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THERMOCHEMICAL AND KINETIC STUDIES OF PERFLUOROAROMATIC AND HALOGEN SUBSTITUTED PERFLUOROAROMATIC COMPOUNDS

BY

WAYNE F. J. YARED

A Dissertation
Submitted to the Faculty of Graduate Studies through the
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ABSTRACT

A new method has been developed in the present work for determining the heat of combustion of perfluoroaromatic and halogen substituted perfluoroaromatic compounds. The basic differences from previous methods are that no auxiliary substances are used and no water is present in the bomb. The combustion of both hexafluorobenzene and octafluorotoluene in a platinum lined bomb yields CO_2, CF_4, and F_2. The combustion of iodopentafluorobenzene in a platinum lined bomb yields CO_2, CF_4, IF_5, I_2, and F_2. In each case the material balance indicates that complete combustion is obtained. The value for $\Delta H^\circ_{f\ 298}(C_6F_6,g)$ obtained by this method is -223.9 kcal/mol, for $\Delta H^\circ_{f\ 298}(C_6F_5CF_3,g)$ is -300.2 kcal/mol, and for $\Delta H^\circ_{f\ 298}(C_6F_5I,g)$ is -104.3 kcal/mol.

Kinetic studies on iodopentafluorobenzene performed by the standard toluene carrier gas flow method yielded a value of 69.2 kcal/mol for $D[C_6F_5\text{-}I]$ based on a mechanism proposed by Krech and Price.

The determination of enthalpies of formation for C_6F_6, $C_6F_5CF_3$, and C_6F_5I along with the bond dissociation energy, $D[C_6F_5\text{-}I]$, allow for the calculation of $\Delta H^\circ_f(C_6F_5,g)$, $D[C_6F_5\text{-}F]$, and $D[C_6F_5\text{-}CF_3]$.

Une nouvelle méthode a été développée pour déterminer la chaleur de combustion des composés aromatiques perfluorés et des composés halogènes substitués aromatiques perfluorés. Les différences de base aux méthodes précédantes, sont l'absence de toute substance auxiliare et de l'eau dans la bombe. La combustion de l'hexafluorobenzène et de l'octafluorotoluène dans une bombe à revêtement de platine, conduit au CO_2,

CF_4, et F_2. La combustion de l'iodopentafluorobenzène dans une bombe à revêtement de platine, conduit au CO_2, CF_4, IF_5, I_2, et F_2. En chaque cas la balance pondérale indique une combustion complète. La valeur de $\Delta H^\circ_{f\ 298}(C_6F_6,g)$ obtenue par cette méthode est -223.9 kcal/mol, pour $\Delta H^\circ_{f\ 298}(C_6F_5CF_3,g)$ est -300.2 kcal/mol, et pour $\Delta H^\circ_{f\ 298}(C_6F_5I,g)$ est -104.3 kcal/mol.

La pyrolyse de l'iodopentafluorobenzène, étudiée dans un système à courant de toluène, conduit au valeur de 69.2 kcal/mol pour $D[C_6F_5-I]$ fondée sur un méchanisme proposé par Krech et Price.

Le détermination des chaleurs de formations de C_6F_6, $C_6F_5CF_3$, et C_6F_5I avec l'energie de dissociation, $D[C_6F_5-I]$, amène au calculation de $\Delta H^\circ_{f\ 298}(C_6F_5,g)$, et $D[C_6F_5-CF_3]$, et $D[C_6F_5-F]$.

PREFACE

> "The researcher must have a hypothesis that tells him what to look for. He can not merely ferret around like the Ashby fox, without purposes. He must have a method or design which persons competent in this particular subject would say was well calculated to turn up the data which would verify or refute the hypothesis. He must have the means and the instruments for measuring the data against the hypothesis, and for testing how far he has achieved what he has set out to do. The best, if not the only way of deciding whether these standards and procedures are adequately provided for the particular case, and whether satisfactory results have been achieved, is review by persons competent and experienced in the area of investigation."

The above statement was taken from Quest for the Optimum: A Report of the Commission to Study the Rationalization of University Research. It is within the framework of the ideas embodied in this statement that this dissertation is presented for review by persons 'competent and experienced' in the particular area of investigation under question.

No statement of printed words can adequately express the thanks that are owing to my research director, Dr. S. J. W. Price. His quest for the optimum and continual encouragement never faltered.

Special thanks must certainly also be extended to Drs. M. Krech, and J. Kominar for their involvement in this present work. Drs. W. Clark, M. Jacko, and J. Richard along with Dr. R. C. Rumfeldt generously provided helpful suggestions during the course of this work.

It is then to these people, together with a wonderful family, many friends, and a great research group, that I dedicate this dissertation.

W.F.J.Y.
February, 1973

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TABLE OF NOMENCLATURE

A, B, C	Moments of inertia of a molecule
C	Energy equivalent of a calorimeter system
C_{cf}	Heat capacity of the contents of a calorimeter system
C_{cor}	Corrected energy equivalent of a calorimeter system
C_f	Energy equivalent of a calorimeter system after combustion
C_p	Heat capacity at constant pressure
D[ ]	Bond dissociation energy
E_{exp}	Experimental activation energy
ε	Energy equivalent of the calorimeter and contents
F	Flow factor
h	Planck's constant
H	Enthalpy
$\Delta H^\circ_{f\ 298}$	Standard enthalpy of formation at 298°K
ΔH_{destab}	$\Delta H^\circ_f(g)(exptl) - \Delta H^\circ_f(g)(calc)$
K	Boltzmann's constant
k_i	Rate constant for process i
κ	Transmission coefficient
ℓ	Thermal leakage modulus
P	Pressure
p	Constant thermal powers
$\Phi(T)$	Total partition function
q_i	Heat from ignition energy
R	Universal gas constant
S	Entropy
σ	Symmetry number
t	Time

T, Θ	Temperature
ΔT_{cor}, $\Delta \Theta_{cor}$	Corrected temperature rise
u	Energy absorbed by a system other than in the form of heat or PV work
t_c	Contact time
t_r	Retention time
V	Volume
ν	Vibrational frequency
w	PV type work
w_g	Weight of a substance in the vapour state
x	Fraction decomposed

CHAPTER I

INTRODUCTION

Introductory Concepts and Definitions

The strength of the chemical bond is of prime importance for the quantitative treatment of chemical reactions. There are several interpretations which can be made of the term bond strength. Bond strength can be viewed as the quantity of energy that is required to break a bond or it can be interpreted as a bond energy term which is characteristic of each bond and which, when summed over all of the bonds in a molecule, yields its heat of formation from atoms.

When the expressions "bond dissociation energy" and "bond strength" are used interchangeably it becomes necessary in the determination of the energy required to break a specific bond to determine with sufficient exactness the fragments into which the molecule is broken. The dissociation energy, $D[R_1\text{-}R_2]$, in the molecule R_1R_2 is the endothermicity of the reaction where R_1R_2 is decomposed into the fragments R_1 and R_2 under the provision that the recombination of R_1 and R_2 proceeds with zero activation energy (1). This endothermicity is calculated for both reactants and products at absolute zero in the ideal gas state.

$$R_1R_2 \rightarrow R_1 + R_2 \qquad [1.1]$$

Considering equation [1.1];

$$D[R_1\text{-}R_2] = \Delta H_f^\circ(R_1) + \Delta H_f^\circ(R_2) - \Delta H_f^\circ(R_1\text{-}R_2) \qquad [1.2]$$

where ΔH_f°, the heat or enthalpy of formation, should properly be referred to 0°K. $\Delta H_f^\circ(R_1\text{-}R_2)$ can generally be determined from ordinary thermochemical results and thus if $D[R_1\text{-}R_2]$ is determined and $\Delta H_f^\circ(R_1)$ is

known for the case where $R_1 = R_2$, $\Delta H_f^\circ(R_2)$ can often be determined. Thus the derivation of one bond energy term may lead to the computation of an entire series of dissociation energies involving that common radical by the sequential use of Hess's Law. Therefore bond dissociation energies and enthalpies of formation can be seen to be integrally interrelated.

Determination of Enthalpies of Formation

Enthalpies of formation, determined from heats of reaction, are found calorimetrically. Calorimetric methods involve the determination of the temperature rise of a given amount of a calorimetric fluid when the process under investigation liberates heat. This determination must be coupled with an independent determination of the energy equivalent of the calorimetric system, either by electrical calibration or by comparison with a reaction of known heat content.

The flame, reaction, and bomb calorimeters are three types of calorimetric apparatus used to measure enthalpies of formation. The bomb calorimeter, which is used almost exclusively in the present work, is a constant volume system in which a reaction occurs under oxygen pressure. The energy released is usually of the order of several thousand calories. The enthalpies of formation of the commonly formed products are normally well established in bomb calorimetry and the instrumentation for energy measurement is well developed.

Determination of Bond Dissociation Energies

The estimation of bond dissociation energies by bond breaking pro-

cesses can be divided into three main divisions, governed by the method in which energy is supplied to the dissociation molecule (2). When energy is in the form of radiation, dissociation energy investigations can be based on absorption spectra, predissociation phenomena, photodecomposition, and photosensitized decomposition. While the first two methods are limited to simple molecules, the latter two only provide an upper limit for the dissociation energy.

In the determination of dissociation energy by electron impact methods, the fragments formed may possess excess kinetic energy. This mathod only produces an upper limit bond dissociation energy.

If the energy supplied is in the form of thermal energy, dissociation energies can be determined by either the equilibrium or the kinetic method.

The equilibrium method measures the equilibrium constant of the reaction in the gas phase where

$$R_1R_2 \rightarrow R_1 + R_2 \qquad [1.1]$$

While the equilibrium method is well suited for diatomic molecules, it is sometimes difficult to apply to the case where radicals are involved due to a combination of attack by the radicals formed on the parent species and reactions between the radicals formed which might lead to products other than the parent compound.

With the kinetic method the assumption is made, and supported by experimentation for small molecules, that the reverse process has zero activation energy. Thus the activation energy, E_{exp}, in a unimolecular process is equated to the bond dissociation energy. The accuracy of the determination of bond energy terms by this method depends, naturally, on the accuracy of the rate constant and on the extent of the temperature range used.

Nature of the Present Research

Presently, there is only limited thermochemical information available on perfluoroaromatic and halogen substituted perfluoroaromatic compounds. A study of their thermodynamic properties is warranted by the increasing importance of many of these compounds to the chemical industry.

The present thermochemical work was undertaken with the aim of developing a more direct method of determining the enthalpies of formation of this group of compounds. The only previous thermochemical studies on this class of compounds was performed by Cox and coworkers (3) using auxiliary materials and water in the combustion bomb. The compounds studied included C_6F_6, $C_6F_5CH_3$, C_6F_5OH, C_6F_5H, and C_6F_5Cl. No previous thermochemical work is reported for $C_6F_5CF_3$ and C_6F_5I. The present work describes thermochemical and kinetic studies on perfluoroaromatic and halogen substituted perfluoroaromatic compounds; specifically, C_6F_6, $C_6F_5CF_3$, and C_6F_5I. The latter compound is the only one to be the subject of a kinetic investigation.

Since each of the compounds studied in the present work as well as all those investigated by Cox (3) contained a common C_6F_5 group, it was thought to be most useful to find ΔH_f° (C_6F_5); a value which would lead to the determination of various $D[C_6F_5\text{-}X]$ because $\Delta H_f^\circ(X)$ is already known.

