time for 63% of the total temperature rise ($0.63 = 1 - 1/e$). Extrapolation of the linear parts of the calorimetric curve to this time gives the corrected temperature change, θ, as the difference. In practice the extrapolation was carried using the time for $0.6\ \Delta T$.

In the electrical calibration the evolution of heat was linear and in this case the extrapolation was carried out using the time for half the temperature rise.

MATERIALS

Dibromophenylphosphine was prepared by heating dichlorophenylphosphine (179 g) with phosphorus tribromide at 150-200 °C for approximately 2 hrs. The resulting mixture was distilled. The initial fractions (up to 175 °C) contained both phosphorus trichloride and mixed halides of phosphorus. The fraction coming over at 255-265 °C was collected (lit.b.p.[33] 259-261 °C). This fraction was redistilled under vacuum (3-4 mm.Hg) and the fraction distilling over at 106-108 °C was collected.

As dibromophenylphosphine reacts with water vapour present in the air the preparation was carried out in thoroughly dried glassware under an atmosphere of dry nitrogen. Teflon sleeves were used on the ground-glass joints as dibromophenylphosphine reacts with the silicone greases normally used to form air-tight seals at ground-glass joints. The flask containing the dibromophenylphosphine was quickly stoppered and transferred to a glovebag having an atmosphere of dry nitrogen and containing phosphorus pentoxide as desiccant.

Dibromophenylphosphine reacts readily with water according to the equation:

$$C_6H_5PBr_2 + 2H_2O \rightarrow C_6H_5PO_2H_2 + 2HBr$$

This reaction, which does not go exactly as written, will be discussed later (p.59). However, stoichiometric quantities of hydrogen bromide are formed and the purity of the dibromophenylphosphine can be determined by performing the well-known Volhard analysis on the hydrolysis products.

An ampoule containing dibromophenylphosphine was placed in a flask of distilled water and the flask was stoppered and then shaken to break the ampoule thereby initiating the reaction. The shaking was continued for several minutes and the flask left standing for a further 5 min. to ensure the reaction had gone to completion. When the flask was unstoppered the strong, garlic-like odour characteristic of phosphines was detected. The solution containing bromide was acidified with dilute nitric acid, an excess of standard (0.1M) silver nitrate solution added, the mixture thoroughly shaken, and the residual silver nitrate determined by titration with ammonium thiocyanate solution (0.1M) using ferric alum as indicator. The purity determined in this way was 100.2%.

The phenylphosphinic acid was taken from the same batch as was used for the combustion experiments.

HANDLING PROCEDURE

Ampoules of dibromophenylphosphine were filled and stoppered in a glove-bag containing phosphorus pentoxide as desiccant and an atmosphere of dry nitrogen. A syringe with a right-angled, glass needle was used to transfer the dibromophenylphosphine from the storage flask to the ampoule. Several ampoules were filled and sealed under vacuum. The results obtained by these two methods of ampoule filling did not differ significantly and so the simpler glove-bag technique was used for the majority of the work.

RESULTS

These are presented in Tables VI, VII, VIII and IX.

TABLE VI

Reaction: THAM (c) + $HCl.nH_2O(aq)$ → $[THAMH^+Cl^-]nH_2O(aq.)$

Ref.No.	m(THAM)/g	n	$-\Delta H$/kcal mol^{-1}
1	1.0148	1321	7.14
3	0.9396	1342	7.12
4	0.9897	1355	7.16
5	0.8925	1502	7.16
6	1.0842	1237	7.14
7	1.0985	1221	7.18
8	0.9936	1349	7.14
9	1.0083	1330	7.14
10	1.3139	1020	7.09
11	1.0328	1298	7.12
12	1.2597	1064	7.01
13	0.9934	1350	7.04
14	0.8667	1547	7.10
15	0.9093	1475	7.08
16	1.0090	1329	7.11
17	1.1137	1204	7.04
19	0.8698	1541	7.09

TABLE VI (continued)

Ref.No.	m(THAM)/g	n	$-\Delta H$/kcal mol^{-1}
20	1.2039	1114	7.12
21	1.1928	1124	7.09
23	1.0658	1258	7.12
24	1.2111	1107	7.04
25	0.9519	1409	7.15
26	1.2323	1088	7.10

Volume of HCl(aq.) = 200 ml. Temperature = 25.0°C

Mean $-\Delta H_r = 7.11 \pm 0.02$ kcal$_{th}$mol^{-1}

TABLE VII

Reaction (4) $C_6H_5PO_2H_2(c) + Br_2(n + 3)H_2O$ (soln) →

$[C_6H_5PO_3H_2 + 2HBr]nH_2O$ (soln)

