HEAT OF COMBUSTION OF SOLVENTS USED
IN NUCLEAR FACILITIES

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ABSTRACT

An adiabatic bomb calorimeter was used to measure the heat of combustion of hexone, normal paraffin hydrocarbon (NPH), tributyl phosphate (TBP), di-butylbutyl phosphonate (DBBP), and di(2-ethylhexyl) phosphoric acid (D2EHPA) and certain of their mixtures. The effects of pressure, temperature, solvent mixing, water, and dilute acid contact on the heat of combustion are briefly discussed.

HEAT OF COMBUSTION OF SOLVENTS USED IN NUCLEAR FACILITIES

INTRODUCTION

Interest in the combustion characteristics of solvents used at facilities operated for the Atomic Energy Commission is a result of two considerations: the safety and disposability of former or current organic extractants. Of interest for both of these reasons is the rate of combustion and the total amount of heat evolved during combustion. This report deals with the latter quantity.

The collection of thermodynamic data of this type can be directed toward either of two uses. The work can be designed to serve a specific purpose or it may be aimed at providing thermodynamic data for general reference. This study is oriented toward the specific problem present in flammability studies and the data are not intended for the calculation of bond energies, heats of formation, or other similar quantities.

In this report ΔH will designate the enthalpy (heat) of combustion and ΔQ the total amount of heat measured in the bomb calorimeter. Both quantities are referenced to one gram of sample unless otherwise noted. For engineering applications it may be convenient to use the unit Btu/pound (1 Btu/pound = 1.80 calories/gram). The gross heat of combustion refers to a final state in which all of the water produced during the reaction is in the condensed phase. The net heat of combustion relates to a final state where the water is in the vapor phase. Since the condensation of water is exothermic, the gross value is always larger than the net value.

SUMMARY

The pressure and temperature dependence of the heat of combustion is negligible. Mixtures of the solvents tributylbutyl phosphate (TBP), di(2-ethylhexyl)phosphoric acid (D2EHPA), and normal paraffin hydrocarbon (NPH) have a heat of combustion that is an additive function of the individual heats of combustion.

Contacting these solvent mixtures with dilute aqueous HNO_3 has a slight depressing effect on the heat of combustion per gram. In the mixtures TBP/NPH (20/80 volume ratio) and 0.3M D2EHPA, 0.2M TBP in NPH this depression is less than 2% but would be expected to increase with increasing TBP content.

Contact of unmixed dibutylbutyl phosphonate (DBBP) and TBP with water substantially reduced the heat of combustion per gram. Further reduction occurred after contact with dilute aqueous HNO_3 , which may be due to an increased water content rather than the HNO_3 itself. The D2EHPA used in this study was affected to a lesser extent by water contact and showed no further depression after HNO_3 contact.

The 6% drop in the heat of combustion of D2EHPA after 1000 watt-hour/liter of cobalt-60 radiation indicates the need for additional work to characterize the effect of radiation on the heat of combustion.

The net heats of combustion of the following solvents were measured in an adiabatic bomb calorimeter.

Solvent	ΔH	Standard Deviation
	cal/g	cal/g
Hexone	8,407	70
NPH	10,512	22
TBP	6,877	59
DBBP	7,513	96
D2EHPA	7,435	2

Solvent mixture heats of combustion follow the relationships

$$\text{TBP in NPH, } \Delta H \text{ cal/g} = \frac{0.973QX + (1-X)(0.745P)}{0.973X + 0.745(1-X)}$$

$$\text{TBP, D2EHPA in NPH, } \Delta H \text{ cal/g} =$$

$$\frac{266.3QY + 322.4ZT + P[745 - 203.9Y - 244.8Z]}{62.4Y + 77.6Z + 745}$$

where:

X = volume fraction of TBP in NPH
 Y = molar concentration of TBP
 Z = molar concentration of D2EHPA
 P = ΔH cal/g NPH
 Q = ΔH cal/g TBP
 T = ΔH cal/g D2EHPA.

EXPERIMENTAL

Experiments were carried out with a Parr Model 1241 adiabatic calorimeter with a stainless steel bomb and stainless steel sample pans. Volatile samples were contained in glass bulbs to minimize soot deposits on the inside of the bomb. The energy equivalent of the calorimeter was established at 2411.6 ± 0.5 cal/°C through benzoic acid combustion.