To determine $\Delta H_f^\circ(C_6F_5)$ it was necessary to investigate one of the compounds chosen for study both thermochemically and kinetically. It was felt to be advantageous to carry out this kinetic study in a toluene carrier flow system so that the toluene might act as a radical scavenger. C_6F_5I was chosen as the subject of the kinetic investigation since it was expected that $D[C_6F_5\text{-}I]$ would be sufficiently low as to allow the kinetic work to be performed at temperatures low enough to prevent decomposition of the toluene carrier.

CHAPTER II

THEORETICAL CONSIDERATIONS

Calorimetric Determination of Bond Energies

General Precepts

For any thermochemical investigation, it is the quantity of energy associated with a unit amount of a given chemical reaction or physical process that is determined (4). As well as the determination of the energy and extent of the process under investigation, it is necessary to determine the nature of the thermodynamic property involved, the temperature of the process, and the corrections required to refer the process to a standard or reference state.

Factors which may influence the value of the energy associated with a reaction or process such as temperature, concentration, pressure, and state of the material must be specified with an accuracy warranted by their individual effects on the value of the measured energy if any degree of significance is to be attached to this measured energy. With the reactants and products so defined, it becomes a simple matter to correct each quantity to its thermodynamic standard state.

As the thermodynamic property measured is either a change in internal energy, ΔE, or a change in the heat content or enthalpy, ΔH, it is important to specify which quantity is under consideration. From the first law of thermodynamics

$$\Delta E = q + w + u \qquad [2.1]$$

where q is the energy absorbed in the form of heat, w is any PV work done on the system, and u is other energy absorbed by the system and is

normally zero since it is involved with such things as changes in motion of the entire system or variations in electric or magnetic field strengths.

At constant volume, V, $P\Delta V = 0$ and $\Delta E = q$, the heat absorbed by a process occurring in a calorimeter at constant volume.

At constant pressure, P, $V\Delta P = 0$ and $w = -P\Delta V$. Substitution into [2.1] gives

$$\Delta E = q - P\Delta V \qquad [2.2]$$

so that

$$\Delta E + P\Delta V = q \qquad [2.3]$$

and

$$\Delta E + \Delta PV = \Delta(E + PV) = q \qquad [2.4]$$

If a definition is stated such that

$$E + PV = H \qquad [2.5]$$

then

$$\Delta H = q \qquad [2.6]$$

Thus for a process in a calorimeter at constant pressure, the heat absorbed by the process is the change in enthalpy, ΔH.

The difference between ΔE and ΔH may be evaluated for a specified process from the relation

$$\Delta H = \Delta E + \Delta PV \qquad [2.7]$$

Any thermochemical process consists of a calorimetric part, involving the determination of a quantity of energy evolved, and a chemical part, involving the measurement of the extent of the given reaction or process which has occurred.

The calorimetric part consists of a determination of the energy equivalent of the calorimeter either by use of a known amount of elect-

rical energy to produce a temperature rise or by use of a known amount of a chemical reaction of well characterized reaction heat. Since the energy equivalent is defined as the known amount of energy divided by the temperature rise it produces, it is intuitive that for the same calorimeter an equal temperature rise produced by a reaction of unknown energy will have released the same energy.

The determination of the nature and completeness of the chemical reaction constitutes the chemical part of a thermochemical investigation. It is preferable that the reaction produces a limited number of products in well defined thermodynamic states, enabling the determination of the completeness of the reaction either by measurement of the amount of one of the reactants consumed or, as is more often the case, by identification and measurement of the products of the reaction.

A method must be determined for correcting the heat evolved from a chemical reaction to a standard state, namely 298°K. At constant pressure

$$\Delta H = H_{products} - H_{reactants} \qquad [2.8]$$

Differentiating with respect to temperature, T

$$\delta\Delta H/\delta T = \delta H_{prod}/\delta T - \delta H_{react}/\delta T \qquad [2.9]$$

But, by definition, $\delta H/\delta T$ (at constant pressure) is the heat capacity at constant pressure, C_p. Therefore,

$$\delta\Delta H/\delta T = C_{p(prod)} - C_{p(react)} = \Delta C_p \qquad [2.10]$$

It is thus only required to know the difference in heat capacities of the products and reactants to determine the variation of the heat of reaction with temperature.

When the calorimetric investigation is not done at the pressure

defined in the standard state definition the first and second laws allow

$$dE = T\,dS - P\,dV \qquad [2.11]$$

so that

$$\frac{\delta E}{\delta T}\,dT + \frac{\delta E}{\delta P}\,dP = T\frac{\delta S}{\delta T}\,dT + T\frac{\delta S}{\delta P}\,dP - P\frac{\delta V}{\delta T}\,dT - P\frac{\delta V}{\delta P}\,dP \qquad [2.12]$$

and

$$\left(\frac{\delta E}{\delta P} - T\frac{\delta S}{\delta P} + P\frac{\delta V}{\delta P}\right)dP + \left(\frac{\delta E}{\delta T} - T\frac{\delta S}{\delta T} + P\frac{\delta V}{\delta T}\right)dT = 0 \qquad [2.13]$$

For the relation to hold

$$\frac{\delta E}{\delta P} = T\frac{\delta S}{\delta P} - P\frac{\delta V}{\delta P} \qquad [2.14]$$

and since

$$\frac{\delta S}{\delta P} = -\frac{\delta V}{\delta T} \qquad [2.15]$$

$$\frac{\delta E}{\delta P} = -T\frac{\delta V}{\delta T} - P\frac{\delta V}{\delta P} \qquad [2.16]$$

and it becomes important to find $\delta V/\delta T$ and $\delta V/\delta P$ data for the quantities concerned. For the enthalpy

$$H = E + PV \qquad [2.5]$$

$$\frac{\delta H}{\delta P} = \frac{\delta E}{\delta P} + P\frac{\delta V}{\delta P} + V \qquad [2.17]$$

Substitution and simplification give

$$\frac{\delta H}{\delta P} = -T\frac{\delta V}{\delta T} + V \qquad [2.18]$$

The temperature assigned to a reaction is either that at which the reactant material is at at the beginning of the calorimetric experiment or is the one that all products material is at at the conclusion of the experiment.

Rotating Bomb Calorimetry

One of the most well developed areas of thermochemistry is the degradative oxidation of organic compounds. The reaction is usually caried out at constant volume under a pressure of approximately thirty atmospheres of oxygen. The reaction vessel is a corrosion resistant steel tubular vessel of about 0.35 litres in internal volume having a screw on cap equipped with valves for the introduction and emission of gases. This vessel is normally termed a bomb. The bomb, containing the sample in a crucible suspended in a gimbal, is immersed in a can of water, the temperature of which rises on ignition of the sample by electrical means. From the measured temperature rise of the water in the can, supplemented by a prior determination of the energy equivalent of the system, the amount of heat liberated by the combustion of the sample can be determined.

Often, the limiting part of a thermochemical investigation is more the chemical than the calorimetric part of the determination (5). It is necessary to have sufficient analytical and physicochemical data to precisely define the amount and states of reactants and products. Such data include: (a) the mass, purity, and state of the primary reactant; and, (b) the masses, chemical nature, and states of the products.

The rotating or moving bomb calorimeter, the use of which was not an absolute necessity for the present experimental work, provides a means for producing a final state of the bomb process that is easy to characterize both chemically and thermodynamically in certain cases.

Calibration of the Bomb with Benzoic Acid

Benzoic acid is often chosen as a calorimetric standard substance because it (a) can be obtained in a stable solid form; (b) can be purified relatively easily; (c) is not noticeably volatile at ordinary room temperatures; (d) does not absorb moisture from the atmosphere; (e) burns quantitatively in the calorimetric bomb; and, (f) can be compressed into tablets (6).

Only if the following conditions are met can the certified value of the heat of combustion for benzoic acid be used to determine the energy equivalent of the calorimeter. These conditions are that (a) the combustion reaction is referred to 298°K.; (b) the sample is burned in a bomb of constant volume in pure oxygen at an initial pressure of thirty atmospheres at 298°K.; (c) the number of grams of benzoic acid burned is equal to three times the internal volume of the bomb in litres; and, (d) the number of grams of water placed in the bomb prior to combustion is equal to three times the internal volume of the bomb in litres.

Small departures from the above conditions are allowed but these require the use of the correction factor

$$f = 1 + 10^{-6}[(20)(P-30) + 42(M_s/V-3) + 30(M_w/V-3) - 45(T-298)] \quad [2.19]$$

where P is the initial pressure in atmospheres of the oxygen at the temperature T, to which the reaction is referred. M_s is the mass of the benzoic acid in grams and M_w is the mass of the water placed in the bomb in grams while V is the internal volume of the bomb in litres. The value of the heat of combustion of benzoic acid as supplied by the Parr Instrument Company is 6318. cal/g.

If the quantity of heat released by a sample of benzoic acid, q,

produces a net temperature rise, ΔT, the energy equivalent of the calorimeter system, C, may be defined as

$$C = q/\Delta T \qquad [2.20]$$

Besides the heat from the combustion of the benzoic acid, there are also contributions from the ignition energy, q_i, and the energy from the formation of nitric acid due to the presence of small amounts of nitrogen in the bomb, q_n. Therefore the energy equivalent of the system after combustion may be written as

$$C_f = (q + q_i + q_n)/\Delta T \qquad [2.21]$$

However, to define a system which is invariant from calibration to calibration, it is necessary to exclude the energy equivalent of the products, so that

$$C_{cor} = C_f - C_{cf} \qquad [2.22]$$

where C_{cf} is calculated from the heat capacities of the crucible, oxygen, carbon dioxide, and water in the bomb at the end of the combustion of benzoic acid. Also included should be the specific heats and differences in mass of any other materials present in different amounts in the standard calorimeter systems and the system as actually used.

Evaluation of the Corrected Temperature Rise

In isoperibol calorimetry, the temperature change of the calorimeter during the main period of a combustion experiment is generally not determined solely by the amount of heat liberated or absorbed by the particular process under investigation. Part of the change is due to heat exchange with the environment and to extraneous thermal effects within the calorimeter such as heat of stirring. The term "corrected temperature rise" is defined as the temperature change which the cal-

orimeter would have experienced in the absence of these perturbations (neglecting thermal gradients within the calorimeter, the effect of which is minimized by the method of comparative experiments) (7). This term multiplied by the energy equivalent of the calorimeter gives the amount of heat attributable to the process under investigation.

A method has been described by Dickinson (8) wherein tangents to the time-temperature curves at the beginning and the end of the main period are extrapolated to a defined time such that the difference of their values at that time is equal to the corrected temperature rise. The extrapolated time is determined from a graphical integration of the time-temperature curve during the main period.

The temperatures of the calorimeter during the initial, main, and final periods are designated as Θ_1, Θ_2, and Θ_3 respectively. The rate of change of temperature during the initial and final periods can be described by Newton's Law.

$$g = d\Theta/dt = \mu + \ell(\Theta_j - \Theta) \qquad [2.23]$$

where

$$\mu = p/\varepsilon \qquad [2.24]$$

and p represents the sum of all constant thermal powers in the calorimeter while ε is the energy equivalent of the calorimeter and its contents. ℓ is defined as the thermal leakage modulus and Θ_j is the jacket temperature.