Ref.No.	m_s/g	n	Br_2 reqd./g	Br_2excess/g	$-\Delta H_r$/kcal mol^{-1}
1	0.3456	4551	0.3887	0.2313	69.06
3	0.0887	17738	0.0998	0.0106	67.51
4	0.0761	20688	0.0856	0.0248	68.32
5	0.0802	19625	0.0902	0.0450	69.05
6	0.1073	14660	0.1207	0.1785	69.35
7	0.1151	13665	0.1295	0.1697	68.74
8	0.1259	12492	0.1416	0.1576	68.92
9	0.1766	8912	0.1986	0.1006	68.27
13	0.1456	10809	0.1638	0.0608	67.88

Volume of solution = 200 ml. Temperature = 25.0 °C

$$-\Delta H_r = 68.57 \pm 0.41\ kcal_{th} mol^{-1}$$

m_s = weight of sample

TABLE VIII

Reaction (1) $C_6H_5PBr_2(1) + Br_2(n+3)H_2O$ (soln) →

$[C_6H_5PO_3H_2 + 4HBr]nH_2O$ (soln)

Ref.No.	m_s/g	n	Br_2 reqd./g	Br_2 excess/g	$-\Delta H_r$ kcal mol^{-1}
16a	0.1670	17766	0.0996	0.0257	107.19
18a	0.1080	27465	0.0644	0.0609	107.56
19a	0.1026	28899	0.0612	0.1011	107.58
20a	0.2043	14525	0.1219	0.0404	107.10
21a	0.1868	15880	0.1114	0.0509	106.99
22a	0.2529	11725	0.1509	0.0114	106.87
23a	0.1585	18697	0.0946	0.0420	107.49
24a	0.2117	14011	0.1263	0.0103	107.82
25a	0.1565	18953	0.0934	0.0432	107.66

Volume of solution = 200 ml. Temperature = 25.0 °C

$$-\Delta H_r = 107.36 \pm 0.22 \text{ kcal}_{th}\text{mol}^{-1}$$

m_s = weight of sample

TABLE IX

Reaction (3) $C_6H_5PBr_2(l) + (n+2)H_2O(l) \rightarrow$

$[C_6H_5PO_2H_2 + 2HBr]nH_2O$ (soln)

Ref.No.	m_s/g	n	Temp./°C	$-\Delta H_r$/kcal mol^{-1}
B2	0.2702	10980	25.0	43.65
B3	0.2257	13145	25.2	44.02
B4	0.2619	11317	25.2	43.15
B5	0.1142	25982	25.2	43.56
B6	0.3035	9769	25.2	43.34
B7	0.3560	8328	25.1	43.74
B8	0.2620	11317	25.1	43.43
*B9	0.3748	7911	25.0	43.05

Volume of solution = 200 ml.

*with deoxygenated water

$-\Delta H_r = 43.56 \pm 0.21$ $kcal_{th} mol^{-1}$ (Mean of B2-B8)

m_s = weight of sample

DISCUSSION

Reaction (4)

$$PhPO_2H_2(c) + [Br_2 + H_2O](aq) \rightarrow [PhPO_3H_2 + 2HBr](aq)$$

It follows from this reaction that

$$\begin{aligned}\Delta H_f^\circ[PhPO_3H_2,c] - \Delta H_f^\circ[PhPO_2H_2,c] &= \Delta H_R - 2\Delta H_f^\circ[HBr,aq] + \Delta H_f^\circ[Br_2,aq] \\ &\quad + \Delta H_f^\circ[H_2O,l] - \Delta H^\circ_{soln}[PhPO_3H_2,c] \\ &= (-68.57) - 2(-29.001) + (-0.62 + (-68.315) - (-0.49) \\ &= -79.01 \pm 0.41 \text{ kcal}_{th}\text{mol}^{-1}\end{aligned}$$

This is in good agreement with the value for the same function obtained from combustion calorimetry, viz., -79.3 ± 5.9 kcal_{th} mol^{-1}. The heat of reaction (4), $\Delta H_R = -68.57 \pm 0.41$ kcal_{th} mol^{-1}, differs significantly from that reported by Hameed[2], $\Delta H_R = -61.31 \pm 0.68$ kcal_{th} mol^{-1}.