A typical experiment proceeded as follows:

One-half gram of TBP was placed in the sample pan and weighed to 0.01 mg. Ten centimeters of Parr fuse wire (≈ 16 mg) were weighed to 0.01 mg and attached to the electrodes so that the wire arced to within $1/32$ "

of the TBP surface. The internal, external, and electrical surfaces of the bomb were checked for moisture and dirt. Three milliliters of distilled water were placed in the bomb, and the top was secured.

Distilled water in the amount of 2000 ± 0.2 g was placed in the bucket. Oxygen was introduced into the bomb until the pressure was 25 atmospheres, at which point the bomb was immersed in the water. At least four minutes were allowed for thermal equilibrium before noting the temperature (26.1 to 26.7 °C) and starting the combustion. The final temperature was recorded 20 min after ignition unless the temperature failed to change for 3 min, in which case that temperature was the final one.

After the run was completed the internal surfaces of the bomb were washed with water which was collected for acid titration. The black residue in the sample pan was transferred to a tared porcelain filter crucible where it was washed and the rinse water added to that from the bomb. The rinse water was titrated with standardized NaOH to endpoints at pH's 4.7 and 8.7. The volume at the first endpoint was assigned to HNO_3 and the first proton from H_3PO_4 . The volume between the two endpoints was assigned to the second phosphoric acid proton.

The black residue was dried at 115 °C and two-thirds absolute atmospheric pressure and weighed. This mass was used as carbon for the purposes of correcting for incomplete combustion. The fuse remaining in wire form was weighed to determine how much was consumed.

In some cases it was desirable to eliminate the formation of HNO_3 during combustion. Repeating four times a cycle of pressurizing the bomb to 5 atmospheres and then

reducing it to atmospheric pressure prevented virtually all HNO_3 formation.

The solvents used in this study were those in use at the Atomic Energy Commission Hanford site. Samples of distilled DBBP and TBP were also used. Solvent mixtures were formulated using graduated cylinders as volume measures. Two molar HNO_3 was used for the contact studies in which one volume of organic was vigorously stirred with four volumes of acid for two to three hours. The heats of combustion are listed in Table I. The approximate water content of the contacted solutions is shown in Table II. The composition of NPH is shown in Table III.

DISCUSSION

The product of the temperature rise and the energy equivalent gives the amount of heat liberated. To convert this to a more accurate heat of combustion it is necessary to take into account the side reactions that occur in a bomb:

- Incomplete combustion.
- Acid formation.
- Fuse consumption.
- Change in the number of moles of gases.
- Condensation of water vapor.
- Reduction of data to standard state.

In this study incomplete combustion was compensated for by taking the weight of the filtered, washed, and dried residue as carbon. The correction for the heat of combustion of carbon, 8.11 kcal/mole,^[1] was added to the observed heat. If the dried residue exceeded 2.6% of the original

TABLE I
HEATS OF COMBUSTION
Heat of Combustion (calories/gram)

<u>Solvent</u>	<u>Gross [No Δ (PV) Correction]</u>	<u>Gross</u>	<u>Net Standard Deviation</u>	<u>Net kcal/mole</u>	<u>Number of Acceptable Runs</u>
NPH (C _{12.23} H _{26.45})	11,340	11,317	10,512 (22)	1820	4
Hexone	9,050	9,035	8,407 (70)	842.0	2
D2EHPA - Batch 1	7,970	7,955	7,435 (2)	2400	2
H ₂ O contact	7,780				1
HNO ₃ contact	7,796				1
- Batch 2	7,921	7,907	7,394	2384	1
Irradiated (1000 watt-hr ⁶⁰ Co/liter)	7,442				1
TBP - distilled	7,365	7,350	6,877 (59)	1932	3
- Batch 1	7,219	7,205	6,732	1793	1
H ₂ O contact	6,790				1
HNO ₃ contact	6,320				2
DBBP - distilled	8,012	7,996	7,513 (96)	1890	3
- Batch 1	7,920	7,905	7,455	1866	2
H ₂ O contact	7,042				1
HNO ₃ contact	6,502				2
TBP/NPH (20/80 vol)	10,298	10,277	9,554 (37)		2
HNO ₃ contact	10,170				2
0.3M D2EHPA + 0.2M TBP in NPH	10,602	10,582	9,813		1
HNO ₃ contact	10,556				3

TABLE II
WATER CONTENT OF CONTACTED SOLVENTS

<u>Solvent</u>	<u>Approximate Gross ΔH (cal/g) - no $\Delta(PV)$ Correction</u>	<u>Approximate Water Content Vol%</u>
TBP		
Batch 1	7,219	1-5
H ₂ O Contact	6,790	4-6
HNO ₃ contact	6,320	8-10
DBBP		
Batch 1	7,920	1-5
H ₂ O contact	7,042	5-8
HNO ₃ contact	6,502	10-12