If $d\Theta/dt = 0$ in equation [2.23] and Θ_∞ is defined as a convergence temperature which Θ approaches with increasing time, then

$$\Theta_\infty = \Theta_j + \mu/\ell \qquad [2.25]$$

Substitution of [2.25] into [2.23] gives

$$g = d\Theta/dt = \ell(\Theta_\infty - \Theta) \qquad [2.26]$$

Integrating [2.26] for Θ_1 and Θ_3 yields

$$\Theta_1 = \Theta_\infty - (\Theta_\infty - \Theta_b)\exp[-\ell(t-t_b)] \qquad [2.27]$$

$$\Theta_3 = \Theta_\infty - (\Theta_\infty - \Theta_e)\exp[-\ell(t-t_e)] \qquad [2.28]$$

where Θ_b and Θ_e are temperatures at times t_b and t_e which represent the beginning and the end of the main period respectively.

It is assumed that μ, ℓ, and Θ_j are constant and that equation [2.26] is a representation of that part of the temperature change in the main period due to heat exchange with the environment and to the constant thermal powers, p, within the calorimeter. Thus the corrected temperature rise may be written as

$$\Delta\Theta_{cor} = \Theta_e - \Theta_b - \delta\Theta \qquad [2.29]$$

where

$$\delta\Theta = \ell \int_{t_b}^{t_e} (\Theta_\infty - \Theta_2)dt \qquad [2.30]$$

The thermal leakage is calculable from

$$\ell = (g_i - g_f)/(\Theta_f - \Theta_i) \qquad [2.31]$$

where equation [2.31] is derived from equation [2.26] and g_i and g_f are the values of $d\Theta/dt$ at the mean temperatures Θ_i and Θ_f of the initial and final periods. Rearranging [2.26] yields a value for the convergence temperature

$$\Theta_\infty = \Theta_f + g_f/\ell = \Theta_i + g_i/\ell \qquad [2.32]$$

Equations [2.27], [2.28], and [2.29] are exact insofar as the assumption that μ, ℓ, and Θ_j are constant is valid. Since the exponents $\ell(t - t_b)$ and $\ell(t - t_e)$ are generally quite small, [2.27] and [2.28] may take on the form of a quadratic expression. Rewriting [2.27] and [2.28] so that they each approximate the equation of a straight line into which the time-temperature data of the initial and final periods may be fit

yields

$$\Theta_1 = \Theta'_b + g'_i(t - t_b) \qquad [2.33]$$

$$\Theta_3 = \Theta'_e + g'_f(t - t_e) \qquad [2.34]$$

The "corrected temperature rise" from these linear equations is then

$$\Delta\Theta'_{cor} = \Theta'_e - \Theta'_b - \delta\Theta' \qquad [2.35]$$

where

$$\delta\Theta' = \ell' \int_{t_b}^{t_e} (\Theta'_\infty - \Theta_2)dt \qquad [2.36]$$

$$\ell' = (g'_i - g'_f)/(\Theta_f - \Theta_i) \qquad [2.37]$$

$$\Theta_\infty' = \Theta_f + g'_f/\ell' = \Theta_i + g'_i/\ell' \qquad [2.38]$$

The difference between the two corrected temperature rises represented in equations [2.29] and [2.35] is

$$\Delta\Theta_{cor} - \Delta\Theta'_{cor} = (\Theta_e - \Theta'_e) - (\Theta_b - \Theta'_b) \qquad [2.39]$$

The difference $(\Delta\Theta'_{cor} - \Delta\Theta_{cor})$ is sufficiently small and constant so that $\Delta\Theta'_{cor}$ may be used in place of $\Delta\Theta_{cor}$. Dickinson showed that

$$\Delta\Theta_{cor} = \Theta_{3xa} - \Theta_{1xa} \qquad [2.40]$$

where

$$\Theta_{1xa} = \Theta_b + g_b(t_{xa} - t_b) \qquad [2.41]$$

$$\Theta_{3xa} = \Theta_e + g_e(t_{xa} - t_e) \qquad [2.42]$$

if the time, t_{xa}, is selected so that

$$\int_{t_b}^{t_{xa}} (\Theta_2 - \Theta_b)dt = \int_{t_{xa}}^{t_e} (\Theta_e - \Theta_2)dt \qquad [2.43]$$

or so that the shaded areas in Figure 1 are equal. The time, t_{xa}, is that time when the temperature rise has reached sixty per cent of its total amount (9) and is the point when the calorimeter is no longer heated at a rate equivalent to that in the initial period and begins to

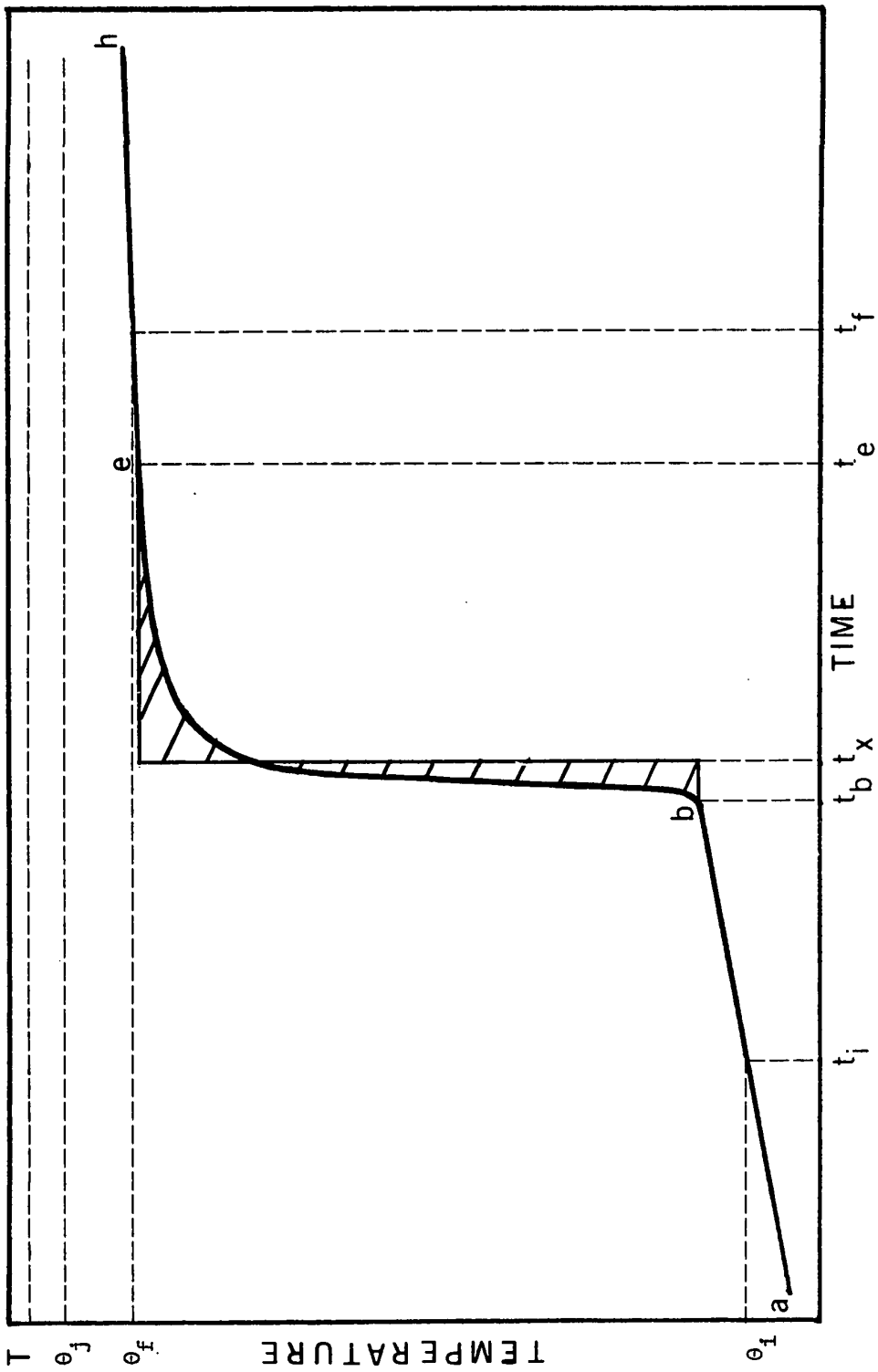


Figure 1: A time-temperature curve for a bomb calorimetric experiment

be heated or cooled at the rate as in the final period.

Calorimeter Design and Temperature Measurement

The determination of the corrected temperature rise is based on the validity of equation [2.23]. It has been found that this equation is valid over the range of temperature differences usually encountered in bomb calorimetry (10, 11) provided the following conditions are satisfied: (a) no insulating material other than air can be used in the space between the calorimeter and the jacket; (b) the thickness of the air space between the calorimeter and the jacket must not exceed 12 mm (for a 3° maximum temperature difference between the calorimeter and the jacket); and, (c) the evaporation of water from the calorimeter must be reduced to a minimum.

The scale of temperature measurement used in bomb calorimetric measurements is, in itself, unimportant. The commonly used temperature measuring instruments are mercury-in-glass thermometers, platinum resistance thermometers, thermocouples, and thermistors.

The mercury-in-glass thermometer has the advantage that it provides a direct reading, and is relatively inexpensive. Short-interval mercury thermometers, particularly the Beckmann type, are quite satisfactory for calorimetric measurement of moderate precision since they are able to be read, with a lens, to 0.002°C. The mercury-in-glass thermometer is subject to several sources of error arising from secular changes in bulb volume, effect of pressure, exposure of the stem and irregular movement of the meniscus (12).

The platinum resistance thermometer is both accurate and reproducible in performance and is thus suited for high precision temperature

measurement. The main disadvantage of the platinum resistance thermometer is the expense of the thermometer and resistance bridge.

In the case of thermocouples, in order to obtain a high degree of accuracy, they must be constructed from carefully selected wires which do not contain regions of inhomogeneity. The e.m.f. developed by a thermocouple is usually quite small, and the accuracy of measurement of it will depend largely on the type of potentiometer used.

The most striking characteristic of the thermistor is the very high negative temperature coefficient of resistance. The greater response of the thermistor as compared to both the platinum resistance thermometer and the thermocouple allows much more latitude in the choice of instruments for measuring the change in resistance, thus allowing for detection of a temperature change of the order of 0.0001°C with a Wheatstone bridge and mirror galvanometer. However, in using thermistors for temperature measurement, as was the case in the present experimental work, it is necessary to take precautions to ensure reproducible behaviour or, failing that, to recalibrate the thermistor periodically.

For the relatively small temperature range usedin calorimetric work the relationship (13)

$$\ln R = A/T + B \qquad [2.44]$$

where ln R is the natural logarithm of the thermistor resistance, R, and T is the absolute temperature, is valid. The constants A, B are determined by a plot of ln R versus 1/T.

Kinetic Determination of Bond Energies

General Precepts

Transition state theory (14) predicts that the rate constant for a unimolecular reaction is

$$k = \kappa \frac{KT}{h} \frac{\Phi^*(T)}{\Phi\ (T)} e^{-D/RT} \qquad [2.45]$$

where $\Phi(T)$ and $\Phi^*(T)$ are the total partition functions for the normal molecule and the activated complex, respectively.