Reaction (1)

$$PhPBr_2(l) + [Br_2 + 3H_2O](aq) \rightarrow [PhPO_3H_2 + 4HBr](aq)$$

The heat of this reaction, $\Delta H_R = -107.36 \pm 0.22\text{kcal}_{th}$ mol^{-1}, may be used to calculate the standard enthalpy of formation of dibromophenylphosphine as follows:

$$\begin{aligned}\Delta H_f^\circ[PhPBr_2,l] &= \Delta H_f^\circ[PhPO_3H_2,c] + \Delta H^\circ_{soln}[PhPO_3H_2,c] + 4\Delta H_f^\circ[HBr,aq] \\ &\quad -\Delta H_f[Br_2,aq] - 3\Delta H_f^\circ[H_2O,l] - \Delta H_R\end{aligned}$$

$$= (-212.6) + (-0.59) + 4(-28.993) - (-0.62)$$

$$-3(-68.315) - (-107.36)$$

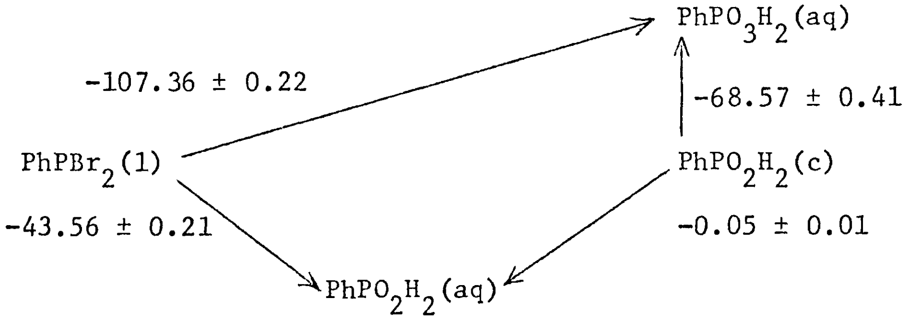
$$= -16.24 \pm 2.81 \text{ kcal}_{th} \text{ mol}^{-1}.$$

The heat observed for this reaction also differs significantly from that reported by Hameed[2] for the same reaction, viz., -104.36 ± 0.26 kcal_{th} mol^{-1}.

Reaction (3)

$$PhPBr_2(l) + 2H_2O(l) \rightarrow [PhPO_2H_2 + 2HBr](aq)$$

The observed enthalpy of reaction, $\Delta H_R = -43.56 \pm 0.21$ kcal_{th} mol^{-1}, differs significantly from that reported by Sen Gupta[1], $\Delta H_R = -41.7 \pm 0.5$ kcal_{th} mol^{-1}. Shown below is the cycle of reactions with the corresponding enthalpies of reaction:



After minor corrections for differences in dilution this cycle sums to 4.83 kcal_{th} mol^{-1} indicating that at least one of these reactions does not proceed entirely as written. The most likely reaction is (3), the hydrolysis of dibromophenylphosphine. According to Frank[34], "While seemingly straightforward the hydrolysis of phosphonous dichlorides (dichlorophosphines) with water does not proceed entirely in accordance with the equation above (3). The phosphonous (phosphinic) acids, themselves odourless, are contaminated by an intense phosphine-like odour and the yields are less than quantitative." However, Sen Gupta[1] reports, "The hydrolyses were performed over a wide concentration range [$1163<N<2829$, where N = moles H_2O/moles $PhPBr_2$] when variation of heat evolved with concentration would indicate an equilibrium; there was no significant variation in $\Delta H_{obs.}$. Although the hydrolysate was contaminated with phenylphosphine (detected by odour), the concentration and hence the extent of side reaction, was small, as post hydrolysis analysis indicated 100% recovery of both the halide and phenylphosphinic acid."

It is likely that the phosphine is produced by the thermal disproportionation of phenylphosphinic acid according to the equation:

$$3PhPO_2H_2 \rightarrow PhPH_2 + 2PhPO_3H_2$$

However, this side reaction is insufficiently exothermic to account for the discrepancy of 4.83 $kcal_{th}$ mol^{-1} in the cycle of solution reactions. After estimation of the enthalpy of formation of $PhPH_2(l)$ to be 17 $kcal_{th}$ mol^{-1} the enthalpy of the disproportionation reaction may be calculated to be approximately -9 $kcal_{th}$ mol^{-1}. This would be insufficient to account for the observed enthalpy of reaction even were it the only reaction to occur.