TABLE III
COMPOSITION OF NPH

<u>Carbon Chain</u>	<u>Mol%</u>
C ₁₅ H ₃₂	0.087
C ₁₄ H ₃₀	14.679
C ₁₃ H ₂₈	31.853
C ₁₂ H ₂₆	25.938
C ₁₁ H ₂₄	19.844
C ₁₀ H ₂₂	7.174
C ₉ H ₂₀	<u>0.120</u>
	99.695

sample weight the run was disregarded as being too error-prone. Neither substituting a quartz sample pan nor increasing the oxygen pressure to 35 atmospheres solved the residue problem. Many of the runs had to be ignored because of the residue. During benzoic acid calibration any residue was unacceptable.

The formation and dissolution of HNO₃ during combustion evolves heat that is not related to the heat of combustion of the sample, and it must be subtracted. Through titration

the number of moles of HNO_3 is determined and the heat is discounted at the rate of 13.81 kcal/mole.^[1] This correction varied, but frequently accounted for 0.2 to 0.4% of the total heat. If the sample itself contained HNO_3 , the bomb was flushed to eliminate the need for this correction.

Many of the samples formed phosphoric acid in the bomb. The enthalpy correction will depend on the defined final state of the phosphorus $\text{P}_2\text{O}_5(\text{s})$, $\text{H}_3\text{PO}_4(\text{s})$, or H_3PO_4 (solution). The final state in this work is $\text{H}_3\text{PO}_4(\text{s})$, and the correction is for the heat of dissolution, 2.9 kcal/mole.^[1] These corrections amounted to less than 0.1% of ΔQ of the undiluted phosphorus-containing solvents. If the final state were $\text{P}_2\text{O}_5(\text{s})$ the additional correction for $\text{H}_3\text{PO}_4(\text{s})$ formation from $\text{P}_2\text{O}_5(\text{s})$ and $\text{H}_2\text{O}(\text{l})$, -36.1 kcal/mole (H_3PO_4), would have to be subtracted. This would amount to a reduction of about 2% or 136 cal/g TBP, 154 cal/g DBBP, or 125 cal/g D2EHPA.

The consumption of the fuse gave rise to another correction that is subtracted at the rate of 1400 cal/g. The amount varied widely around 15 calories or $\approx 0.3\%$ of the total energy.

A change in the number of moles of gas affects the enthalpy according to the relation:

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + \Delta n(RT)$$

In these experiments the correction never surpassed 0.2% of the energy involved in the combustion.

The presence of three milliliters of water in the bomb saturates the bomb, thus insuring that all of the water produced in the combustion condenses. At 26 °C this condensation evolves 10.48 kcal/mole.^[2] The energy supplied by

water condensation varies from solvent to solvent, but amounts to roughly 6 or 7% of the total measured energy.

The Washburn reduction to standard state^[3] is used to correct for several side reactions that occur in the bomb, including compression of condensed and gaseous phases, dissolution of gases in aqueous phase, changes in the vaporization of water with temperature, and acidity rise and dilution of the final acidic solution.

Some studies reported in the literature^[1,4] used organophosphorus compounds and experimental conditions similar to those used here. The corrections were calculated and amounted to 0.005 to 0.05% of the measured heat. These corrections were not evaluated in this current study because of the small effect.

The data indicate that the value of ΔH after aqueous contact varies inversely with the water content of the solvent. When the more polar HNO_3 molecules are present, additional water is contained in the organic solvent and depresses ΔH . The same effect might happen in the TBP, D2EHPA, or NPH mixtures; as the more polar TBP concentration increases the effect of HNO_3 contact would become more pronounced.

HEXONE

This volatile solvent, methylisobutyl ketone, indicated a ΔH gross of 905 kcal/mole. This is close to an unpublished value^[5] of 896 for methyl t-butyl ketone. A large volume of combustion data^[6] indicates that ΔH differs only slightly for different isomers.

NPH

The normal paraffin hydrocarbon (NPH) measured ΔH gross of 11,317 cal/g gives excellent agreement with an estimated value of 11,325 cal/g based solely on the composition of NPH (Table III). This value is close to that of kerosene,^[2]-- 11,006 cal/g. The density of NPH was measured as 0.745. The solvent density can be used to calculate the heat of combustion of solvent mixtures.