These total partition functions $\Phi(T)$ and $\Phi^*(T)$ may be divided into their translational, rotational, and vibrational components.

The translational portion of the partition function is

$$\Phi_t(T) = (2\pi mKT)^{3/2}/h^3 \qquad [2.46]$$

and it will be the same for both $\Phi(T)$ and $\Phi^*(T)$.

The rotational partition function is

$$\Phi_r(T) = 8\pi^2(2\pi mKT)^{3/2}(ABC)^{1/2}/h^3 \qquad [2.47]$$

As in the translational case, the rotational partition function will be the same for both $\Phi(T)$ and $\Phi^*(T)$.

If each mode of internal vibration behaves as a harmonic oscillator, the expression for the rate constant, k, becomes

$$k = \kappa \frac{\sigma}{\sigma^*} \frac{(A^*B^*C^*)^{1/2}}{(ABC)} \frac{3n-7}{3n-6} \frac{(1 - e^{-h\nu^*/KT})}{(1 - e^{-h\nu/KT})} e^{-D/RT} \qquad [2.48]$$

If the temperature is relatively high such that $h\nu << KT$, the terms $(1 - e^{-h\nu/KT})$ may be replaced by $KT/h\nu$, such that

$$k = \kappa \frac{\sigma}{\sigma^*} \frac{(A^*B^*C^*)^{1/2}}{(ABC)} \frac{3n-6}{3n-7} \frac{\nu}{\nu^*} e^{-D/RT} \qquad [2.49]$$

For the case where $h\nu >> KT$, taking natural logaritms of equation [2.48] and differentiating with respect to T yields

$$\frac{d(\ln k)}{dT} = D/RT^2 \qquad [2.50]$$

Thus examining equation [2.50], it can be seen that the Arrhenius activation energy $E_{exp} = D$.

Performing the same operation on equation [2.49] where $h\nu << KT$ yields

$$\frac{d(\ln k)}{dT} = (D + RT)/RT^2 \qquad [2.51]$$

Equation [2.5]] yields $E_{exp} = D + RT$, and hence

$$D \leqslant E_{exp} \leqslant D + RT \qquad [2.52]$$

It should be mentioned that in the preceeding discussion the experimental energy involved is the high pressure activation energy determined in the pressure independent region.

Toluene Carrier Gas Technique

The toluene carrier gas technique is an elegant and useful method of ensuring that complicating side reactions do not confuse the kinetics of unimolecular dissociation reactions.

Generally in order to measure the activation energy of a process such as

$$R_1R_2 \rightarrow R_1 + R_2 \qquad [1.1]$$

it is necessary to be able to determine the rate of the primary dissociation process. In order to accomplish this accurately, the strength of the bond under study must be considerably less than that of any other bond in the molecule. The primary dissociation process is followed by reactions of the radicals produced either with themselves or with other undecomposed molecules.

The primary dissociation process may be isolated to some extent

by using a flow system in which reactants pass through the hot reaction zone in a short time so that the radicals produced have little time to undergo subsequent reaction. However, even very high flow rates would not, in all probability, eliminate all reaction and these high flow rates would cause problems in thermal equilibrium.

The use of a scavenger which does not lend itself to the initiation of chain processes combines the advantages of a flow system and allows for contact times which do not produce thermal equilibrium difficulties. Toluene overcomes the threat of chain processes by producing benzyl radicals on reaction with other radicals (15).

$$C_6H_5.CH_3 + R \rightarrow C_6H_5.CH_2 + RH \qquad [2.53]$$

Under the conditions normally used, benzyl radicals are thermally stable and are removed either by combination with a radical or dimerization.

The toluene carrier gas technique may be used at temperatures which produce decomposition of the toluene itself provided that either the products coming from this fragmentation process are identifiable or that suitable corrections for this fragmentation are made (16).

CHAPTER III

DETERMINATION OF ENTHALPIES OF FORMATION

Materials

Hexafluorobenzene

The hexafluorobenzene used was obtained from the Imperial Smelting Corporation and was analyzed by means of a gas chromatograph equipped with a thermal conductivity detector using a 6 ft x 1.4 in. o.d. polypropylene glycol column. The column temperature was 110°C and the flow rate of helium, which was used as the carrier gas, was set at 60 cc/m. The only detectable impurity was approximately 0.02% pentafluorobenzene.

Physical properties of the compound including index of refraction, boiling point, and melting point, were measured and compared to those previously published (17). These values are shown in Table 1.

Octafluorotoluene

The octafluorotoluene used was obtained from the Imperial Smelting Corporation and was fractionally distilled to remove any impurities which might be present. Analysis by means of a gas chromatograph equipped with a thermal conductivity detector and using a 6 ft x 1/4 in. o.d. polypropyleneglycol column operated at 110°C with a helium carrier flow rate of 60 cc/m showed approximately 0.01% impurity.

Physical properties of this compound including index of refraction, boiling point, and specific gravity were measured and compared to

published values (17). These values are shown in Table 1.

Iodopentafluorobenzene

The iodopentafluorobenzene used was obtained from the Imperial Smelting Corporation and was fractionally distilled to remove any traces of impurities which might be present. Analysis was done by a gas chromatograph equipped with both a flame ionization and electron capture detector and fitted with a 6 ft x 1/8 in. o.d. Silicone Oil DC-710 column operated at 105°C with a nitrogen carrier gas. The compound showed approximately 0.01% impurity.

Physical properties of the compound including index of refraction, boiling point, and specific gravity were measured and compared to published values (17). These values are shown in Table 1.

Sodium Arsenite Solution

The arsenic (III) oxide used was obtained from Anachemia Chemicals Limited. 2.4725 g of dry arsenic (III) oxide were completely dissolved in 20 ml of 1N sodium hydroxide solution. To achieve neutrality, 1N sulphuric acid was added. The solution was diluted to 500 ml to produce a 0.1N sodium arsenite solution.

When $5 \leqslant pH \leqslant 9$ the titration is accurate to ±0.1% (18), however when $pH \lesssim 5$ the reaction is retarded and the end point is vague. The pH may be adjusted to the correct range by the careful addition of sodium bicarbonate solution.

Table 1: Physical Properties of Perfluoroaromatic and Halogen Substituted Perfluoroaromatic Compounds

Compound	Source	Index of Refraction n_D^{25}	Boiling Point °C	Melting Point °C	Specific Gravity g/ml
Hexafluorobenzene	Present Work	1.3762	80.1	5.2	
	Ref. (17)	1.3761	80.	5.2	
Octafluorotoluene	Present Work	1.3649	103.8		1.762
	Ref. (17)	1.3656	104.		1.766
Iodopentafluorobenzene	Present Work	1.4954	165.		2.114
	Ref. (17)	1.4950	166.		2.2122

Apparatus

The rotating bomb calorimeter used, as shown in Figure 2, made from plated brass, was similar, in design, to that used in the Bureau of Mines Laboratories, Bartlesville (19). The major modification was the rotating mechanism which involved the use of a low r.p.m. high torque motor coupled to the rotating mechanism on the bomb by a series of gears and shafts. The shaft going through the lid of the calorimeter was of two portions, one fixed, and one capable of being raised and lowered which allowed coupling to the gear on the motor when rotation was desired.

The stirring and circulation of water in the calorimeter jacket and lid was accomplished by a blade stirrer and a circulating pump driven by two Electrohome 115 V, 1.25 amp motors of r.p.m. 1550. One of these motors, as well as driving the circulating pump, also supplied power to the blade stirrer in the calorimeter bucket.

The calorimeter jacket contained two circular heaters, one 500 watt and one 250 watt, and a set of cooling coils. Cool, thermostated water from an external bath regulated to 16 ±0.01°C, was circulated through the coils and worked against the heaters in keeping the jacket at 25.000°C. The temperature of the external bath was monitored by a Häcke temperature controller working against a cooling coil from a portable cooling unit supplied by Precision Scientific Company. Power to the circular heaters contained in the calorimeter jacket was supplied by a Thermotrol Proportional Temperature Controller, Model 1053. This device allowed the temperature of the jacket to be controlled to ±0.001°C.

In addition to the blade stirrer and part of the rotating mechan-

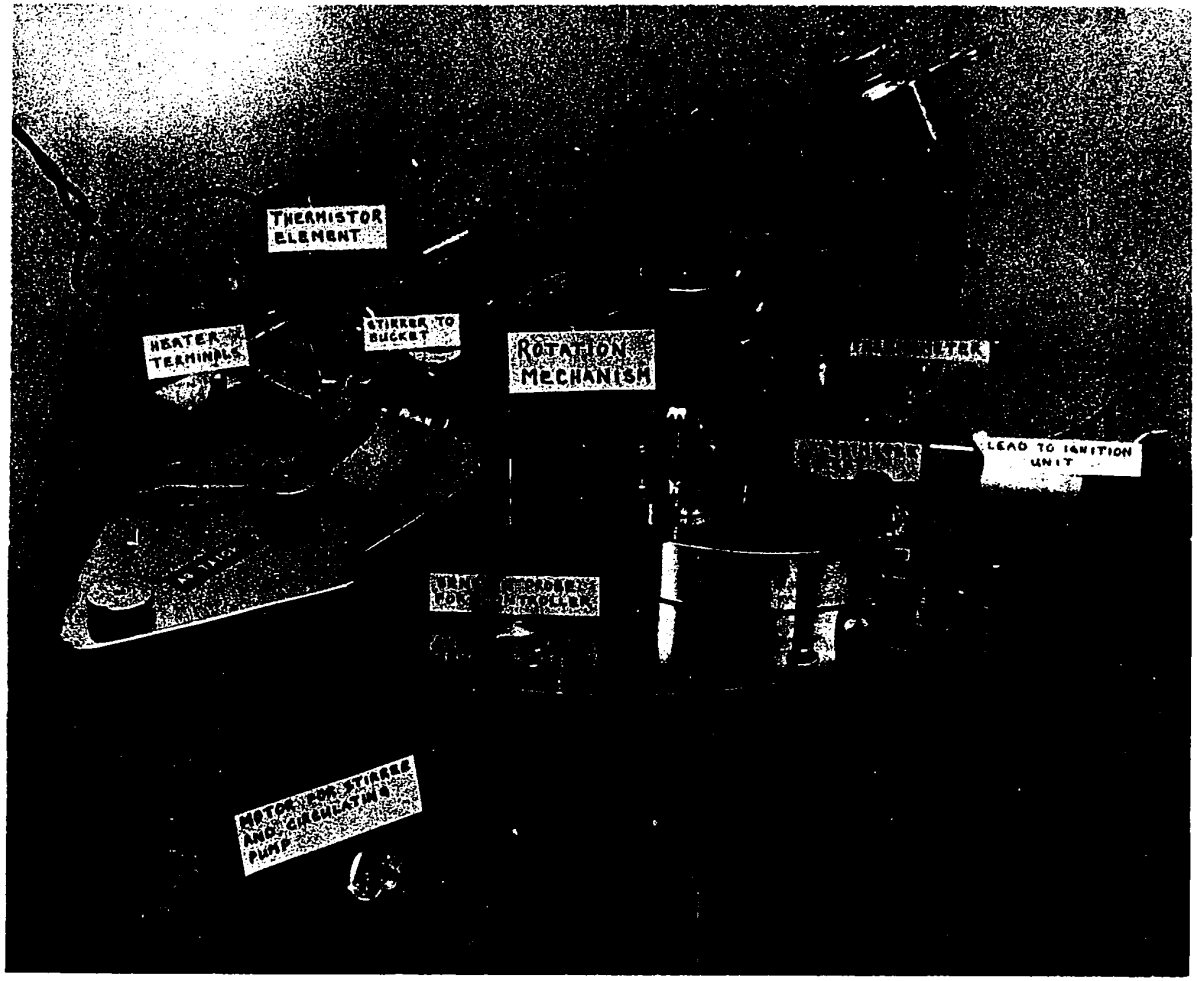


Figure 2: A photograph of the rotating bomb calorimeter (20)

ism, as illustrated in Figure 3, the calorimeter bucket also contained a 15 watt rod heater and the mechanism for coupling the bomb to the ignition unit. The rod heater was used to adjust the temperature of the water in the calorimeter bucket to a desired starting point. The coupling mechanism involved a spring clip which released when the rotation mechanism was activated.