Post hydrolysis analysis with standard base, 0.1 M NaOH, gave 100.5% acid based on the equation:

$$PhPBr_2 + 2H_2O \rightarrow PhPO_2H_2 + 2HBr$$

and is consistent with 4% of the phenylphosphinic acid being involved in the disproportionation side reaction. The thermal disproportionation reaction is only approximated by the equation given above and "the actual yields of these products, especially of the phosphines, are far below the theoretical"[35] possibly because of their oxidation by atmospheric oxygen to $PhPO_2H_2$. This oxidation is highly exothermic, approximately 150 $kcal_{th}mol^{-1}$, and may account for the discrepancy in the cycle. The possibility that dissolved oxygen might be involved in the oxidation was eliminated by carrying out one hydrolysis in boiled-out distilled water which was saturated with nitrogen. The observed enthalpy of reaction did not differ significantly from the results obtained with distilled water containing dissolved oxygen.

It should be noted that in all calculations made above involving the enthalpies of solution reactions the enthalpies of mixing of the reaction products have been assumed to be negligible.

BOND ENERGIES IN HALOPHENYLPHOSPHINES

For a molecule of the type AB_n having only A-B bonds it is reasonable to divide the enthalpy of atomisation of the compound equally amongst the n bonds A-B, provided these bonds are known to be equivalent, so that the bond energy of the A-B bond, E(A-B), in the gaseous state is defined by the expression

$$E(A\text{-}B) = (\Delta H_f^a[AB_n, g, 298.15\ K])/n$$

where $\Delta H_f^a = \Delta H_f^\circ[\text{atoms}] - \Delta H_f^\circ$, the enthalpy of formation of the molecule AB_n from the atoms.

When a molecule contains bonds of more than one type the calculation of bond energies becomes more complicated. One possible solution to this problem is to arbitrarily assign an energy to one bond type in order to estimate the strength of another bond type. This method is obviously too simplistic as it involves the transfer of unmodified bond energies, derived from molecules of one type, to molecules in which that bond may be in a very different environment. However, allowances may be made for the changed environment of a particular bond by considering evidence about variations in bond length, vibration frequency, or force constant of the transferred bond, obtained from infrared, Raman, microwave, electron diffraction, and X-ray experiments. Such relevant data for halophenylphosphines are summarised below.

	Ph_3P	$PhPBr_2$	PBr_3	
ν^* cm^{-1}		389	390	Ref. 36
Bond Order P-Br		1.30	1.25	Ref. 36
Bond Order P-Ph	1.18	1.30		Ref. 36
Bond Length P-X /Å	1.828		2.20	Ref. 37
Bond Angle X/P/X	103°		101°	Ref. 37

X = Ph,Br $\nu = (\nu_s + \nu_{as})/2$ = average of the frequencies of the symmetric and asymmetric bond vibrations.

The nearly identical average frequency values for the P-Br bond vibrations in PBr_3 and $PhPBr_2$ together with the general insensitivity of the P-Br bond length to the presence of other atoms attached to phosphorus[37], provides some justification for the assumption that the P-Br bond energies in PBr_3 and $PhPBr_2$ are nearly equal.

The standard enthalpy of formation of $PhPBr_2(1)$ has been calculated above (p.68), $\Delta H^\circ_f[PhPBr_2,1] = -16.24 \pm 2.81$ $kcal_{th}$ mol^{-1}. The enthalpy of vaporisation has been estimated by fitting $\log_{10} p = A + B/T$, (where p is the vapour pressure, T is the boiling point, A and B are constants) to boiling point/vapour pressure data[25], as $\Delta H^\circ_{vap} = 14.5 \pm 1.5$ $kcal_{th}$ mol^{-1}, which gives $\Delta H^\circ_f[PhPBr_2,g] = -1.74 \pm 3.2$ $kcal_{th}$ mol^{-1}.

Consideration of the equation

$$PhPBr_2(g) \rightarrow Ph(g) + P(g) + 2Br(g)$$

gives

$$\begin{aligned} E[Ph\text{-}P] &= \Delta H^\circ_f[Ph,g] + \Delta H^\circ_f[P,g] + 2\Delta H^\circ_f[Br,g] - \Delta H^\circ_f[PhPBr_2,g] - 2E[P\text{-}Br] \\ &= 77.7^{[38]} + 75.584^{[39]} + 2(26.735)^{[40]} - (-1.74) \quad - 2(63)^{[39]} \\ &= 82.5 \pm 3.8 \text{ kcal}_{th} \text{ mol}^{-1}. \end{aligned}$$

This value may be compared with E[P-Ph] = 77 $kcal_{th}$ mol^{-1} calculated from the gas phase enthalpy of formation of triphenylphosphine[41] and