TBP

Tributyl phosphate (TBP) showed a lessened heat of combustion per gram after water contact, and contact with dilute HNO_3 depressed it even further. The plant TBP showed a slight depression relative to the distilled compound in agreement with the analysis that showed some water is present in the plant TBP. The density of TBP was measured as 0.973.

DBBP

The remarks about contacted TBP apply also to dibutylbutyl phosphonate (DBBP).

D2EHPA

The plant di(2-ethylhexyl) phosphoric acid (D2EHPA) gave an indication of a lowering of ΔH upon contact with water, but showed no further decrease after HNO_3 contact as did TBP and DBBP. Di(2-ethylhexyl) phosphoric acid was the only solvent burned after exposure to radiation (^{60}Co), and it demonstrated a lessened heat of combustion. The density of D2EHPA was determined to be 0.981.

TBP IN NPH

Based on the assumption that the enthalpy of mixing would not be detectable, an *a priori* relationship for the heat of combustion of mixtures of TBP/NPH was derived. Comparison of the experimental value of TBP/NPH, 20/80 (vol), with the calculated value shows a discrepancy of approximately 0.7%.

$$\Delta H = \frac{0.973QX + 0.745P(1-X)}{0.973X + 0.745(1-X)}$$

where

$$Q = \Delta H \text{ TBP}$$

$$P = \Delta H \text{ NPH}$$

$$X = \text{volume fraction of TBP (e.g., 0.20 in the example).}$$

TBP, D2EHPA IN NPH

Using the same approach as for the TBP/NPH case, the equation for the heat of combustion of this solvent mixture was derived. Comparison of the calculated ΔH gross with experiment for 0.3M D3EHPA and 0.2M TBP in NPH again shows a discrepancy of 0.7%.

$$\Delta H \text{ cal/liter} = 266.3YQ + 322.4ZT + P[745-204.9Y-244.8Z]$$

$$\Delta H \text{ cal/gram} = \frac{266.3YQ + 322.4ZT + P[745-203.9Y-244.8Z]}{62.4Y + 77.6Z + 745}$$

where

$$\text{TBP} = \underline{Y} \text{ molar in NPH}$$

$$\text{D2EHPA} = \underline{Z} \text{ molar in NPH}$$

$$T = \Delta H \text{ D2EHPA}$$

$$Q = \Delta H \text{ TBP}$$

$$P = \Delta H \text{ NPH}$$

FACTORS AFFECTING THE HEAT OF COMBUSTION

PRESSURE

This effect could be corrected for by the Washburn reduction to standard state, which was mentioned as being a very small correction.

INERT IMPURITIES

Water is the most important compound in this group and can affect the enthalpy change by requiring energy for vaporization and mixing. Water can substantially depress the heat of combustion if present in large amounts, diluting the solvent and thereby lowering ΔH . The presence of HNO_3 increases the water content of contacted solvents and further lowers the heat of combustion.

FLAMMABLE IMPURITIES, SOLVENT MIXTURES

The data confirm that solvent mixtures have an ΔH determined by the individual heat of combustion of the component and the fractional makeup of the mixture. The other possible effect, a change due to the heat of dissolution, is not significant. This is expected since in order to affect the heat of combustion of an equimolar solution of TBP and NPH by 1%, the heat of dissolution would have to be 36 kcal/mole.

The vigorously exothermic dissolution of H_2SO_4 in water yields only 18 kcal/mole.^[7] The heat of dissolution of these organics in one another would be expected to be much less.

INCOMPLETE COMBUSTION

The formation of soot and organic residues in a fire will lessen the heat output.

TEMPERATURE

The bomb calorimeter was unable to measure the effect of temperature because its operating range was temperature-limited. However, using estimated heat capacities for several solvents it was calculated that in order to affect the heat of combustion by 1% over the temperature range 27 to 77 °C, the solvent heat capacity would have to increase seven-fold, assuming a linear rise with temperature. Such a rise in the heat capacity over that temperature range, where an unusual compound might double its heat capacity, is highly improbable. The effect of temperature is negligible for the purposes of this report.

RADIATION

A single sample of irradiated solvent (D2EHPA) was run and it showed a significant decrease ($\approx 6\%$) in the heat of combustion. The dose was approximately 1000 watt-hr/liter of ^{60}Co radiation. Since irradiation affects ΔH by changing the identity of the solvent molecules, it is expected that the effects of low doses would go unnoticed in burning. The effect should be linear with dosage until very high doses are encountered.

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