The rotating bomb calorimeter was used only as a matter of convenience in the present work. A static system of the same precision would have worked equally as well provided it was equipped with a platinum lined bomb.

The temperature of the water in the bucket was monitored by a 2000 ohm thermistor used in conjunction with a Honeywell Wheatstone Bridge, Model 1081 and a Leeds and Northrup D. C. Null Detector with variable sensitivity. The thermistor was calibrated against a Parr certified thermometer capable of being read to ±0.001°C. The resistance of the thermistor could be estimated to 0.01 ohm (about 0.0001°C) with the null detector set at low to moderate sensitivity. Time was measured and recorded on a Simplex timer capable of recording time to 0.01 m.

The ignition unit consisted of two 250 microfarad capacitors, a 2000 ohm resistor, and a 250 V diode. The diode rectified the current from a 115 V alternating current powerstat.

The bomb used was a platinum lined, high pressure Parr Bomb, Model 1004C. A collar and a gear which produced a twisting end over end motion when the rotation was effected, was attached to the exterior of the bomb. A special clamping handle which fitted into two small holes near the bottom of the bomb was used to lower the bomb in an inverted posit-

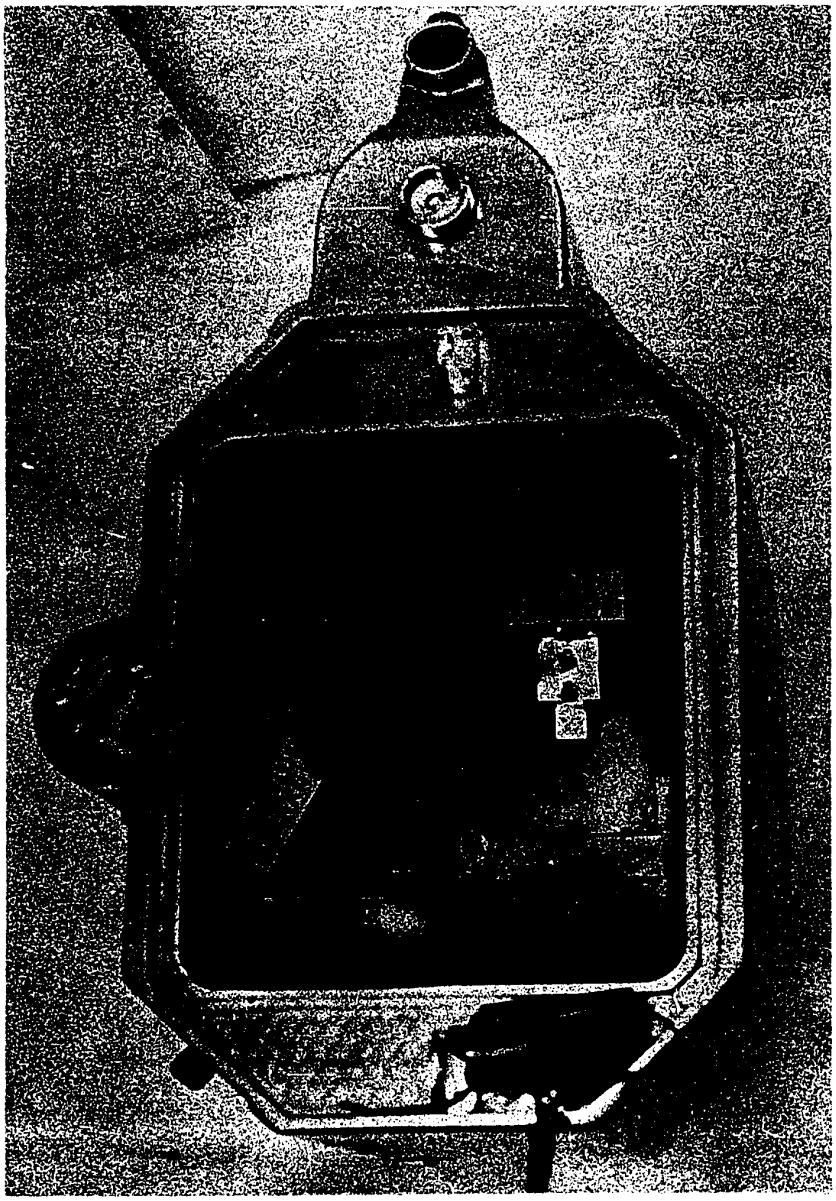


Figure 3: A photograph of the calorimeter bucket (20)

ion into the calorimeter bucket. The inverted position of the bomb directs the flame of the combustion towards the bottom of the bomb and thus protects the interior fittings from damage. Platinum crucibles used in the combustions were purchased from Fisher Scientific Company.

In order to fill the bomb in an inverted position, a brass ring, the interior of which was capable of accomodating the bomb, was fitted with three large set screws to hold the bomb inverted and steady while it was being prepared for a combustion experiment.

In sealing the bomb prior to a combustion, the head was placed in the bomb and the cap screwed down. The set screws in the head were tightened from side to side until all had been tightened. The bomb was allowed to set for ten minutes to allow the Teflon gaskets in the head to flow and subsequently the set screws were given a final tightening.

The calorimeter bucket contained approximately 3800 g of weighed water. The bucket was placed in the calorimeter and the bomb set into the bucket and the firing mechanism was engaged. The calorimeter was closed and the system was allowed twenty to thirty minutes to equilibrate.

Characterization of the Thermistor and Calorimeter

In bomb calorimetric work, one of the important aspects of the calorimetric, as opposed to the chemical, part of the investigation, is the measurement of the temperature increase with time and the subsequent calculation of the corrected temperature rise, ΔT_{cor}. The use of a thermistor as the temperature measuring device requires calibration over the temperature range to be used. This calibration is shown in Table 2.

Table 2: Thermistor Calibration

Temperature °K	Resistance ohm
295.860	2543.3
296.022	2524.3
296.198	2505.2
296.363	2487.2
296.555	2463.3
296.878	2428.2
297.202	2393.2
297.528	2359.5
297.856	2325.7
298.150	2297.4

For the thermistor used, the following formulae have previously been tested (20).

$$\ln R = (A/T) + B \quad (13) \qquad [3.1]$$

$$\ln R = [C/(T + \Theta)] + D \quad (21) \qquad [3.2]$$

$$T = A' \ln R \quad (22) \qquad [3.3]$$

where R is the resistance, T the absolute temperature and A, B, C, D, and A' are constants. Of these equations, [3.2] is reported to be the most accurate (23) while [3.3] is only applicable for small temperature changes of about 0.75°C (23).

A plot of 1/ln R versus T, as shown in Figure 4, was necessary to determine Θ in equation [3.2] which was confirmed to be 121.6 as previously reported (20).

In order to use the equations presented in Chapter II to determine the corrected temperature rise, a study of the effects of stirring and heat exchange for the calorimeter were necessary. These studies, which had previously been conducted by Clark (20), involved taking time and temperature readingsfor the calorimeter system with an empty bomb over the range of temperatures used both with the bomb stationary and rotating. Clark (20) plotted the slopes of the time and temperature readings against the mid-point of each temperature interval used and a representation of his data on the calorimeter used in the present work is shown in Figure 5. Figure 5 shows a linear relation for the calorimeter whether or not it was rotating. It was therfore assumed that equation [2.23], that is

$$g = d\Theta/dt = \mu + \ell(\Theta_j - \Theta) \qquad [2.23]$$

holds for the calorimeter and the temperature range used.