$E[P\text{-}Me] = 66.7\ kcal_{th}\ mol^{-1}$[41]. Bedford and Mortimer[12] account for the difference between the P-C bond energy in triphenylphosphine and trimethylphosphine by the possibility of additional bonding in the former compound involving 3d orbitals of the phosphorus atom and the π-orbitals of the benzene ring. However, the use of d orbitals in bonding is one of the most controversial features of phosphorus chemistry[42,43]. The d orbitals of an uncharged phosphorus atom are too diffuse for significant overlap with pσ or pπ orbitals[44]. A formal positive charge contracts the 3d orbitals which become commensurate with other orbitals[44]. It is possible that the higher electronegativity of carbon in phenyl (2.9)[36] over that in methyl (2.5)[36] (cf. P = 2.1) may be sufficient to make dπ-pπ bonding significant in phenylphosphines. However, the greater electronegativity difference will also lead to bond strengthening due to electrostatic factors.

The phenyl groups in triphenylphosphine are in a staggered conformation[37] which means they are not free to rotate independently about the P-C bonds. Although the symmetry requirements for dπ - pπ bonding are more complex than those for pπ -pπ bonding the staggered conformation makes it impossible for all three phenyl groups to simultaneously adopt the most favourable position for overlap of the 3d and 2p orbitals. In dibromophenylphosphine the rotation of the phenyl group is unrestricted and the phenyl group is therefore free to adopt the conformation giving maximum

3d-2p orbital overlap. The strengthening of 5.5 $kcal_{th}$ mol^{-1} of the P-Ph bond in dibromophenylphosphine in comparison to that in triphenylphosphine may be due primarily to this unrestricted rotation as the electronegativity of bromine (2.8) is very close to that of carbon in a phenyl group (2.9).

CONCLUSION

The aim of this project was to gain some insight into the nature of the bonding in the series of phosphines Ph_3P, Ph_2PX, $PhPX_2$, PX_3, where X = Br and Cl, by determining the bond energies in these compounds. This required a knowledge of the enthalpies of formation of these compounds in the gaseous phase. The standard enthalpies of formation of the halophenylphosphines in the liquid phase were to be calculated from the standard enthalpies of formation of phenylphosphinic acid, $PhPO_2H_2$, and diphenylphosphinic acid, Ph_2PO_2H, and the enthalpies of the following reactions:

$$Ph_2PX(l) + H_2O_2(aq) \rightarrow Ph_2PO_2H(c) + HX(aq) \quad \ldots\ldots(5)$$

$$PhPX_2(l) + H_2O(l) \rightarrow [PhPO_2H_2 + 2HX](aq) \quad \ldots\ldots(3)$$

where X = Br,Cl. These reactions, the enthalpies of which have been reported[1], have been shown not to proceed as written above.

However, the standard enthalpy of formation of $PhPX_2$ may be determined from the enthalpy of the reaction

$$PhPX_2(l) + [Br_2 + 3H_2O](aq) \rightarrow [PhPO_3H_2 + 2HBr + 2HX](aq)$$

and the standard enthalpy of formation of phenylphosphonic acid, $PhPO_3H_2$, as has been reported for $PhPBr_2$ (p.68). Reaction (5), if carried out in the presence of dilute alkali, may yield the standard enthalpy of formation of Ph_2PX. Corrections would have to be made for the neutralisation of the halogen acid by the alkali.

The standard enthalpies of vaporisation of $PhPX_2$ and Ph_2PX, where X = Br,Cl, are at present being measured in these laboratories.[45]

CHAPTER IV

THE STANDARD ENTHALPY OF FORMATION OF TRI(p-tolyl) METHANOL

INTRODUCTION

In connexion with solution calorimetric studies on triarylcarbonium perchlorates[46] the standard enthalpies of formation of the corresponding methanols were required. The only literature value available[47] is that for triphenylmethanol so the determination of that for tri(p-tolyl) methanol was undertaken using combustion calorimetry.

EXPERIMENTAL

Tri(p-tolyl) methanol was prepared from p-tolylmagnesium bromide and methyl p-toluate according to the method of Mothwurf[48] by Coley[46]. Two crystallizations from petroleum ether (boiling range 333 to 353 K) were used to purify this material. Microanalysis (A.Bernhardt, Mikroanalytisches Laboratorium) gave C,87.25 mass per cent; H, 7.28 mass per cent; $C_{22}H_{22}O$ requires C, 87.38 mass per cent; H, 7.33 mass per cent. The purity was determined using a Perkin Elmer Differential Scanning Calorimeter 1B as 99.4 moles per cent. (See Appendix B). The residual impurity could not be removed by prolonged heating just below the melting temperature (365 K) and in the calculations it was assumed to have the same energy of combustion as tri(p-tolyl) methanol. The density of tri (p-tolyl) methanol at 298.15 K was determined pynometrically as 1.087 g cm^{-3}.