Clark (20), by means of generating hyperbolae similar to the time-

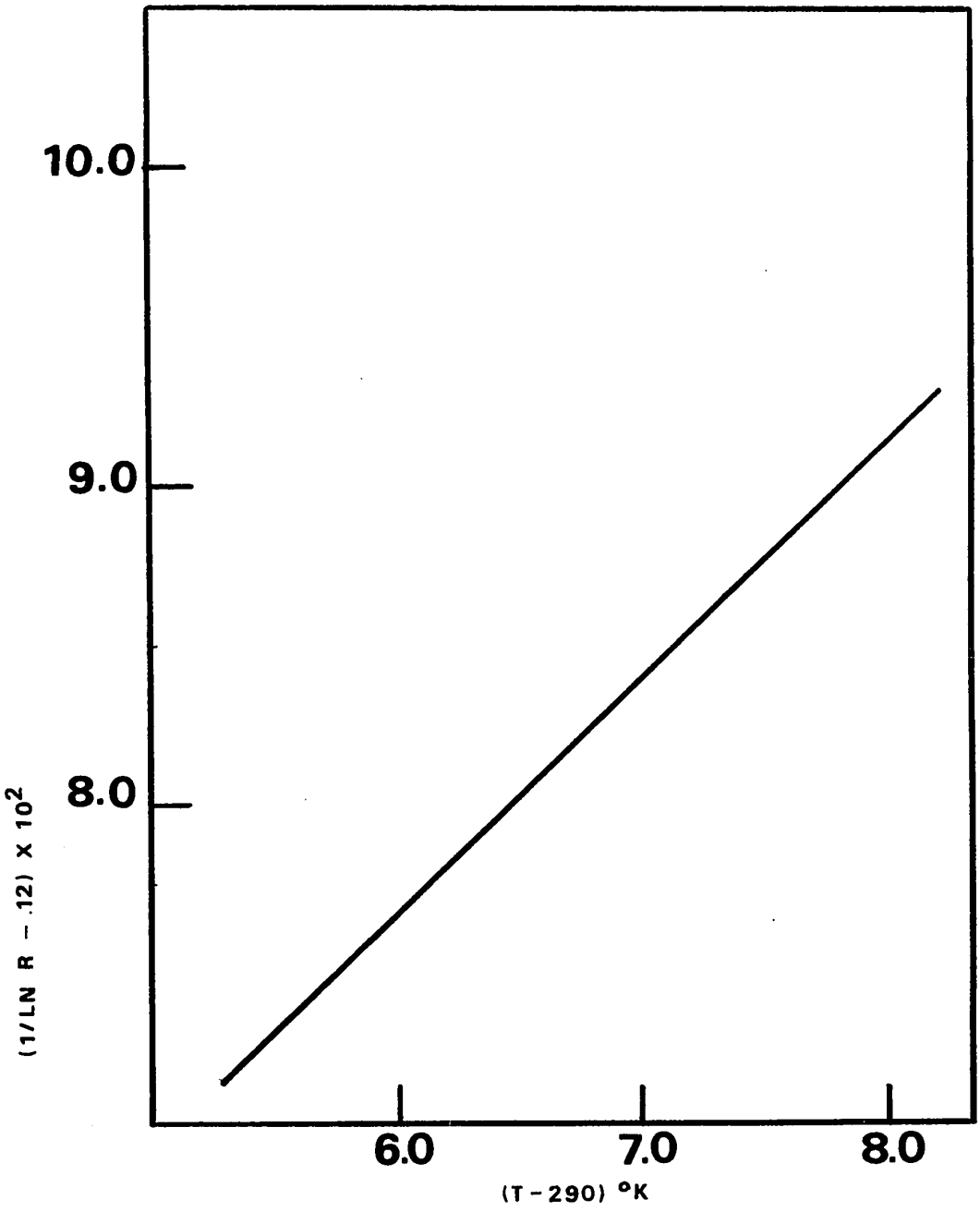


Figure 4: Thermistor calibration: A plot of 1/ln R versus T

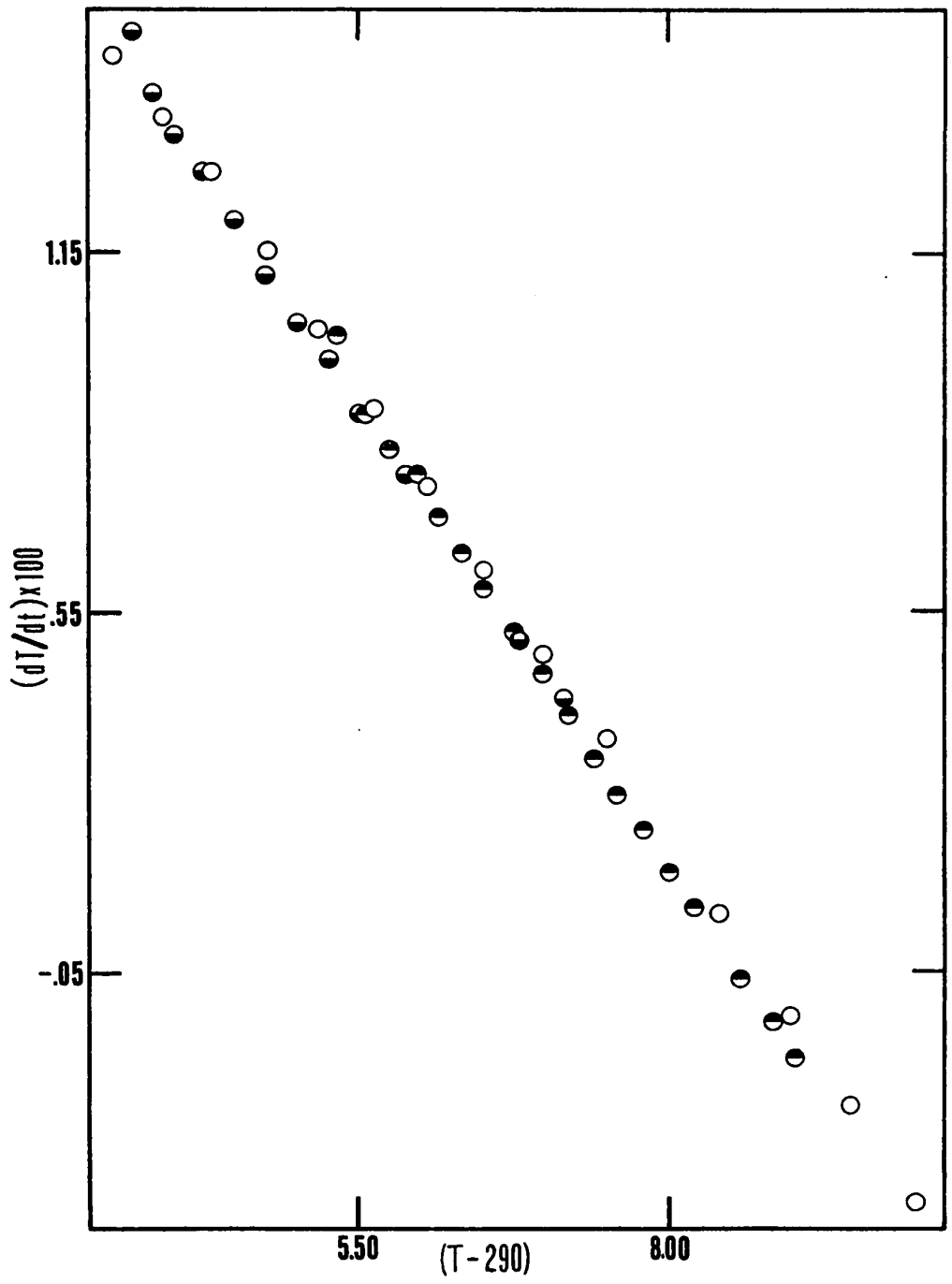


Figure 5: Characterization of the calorimeter: A plot of dT/dt versus T [0 ≡ bomb rotating, ⊖, ⊖ ≡ bomb stationary]

temperature curve produced in a combustion, developed a numerical method based on the equation

$$\int_{x_o}^{x_m} y\,dx = \sum_{k=0}^{m} [y_k/P_k(x_k)] \int_{x_o}^{x_m} P_k(x)\,dx \qquad [3.4]$$

which approximated the area under the curve generated to the fifth significant figure when time intervals of 0.07 m were employed. The results of Clark's work in this regard are shown in program subroutine G05ARA which was based on Lagrangian interpolation. Program subroutine G05ARA was used in the present work to determine ΔT_{cor}.

The critical factor in the calculation of ΔT_{cor} is the choice of the time at the end of the main period. This problem was solved by Clark (20) by incorporating an iterative feature into the calibration program of evaluating ΔT over a time range judged to extend from the main period into the final period of time and temperature readings. At the point at which the end of the main period was reached the ΔT values would start to converge. This convergence is shown in Table 3 for sample combustions and illustrates a refinement of Clark's original program in that the number of iterations was doubled to forty in an effort to follow the temperature rise through the main period and well into the final period.

Determination of the Energy Equivalent of the Calorimeter

Benzoic acid which was standardized for calorific purposes and obtained from Parr Instrument Company was used to determine the energy equivalent of the calorimeter used. The benzoic acid was purchased in the form of tablets of approximately 1 g in weight and was stored in a desiccator over calcium chloride. The results of the combustion of

Table 3: Convergence of Values in a Calibration Program

E_C, CAL/ ^oK	$U + \ell\Theta_J$	ℓ	ΔT_{COR}, ^oK
0.93607420E 04	0.12163020E-01	0.12522080E-01	0.79427230E 00
0.76950500E 04	0.12428220E-01	0.88692040E-02	0.96610170E 00
0.65247610E 04	0.12650930E-01	0.58014720E-02	0.11392630E 01
0.56566830E 04	0.12824530E-01	0.34103170E-02	0.13139550E 01
0.53016050E 04	0.12951460E-01	0.16619020E-02	0.14018830E 01
0.49864290E 04	0.13055500E-01	0.22880230E-03	0.14904110E 01
0.47091320E 04	0.13131780E-01	-0.82198290E-03	0.15780900E 01
0.45568670E 04	0.13174030E-01	-0.14038840E-02	0.16307690E 01
0.45085110E 04	0.13204820E-01	-0.18279680E-02	0.16482410E 01
0.44601910E 04	0.13231810E-01	-0.21996570E-02	0.16660800E 01
0.44144490E 04	0.13253680E-01	-0.25009590E-02	0.16833270E 01
0.43719170E 04	0.13269310E-01	-0.27162360E-02	0.16996860E 01
0.43486950E 04	0.13277050E-01	-0.28228690E-02	0.17087520E 01
0.43408320E 04	0.13282150E-01	-0.28930540E-02	0.17118450E 01
0.43338120E 04	0.13286500E-01	-0.29531050E-02	0.17146150E 01
0.43280350E 04	0.13289820E-01	-0.29987140E-02	0.17169000E 01
0.43232920E 04	0.13292230E-01	-0.30319250E-02	0.17187830E 01
0.43205540E 04	0.13293540E-01	-0.30500670E-02	0.17198700E 01
0.43188470E 04	0.13294140E-01	-0.30582770E-02	0.17205490E 01
0.43179370E 04	0.13293660E-01	-0.30517530E-02	0.17209110E 01
0.43195230E 04	0.13293160E-01	-0.30447640E-02	0.17202800E 01
0.43192730E 04	0.13293050E-01	-0.30432200E-02	0.17203800E 01
0.43193550E 04	0.13293020E-01	-0.30428860E-02	0.17203480E 01
0.43199100E 04	0.13293320E-01	-0.30470190E-02	0.17201280E 01
0.43196560E 04	0.13293560E-01	-0.30503080E-02	0.17202280E 01
0.43194020E 04	0.13294150E-01	-0.30583880E-02	0.17203290E 01
0.43184450E 04	0.13294940E-01	-0.30692670E-02	0.17207100E 01
0.43184020E 04	0.13294900E-01	-0.30688370E-02	0.17207260E 01
0.43180620E 04	0.13295390E-01	-0.30755520E-02	0.17208630E 01
0.43176870E 04	0.13295850E-01	-0.30818940E-02	0.17210120E 01
0.43177460E 04	0.13296130E-01	-0.30857390E-02	0.17209890E 01
0.43168710E 04	0.13297230E-01	-0.31008660E-02	0.17213370E 01
0.43167100E 04	0.13297680E-01	-0.31071040E-02	0.17214000E 01

Table 4: Determination of the Energy Equivalent of the Calorimeter

Run	Mass of Benzoic Acid g	ΔT_{cor} °C	q_i cal	C_{cf} cal	Theoretical CO_2 yield g	Actual CO_2 yield g	% CO_2 %	Energy Equivalent cal/g
1	1.085	1.613	2.65	4.48	2.738	2.732	99.78	4252.7
2	1.071	1.591	2.62	4.47	2.701	2.680	99.22	4254.4
3	1.036	1.541	2.69	4.46	2.614	2.599	99.43	4253.0
4	1.017	1.512	2.68	4.45	2.565	2.559	99.77	4251.4
5	1.125	1.672	2.63	4.49	2.837	2.804	98.84	4252.7
6	1.041	1.549	2.64	4.46	2.625	2.603	99.16	4248.4

benzoic acid are shown in Table 4. Runs 1 and 2 represent determinations of the energy equivalent of the calorimeter where 1 ml of water was used in the bomb and the nitrous and nitric acids produced in the combustion were titrated with standardized sodium hydroxide solution. Runs 3 to 6 inclusive in Table 4 represent combustions where the bomb containing the benzoic acid to be combusted was flushed for fifteen minutes with analytical grade oxygen prior to pressurizing, in an effort to remove all the nitrogen from the system and hence eliminate the need for corrections due to the enthalpies of formation of nitrous and nitric acids.

Table 4 also illustrates the per cent recovery of carbon dioxide produced in the reaction. This was determined in runs 1 to 3 inclusive with Indicarb 6-10 Mesh and in runs 4 to 6 inclusive with Lithasorb, both being obtained from Fisher Scientific Company.

Using the heat of combustion of benzoic acid as 6318. cal/g, the average energy equivalent of the calorimeter used is calculated to be 4252.1 ±1.6 cal/g.

Development of the Experimental Method

One of the purposes behind the present experimental work was to develop a method which would facilitate the determination of enthalpies of formation of perfluoroaromatic and halogen substituted perfluoroaromatic compounds without the use of any auxiliary materials. To accomplish this stated purpose several preliminary experimental methods were attempted before an acceptable procedure was devised.

The first of these experimental methods included combustion of the compound under investigation in an open steel crucible in a steel bomb.

The compound was weighed into a previously weighed steel crucible and sealed immediately after removal from the balance into a steel bomb which was in the upright position. Combustions in an open steel crucible in a steel bomb are represented by run 1, Table 5 on page 49. This method was soon abandoned because these combustions produced a green colouration on the inside of the bomb which was visual indication of compounds presumed to be iron fluorides. Subsequent testing of the coating on the bottom and walls of the bomb for Fe^{+++} and Fe^{++} gave a positive reading with potassium thiocyanate. Henceforth a platinum lined bomb and platinum crucible were used in all combustions.

The second method involved sealing the compound to be studied into glass ampoules. The ampoules were constructed from Pyrex glass and were in the form of flat discs with one very thin wall to facilitate breaking of the ampoule when ignition was effected. The ampoules were weighed prior to filling with the compound under investigation, and then after sealing were reweighed along with any glass which was removed during the sealing process. Aside from the practical problem that the ampoule containing the compound often did not survive intact under the pressure inside the bomb until ignition had occurred, great difficulty was experienced in obtaining consistent results from combustions in ampoules. This was attributed, in part, to occlusion of some portion of the compound in pieces of the ampoule when the ampoule was broken, and to incomplete combustions, partial evidence for which included the presence of a sooty deposit in the platinum crucible after a combustion. Combustions attempted using the sealed glass ampoule are represented, in part, in Table 5, page 49, by runs 2 to 4 inclusive. With the seeming failure of this particular method it became necessary to devel-

op an alternate experimental procedure, keeping in mind the stated purpose of the experimental work.

Subsequently an experimental method was attempted which did not involve the use of any type of containment for the compound other than the platinum crucible. The bomb and its fittings, the crucible, the compound to be studied, an electric balance, and other necessary tools were kept in a cold room set a -20°C. This method involved weighing the now solid compound that was to be combusted into the weighed crucible, sealing the crucible and compound into the bomb, and pressurizing with the necessary amount of oxygen. Besides the obvious practical problems for the experimentor in pursuing this method, there were difficulties involved in condensation of water vapour on the platinum crucible and in the interior and on the lid of the bomb. The presence of this albeit small amount of water vapour was not tolerable if, as was previously stated, the purpose of producing combustions of these compounds without the use of any auxiliary materials whatsoever was to be maintained. The failure of this particular method, as related to the object of the experimentation, can be evidenced in Table 5, page 49 by representative runs 5 and 6 in which liquid was found in the bomb at the conclusion of a combustion experiment.

Despite the fact that it had been reported (24) that it was not possible to obtain complete combustions of perfluoroaromatic compounds without containing them and without the use of auxiliary materials, the next method attempted, which eventually with minor refinements, proved to be quite acceptable, involved no containment for the compound with the exception of the platinum crucible and the use of no auxiliary materials whatsoever.

Before each calorimetric experiment the bomb was baked out in a drying oven at 110°C for 1/2 h to remove any traces of moisture. The bomb was then removed from the drying oven and allowed to come to room temperature. Approximately one ml of the compound to be combusted was pipetted into a previously weighed platinum crucible. The weight was recorded and a stopwatch was started. After several weight-time readings were taken, the crucible and compound were removed from the balance and fitted into the gimbal which had previously been fitted with a weighed platinum fuse wire (12 cm long, 36 guage). A diagram illustrating this may be found in Figure 6. The lid assembly, including the crucible, compound and fuse wire was fitted as quickly as possible into the bomb which was clamped in an inverted position.

The bomb was sealed by means of a screw cap and sealing bolts. The length of time from taking the weight of the crucible and compound to the insertion of the lid into the bomb was measured to the nearest 0.1 s. The amount of compound lost by evaporation could then be calculated from the rate of evaporation of that compound which was determined from the weight-time readings taken prior to removal of the crucible and compound from the balance.

Prior to, and just up to, insertion of the lid containing the crucible, compound, and fuse wire into the inverted bomb, analytical grade oxygen was flushed into the open bomb in an effort to eliminate the need for corrections due to the formation of nitric and nitrous oxides produced in a combustion from the presence of nitrogen in the bomb. After the bomb had been sealed, it was pressurized to 450 p.s.i. with analytical grade oxygen. Table 5, page 49, runs 7 to 24 inclusive and all runs in Table 7 and Table 9 (pages 58 and 67 respectively) illustrate

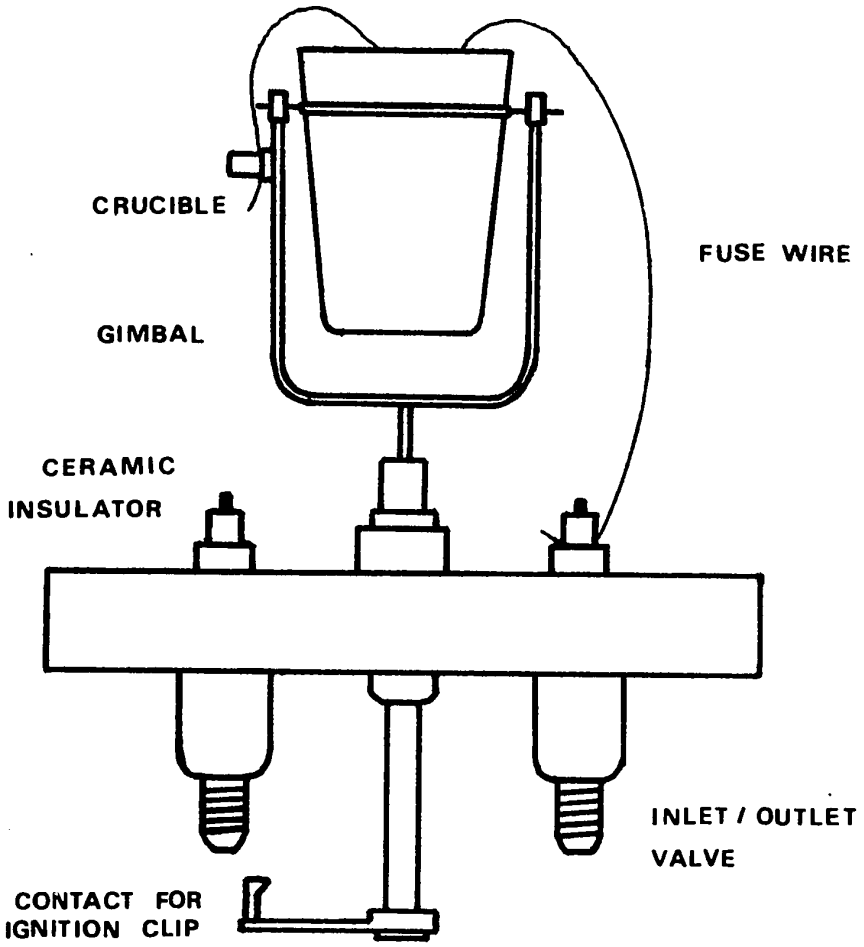


Figure 6: Diagram of the bomb lid assembly

the use of this method.

Since the sample undergoing combustion was not contained in any manner, it was necessary, in the computation of a valid $\Delta H^{\circ}_{f\ 298}(g)$, to determine the amount of that compound which would exist in the vapour state at the conditions inside the bomb prior to combustion. To that end the Gibb's equation in the form

$$\ln(P_1/P_2) = [\bar{V}_{\ell}(P_{e1} - P_{e2})]/RT \qquad [3.5]$$

was employed. In equation [3.5], T represents the absolute temperature of the bomb at the beginning of a combustion experiment, P_{e1} is the pressure in atmospheres in the bomb when filled with the appropriate amount of oxygen, and P_{e2} equals one atmosphere. $\bar{V}_{\ell}$ is the molar volume of the liquid being combusted and P_2 is the vapour pressure of that compound when the external pressure is P_{e2}. The Gibb's equation is then solved for P_1 which is the vapour pressure of the compound under an external pressure of P_{e1}. The value obtained for P_1 is substituted into

$$P_1V = nRT \qquad [3.6]$$

which can be rewritten as

$$P_1V = (w_g/M)RT \qquad [3.7]$$

where w_g is the weight of the substance which will be in the vapour state and M is its molecular weight. R is expressed in l.atm/deg.mol.

Substitution into equation [3.7], where V is the internal volume of the bomb in litres, will give a numerical value to w_g and hence allow for a determination of a correction to $\Delta H^{\circ}_{f\ 298}$(compound,l) for the compound which is to be combusted that reflects only that portion of the compound in the liquid state when combustion occurs.

The Enthalpy of Formation of Hexafluorobenzene

In the determination of the heat of combustion of hexafluorobenzene, by the method previously described, only the compound and oxygen were used in the calorimetric bomb. Figure 7 illustrates a typical weight lost from evaporation versus time curve for hexafluorobenzene. The average rate of evaporation for the hexafluorobenzene was determined to be 0.274 mg/s. The time between weighing the crucible and hexafluorobenzene and the sealing of the bomb was such that evaporation of the hexafluorobenzene was 0.5% of the total sample weight or less.

This correction for evaporation is estimated to be accurate to within at least ±3%. The error in weight generated by this correction procedure should therefore be less than 0.02% of the total sample weight.

After a fifteen minute period during which the bomb achieved thermal equilibrium with the water in the calorimeter bucket, time and temperature readings were taken every 10 to 15 s for approximately 10 m. Subsequent to this pre-combustion period, ignition was effected and time and temperature readings were taken as often as every 0.05 m for the ensuing 25 m. Rotation of the bomb was started 3m after ignition and was continued throughout the remainder of the calorimetric experiment.