RESULTS AND DISCUSSION

The mean of ten experiments gave $-\Delta U_c^\circ[(CH_3C_6H_5)_3COH,c,298.15\ K] = 38.796 \pm 0.080\ kJ\ g^{-1}$ (see Table X). This result combined with recommended ancilliary data[49] gave $\Delta H_f^\circ[C_{22}H_{22}O,c,298.15\ K] = -13.5 \pm 5.8\ kcal_{th}\ mol^{-1}$. The standard enthalpy of formation of crystalline triphenylmethanol at 298.15 K is $-0.59 \pm 0.60\ kcal_{th}\ mol^{-1}$[47] and, assuming that its enthalpy of sublimation is equal to that of tri(p-tolyl) methanol, the gas-phase enthalpy of formation increment per p-methyl group is $-4.3 \pm 1.9\ kcal_{th}\ mol^{-1}$. This value may be compared with $-7.8 \pm 0.2\ kcal_{th}\ mol^{-1}$ for the same function obtained from the difference in the gas-phase enthalpies of formation of benzene and toluene[41].

TABLE X

COMBUSTION DATA FOR TRI(p-tolyl) METHANOL

$$C_{22}H_{22}O(c) + 27\ O_2(g) \rightarrow 22\ CO_2(g) + 11\ H_2O(l)$$

Ref.No.	m*(Tpt.)/g	m(Fuse)/g	m(Cruc.)/g	m(Pt wire)/g	m(Soot)/g
39	0.85633	0.00331	3.62239	0.00868	0.00040
40	0.91476	0.00353	3.62302	0.00975	0.00000
41	0.78609	0.00322	3.61766	0.00836	0.00052
42	0.69176	0.00354	3.61556	0.00848	0.00084
43	0.87180	0.00331	3.61567	0.00718	0.00000
44	0.69708	0.00326	3.61246	0.00986	0.00000
45	0.75654	0.00374	3.61104	0.00729	0.00132
46	0.75914	0.00358	3.60799	0.00862	0.00067
47	0.89527	0.00364	3.60646	0.00880	0.00064
48	0.87616	0.00334	3.60272	0.00766	0.00188

m* = in vacuo mass m = weight in air

Tpt = tri (p-tolyl) methanol

COMBUSTION DATA FOR TRI(p-tolyl) METHANOL (continued)

Ref.No.	$\Delta R/\Omega$	$f/\Omega K^{-1}$	q_i/kJ	q_n/kJ	q_c/kJ	E_{cf}/kJ $deg.^{-1}$
39	1.30528	0.387629	0.05972	0.00472	0.01320	0.016651
40	1.38553	0.387615	0.06358	0.00472	0.00000	0.016826
41	1.19615	0.387645	0.05816	0.00472	0.01716	0.016439
42	1.05216	0.387667	0.06375	0.00472	0.02772	0.016155
43	1.32319	0.387625	0.05973	0.00472	0.00000	0.016696
44	1.05500	0.387666	0.05886	0.00590	0.00000	0.016171
45	1.14654	0.387654	0.06725	0.00590	0.04356	0.016349
46	1.16008	0.387651	0.06445	0.00472	0.02211	0.016357
47	1.36067	0.387619	0.06550	0.00590	0.02112	0.016765
48	1.33328	0.387624	0.06026	0.00472	0.06204	0.016707

COMBUSTION DATA FOR TRI(p-tolyl) METHANOL (continued)

Ref.No.	q_w/kJ	$-\Delta U_c^\circ$/kJ g^{-1}
39	0.017113	38.878
40	0.019522	38.618
41	0.014752	38.810
42	0.012133	38.792
43	0.017152	38.699
44	0.012408	38.566
45	0.014662	38.672
46	0.014687	38.970
47	0.017192	38.771
48	0.017163	38.871

Mean = 38.796 ± 0.080 kJ g^{-1}

APPENDIX A

Platinum resistance thermometer characteristics.

$R_t = R_o(1 + aT + bT^2)$

R = resistance in ohms.

T = temperature in °C

a,b = constants

$R_T = 99.930(1 + 0.003912T - 0.0000006191T^2)$

$dR_T/dT = 99.930(0.003912 - 0.0000012382T)$

$T/°C$	R_T/Ω	$dR_T/dT/\Omega\ K^{-1}$
24.0	109.276593	0.387956
25.5	109.858388	0.387771
25.6	109.897165	0.387759
25.7	109.935940	0.387746
25.8	109.974714	0.387734
25.9	110.013487	0.387721
26.0	110.052258	0.387709
26.1	110.091028	0.387697
26.2	110.129797	0.387684
26.3	110.168565	0.387672
26.4	110.207332	0.387660
26.5	110.246098	0.387647
26.6	110.284861	0.387635
26.7	110.323624	0.387623
26.8	110.362386	0.387610
26.9	110.401146	0.387598
27.0	110.439906	0.387585

The constants a and b were supplied by the manufacturer.

APPENDIX B

PURITY DETERMINATIONS BY DIFFERENTIAL SCANNING CALORIMETRY

The Perkin-Elmer DSC-1B with the Leeds and Northrup Speedomax W recorder was used in all experiments. The DSC consists essentially of a sample cell and a reference cell. At the bottom of each cell are platinum resistance thermometers and small heaters used to provide temperature control. During one-half of the 60 Hz operation, the circuit into which the heating rate is programmed controls the instrument. This circuit reads the two thermometers, averages their readings, compares this average with the programmed temperature, and applies sufficient power to the cells to bring them into accord with the programmed temperature. This circuit also activates an event marker for each Kelvin.

A different circuit controls the other half of the cycle. It reads the two thermometers and supplies enough differential power to the cell having the lower temperature to make the cells isothermal again. The differential power supplied is recorded as millicalories per second and the direction of pen excursion indicates whether the transition is exo- or endo-thermic. The pen deflection records the rate of differential heat supplied and the chart movement is in seconds so that the area under the peak is directly proportional to the quantity of heat evolved or absorbed during the transition.

The use of the DSC for purity determinations is based on the van't Hoff equation which may be developed[50] to give the following equation:

$$T_s = T_o - (RT_o^2 X)/\Delta H.F$$

where T_s is the instantaneous temperature of the sample (K); T_o is the melting point of the infinitely pure sample (solvent, K); R is the Gas Constant (1.987 cal mol^{-1} K^{-1}); ΔH is the heat of fusion of the sample (solvent,cal/mole); X is the mole fraction of impurity; F is the fraction of the total sample melted at T_s.A plot of T_s against 1/F should give a straight line of slope $-RT_o^2X/\Delta H$ with an intercept of T_o.ΔH may be obtained from the area under the DSC curve, T_s from the projection of any point on the curve onto the temperature/time axis and 1/F may also be obtained from the thermogram as it is the reciprocal of the partial area under the DSC curve up to T_s divided by the total area.

In applying the van't Hoff equation for purity determinations two assumptions are made:

(1) the impurity is insoluble in the predominant solid phase;

(2) the impurity is completely soluble, i.e., ideal solution, in the molten or liquid phase.

In order to make use of the van't Hoff equation it is necessary to apply two corrections to account for instrumental factors:

(1) the thermal resistance of the instrument;

(2) the undetected melting.

THERMAL RESISTANCE

The thermal resistance between the heater/sensor platform and the base of the sample pan may be corrected for to a first approximation by melting a material of very high purity (>99.99%) and recording the melting curve. The leading edge slope is directly proportional to the thermal resistance. To correct any temperature in a recorded transition it is necessary to superimpose this slope on the curve and extrapolate to the isothermal base line. High purity indium is normally used. Maximum precision is obtained when the pure material melts in or near the range for which it is being used as a correction. To make the correction the standard thermogram must be recorded at the same sensitivity, heating rate and chart speed as the sample.

UNDETECTED MELTING

If the sensitivity is chosen so as to keep the complete record on the chart then the low temperature portion of the melting curve will contain undetected melting because of the low sensitivity employed. This means that the area under the curve will be too small to truly represent the fraction of melted sample. This small amount of heat is detected by the DSC and is compensated for in the differential circuit but it is not shown on the pen recorder trace. To recover this small amount of heat it is necessary to linearise the T_s vs. 1/F plot. This is done by trial and error using progressively larger area increments and determining the effect on the plot. The formula for compensation is:

$$\text{true } F_1 = \frac{a_1 + x}{A + x} \quad ; \quad \text{true } F_2 = \frac{a_1 + a_2 + x}{A + x} \quad ; \quad \text{etc.}$$

where a_1 and a_2 are the partial areas; A is the total area under the curve; x is the small area missed in the low temperature portion of the melting curve. This linearisation is a requirement of the assumptions of the van't Hoff equation.

PROCEDURE

All samples were ground in an agate mortar and pestle prior to encapsulation in a hermetically sealed aluminium container. The reference pan was empty. Each run was begun at least 20°C below the melting point to ensure thermal equilibrium was established well before the melting transition occurred.

Temperature and area calibration were carried out using indium (99.999% pure) under the same conditions as were employed for the samples whose purities were to be determined. Because of the age and consequent condition of the sample holder assembly it was not possible to use the most sensitive range nor the slowest scanning speed as the noise level was prohibitively high. However, when a new sample holder assembly became available a determination of the purity of tri(p-tolyl) methanol was made using the optimum conditions[51,52,53] with the same results as those obtained under less favourable conditions. The purity of succinic acid was not re-determined.

Areas were measured with a polar planimeter. Each area was measured five times and an average value was used in the subsequent calculations. It was necessary to add an area equal to approximately 10% of the total area under the melting peak to each of the fractional areas in order to linearise the T_s vs. $1/F$ plot.

RESULTS

Succinic Acid

Indium calibration

Weight = 6.67 mg.
Range = 4
Scan speed = 4 K min.$^{-1}$
Chart speed = 120 in.hr.$^{-1}$
Area = 201.0 p.u.

Succinic Acid

Weight = 1.12 mg.
Range = 4
Scan speed = 4 K min.$^{-1}$
Chart speed = 120 in.hr.$^{-1}$

The indium was 99.999 per cent pure, had a melting point of 429.7 K, atomic weight = 114.8 and heat of fusion = 780 cal mol^{-1}[51].

$$k = \frac{(780)(6.67)10^{-3}}{(201.0)(114.8)} \quad \text{cal}_{\text{th}}\text{p.u.}^{-1}$$

$$= (2.255)10^{-4} \quad \text{cal}_{\text{th}}\text{p.u.}^{-1}$$

where k is the calibration constant and p.u. are planimeter units.

Temp./K	Area sum	1/F	Area sum + 3%	1/F
461.74	5.0	70.2	15.5	23.3
462.12	11.0	31.9	21.5	16.8
462.45	22.0	16.0	32.5	11.1
462.83	65.0	5.4	75.5	4.8
	351.0		361.5	

$$\text{Mole \% impurity} = \frac{100.\Delta H_f.\Delta T}{RT_o^2}$$

$$\Delta H_f = \frac{k(361.5)\,118.09}{(1.12)\quad 10^{-3}} = 8594.5 \text{ cal mol}^{-1}$$

T_o = 463.12 K, ΔT = 0.06 K

$$\text{Mole \% impurity} = \frac{100 \quad (8594.5) \quad 0.06}{1.9872 \quad (463.12)^2}$$

$$= 0.12$$

Mole % purity = 99.88

Tri (p-tolyl) methanol

Indium calibration		Tri (p-tolyl) methanol	
Weight	= 6.42 mg.	Weight	= 9.04 mg.
Range	= 4	Range	= 4
Scan speed	= 4 K min.$^{-1}$	Scan speed	= 4 K min.$^{-1}$

Chart speed = 120 in. hr.$^{-1}$ Chart speed = 120 in. hr.$^{-1}$

Area = 190 p.u.

$$k = \frac{780 \quad (6.42) \quad 10^{-3}}{(190.0) \quad 114.8}$$

$$= 2.296 \quad (10^{-4}) \text{ cal p.u.}^{-1}$$

Temp./K	Area sum	1/F	Area sum + 8%	1/F
361.20	30.0	17.5	71.9	7.9
361.77	46.5	11.3	88.4	6.4
362.35	80.0	6.5	121.9	4.6
362.70	113.0	4.6	154.9	3.7
	523.8		565.7	

$$\text{Mole \% impurity} = \frac{100 \ . \ \Delta H_f \ . \ \Delta T}{RT_o^2}$$

$$\Delta H_f = \frac{k \quad (565.7\,) \quad 302.42}{9.04 \quad 10^{-3}} = 4344.7 \text{ cal mol}^{-1}$$

T_o = 363.96 K, ΔT = 0.34 K

$$\text{Mole \% impurity} = \frac{100 \quad (4344.7\,) \quad 0.34}{1.9872 \quad (363.96)^2}$$

$$= 0.57$$

Mole % purity = 99.43

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