Before analysis, the exterior of the bomb's lid was thoroughly dried with acetone with special attention being given to the inlet and outlet valves to insure that no moisture was present. As a precaution that no acetone remained in the inlet or outlet valves, house vacuum was applied to them for a short period of time. The bomb was then connected by means of copper tubing and a short Tygon sleeve to an

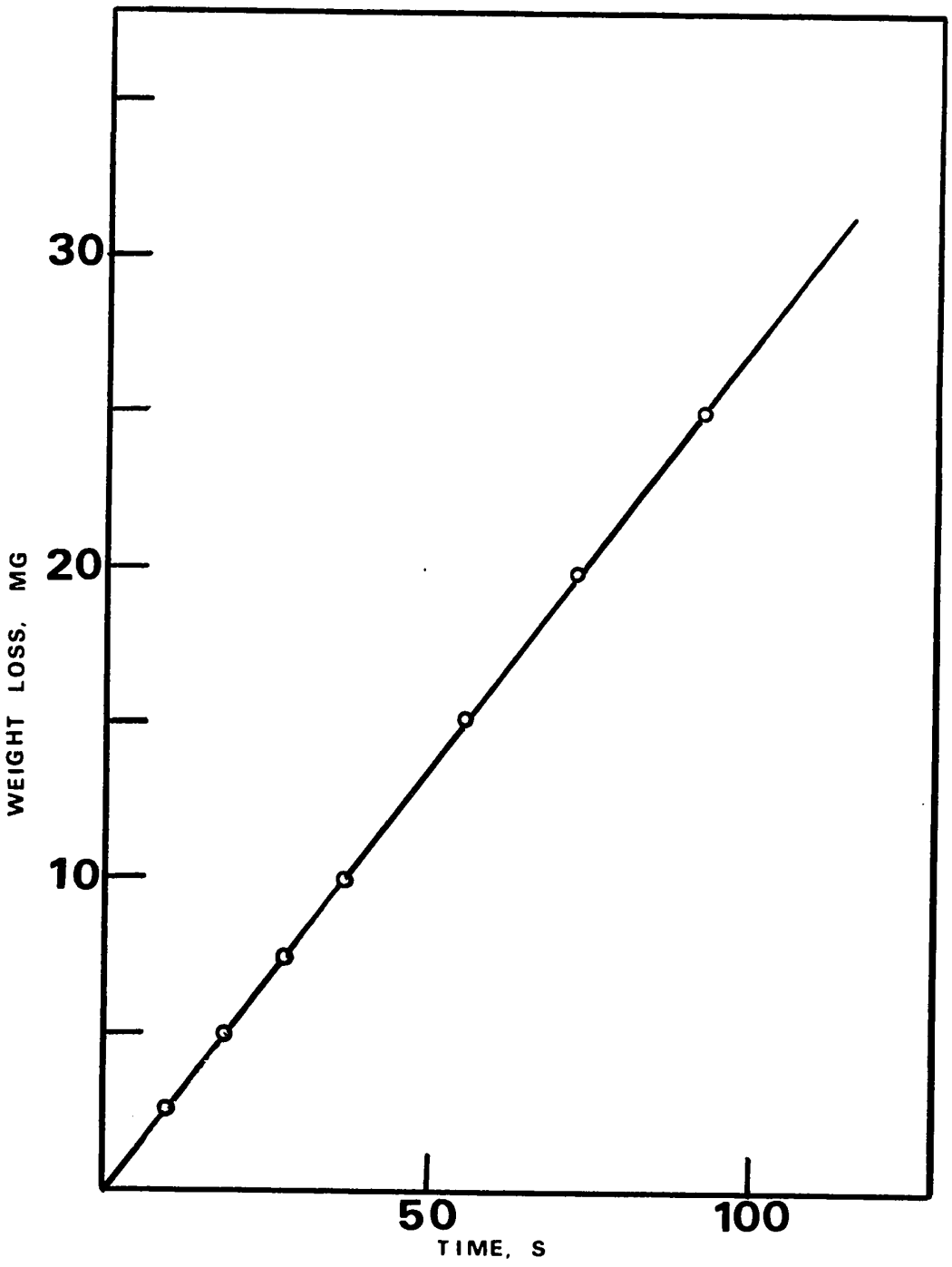


Figure 7: Weight lost from evaporation versus time plot for C_6F_6

analysis train consisting of a Teflon bubbler, a drying tube containing magnesium perchlorate, a gas sample collection vessel, and a carbon dioxide collection vessel. The bomb outlet valve, now connected to the analysis train, was opened and the gases were allowed to pass through the analysis train until the bomb had been emptied. Analytical grade oxygen was then passed through the inlet valve of the bomb and allowed to escape from the outlet valve and into the analysis train for about 1 1/2 h to flush the bomb of any remaining combustion products. With an initial oxygen pressure of 450 p.s.i., the total emptying and flushing of the bomb took approximately 16 h.

The Teflon bubbler was a Teflon graduated cylinder equipped with a 2-hole rubber stopper into which was fitted two lengths of Teflon tubing. The Teflon tubing through which the effluent gases from the bomb entered the bubbler portion of the analysis train extended very nearly to the bottom of the bubbler and was drawn there to a point. The second piece of Teflon tubing provided for the exit of gases from the bubbler and extended just beneath the rubber stopper but not into the solution which was contained in the bubbler. The bubbler contained 100 ml of solution comprised of 5 ml of concentrated hydrochloric acid and 95 ml of distilled water. The presence of the hydrochloric acid was a precaution to prevent carbon dioxide, which is present in the effluent gases, from dissolving in the bubbler solution.

A 10 ml aliquot of the solution contained in the Teflon bubbler was removed from the bubbler, after the bomb had been emptied and flushed, and added to 25 ml of Total Ionic Strength Activity buffer solution from Orion Company which caused the pH to be adjusted to approximately 5.5. This mixture of the bubbler solution and the buffer solution was

analyzed for F^- using a fluoride specific ion electrode in conjunction with an Orion, Model 701 digital pH meter, capable of reading relative millivolts to the nearest 0.1 mv. The meter was calibrated prior to each determination of F^- using a series of standard solutions ranging in concentration of F^- from 1×10^{-4} to 1×10^{-1} molar and prepared by the addition of 0.1 molar fluoride standard solution from Orion Company to the appropriate amount of distilled water and Total Ionic Strength Activity buffer solution.

The gas collection tube was constructed from a short length of Pyrex tubing with high vacuum stopcocks at each end. The stopcocks were obtained from Ace Glass Company and had a Teflon barrel with Viton O-ring seals. The gas collection tube of 4 cc volume was normally connected in the analysis train immediately after the Teflon bubbler, but from time to time its position in the analysis train was altered to test the composition of the effluent gases at all stages of the analysis train. When the gas collection tube was removed from the analysis train for analysis on a gas chromatograph it was replaced with either a similarly constructed collection vessel or a short length of Tygon tubing.

Analysis of the contents of the gas collection tube was performed on a Perkin Elmer, Model 154, gas chromatograph equipped with a thermal conductivity detector. A silica gel column of dimensions, 6 ft x 1/4 in. o.d. operated at 25°C and a helium carrier flow rate of 15 cc/m was used in the analysis. The chromatographic conditions employed gave separation of the tetrafluoromethane peak from the massive oxygen peak and thus permitted a determination of the ratio of carbon dioxide to tetrafluoromethane. A sample chromatogram, obtained in the analysis

of the contents of the gas collection vessel for a hexafluorobenzene combustion, is shown in Figure 8.

The vessel containing the magnesium perchlorate, which was placed before the carbon dioxide collection tube,was used to remove any moisture from the effluent gases which might have been picked up from the Teflon bubbler.

A drawing of the U-shaped Pyrex carbon dioxide collection tube is shown in Figure 9. Both Indicarb 6-10 Mesh Carbon Dioxide Absorbant and Lithasorb, an indicating, high capacity carbon dioxide absorbant, each provided by Fisher Scientific Company, were used in separate carbon dioxide determinations. Lithasorb, because of its ease of handling and high capacity, was used in all combustions beginning with run 9 in Table 5. When Lithasorb is used it must be followed in the carbon dioxide collection vessel by a drying agent such as magnesium perchlorate to retain the water liberated when Lithasorb absorbs carbon dioxide. The collection tube was evacuated to a constant weight prior to use in the analysis train and was again evacuated to a constant weight subsequent to the flushing procedure (through the magnesium perchlorate end to prevent loss of liberated water).

Allowance was made for the small amount of carbon dioxide removed in the gas chromatography sample in the determination of the total yield of carbon dioxide.

The results of the hexafluorobenzene combustions are shown by representative experiments in Table 5. As noted earlier, run 1 was performed in a steel bomb, runs 2, 3, and 4 represent combustions in sealed glass ampoules and runs 5 and 6 were those done when the bomb was filled in a cold room set at -20°C.

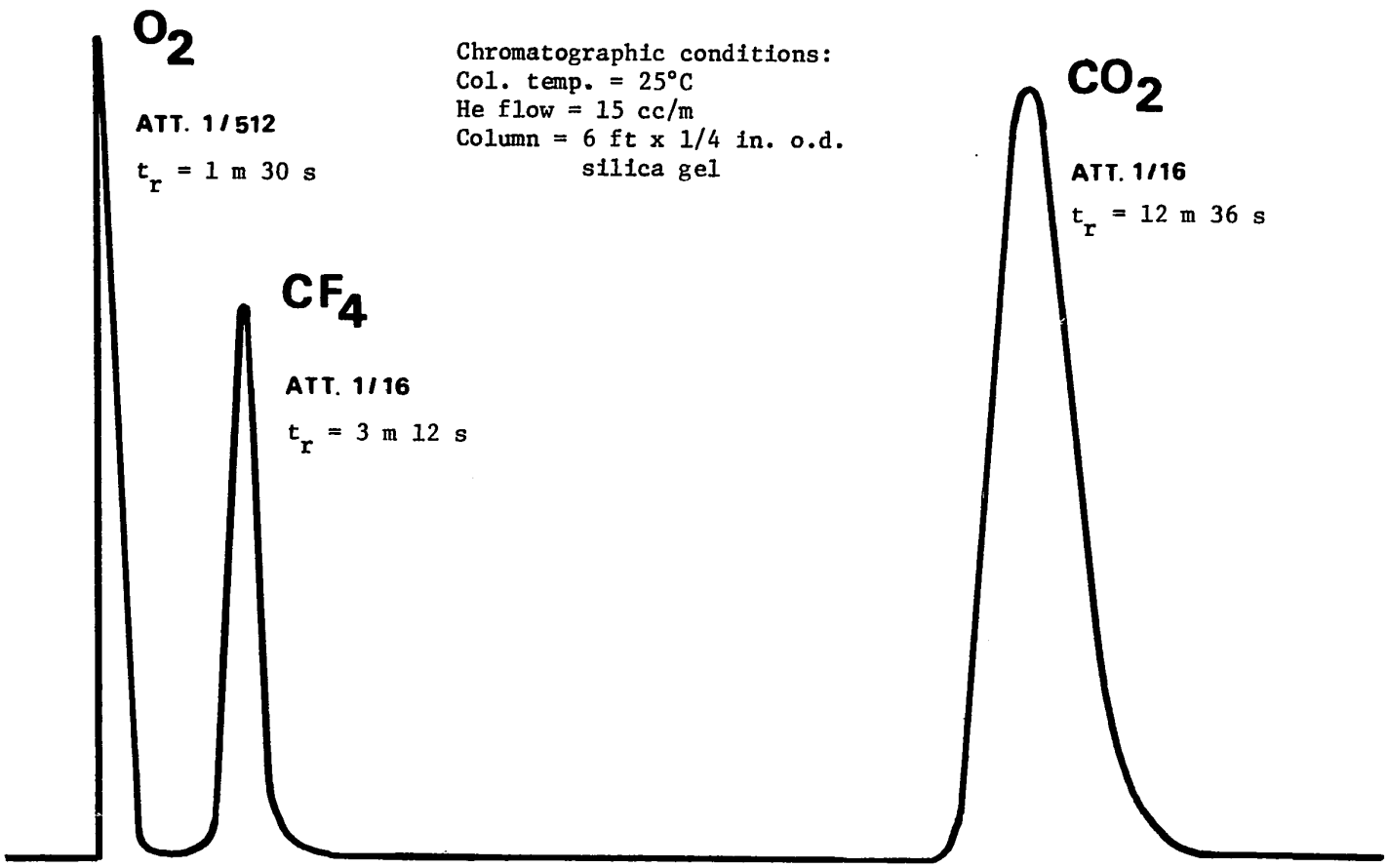


Figure 8: A sample chromatogram for the analysis of the contents of the gas collection vessel in a combustion of C_6F_6

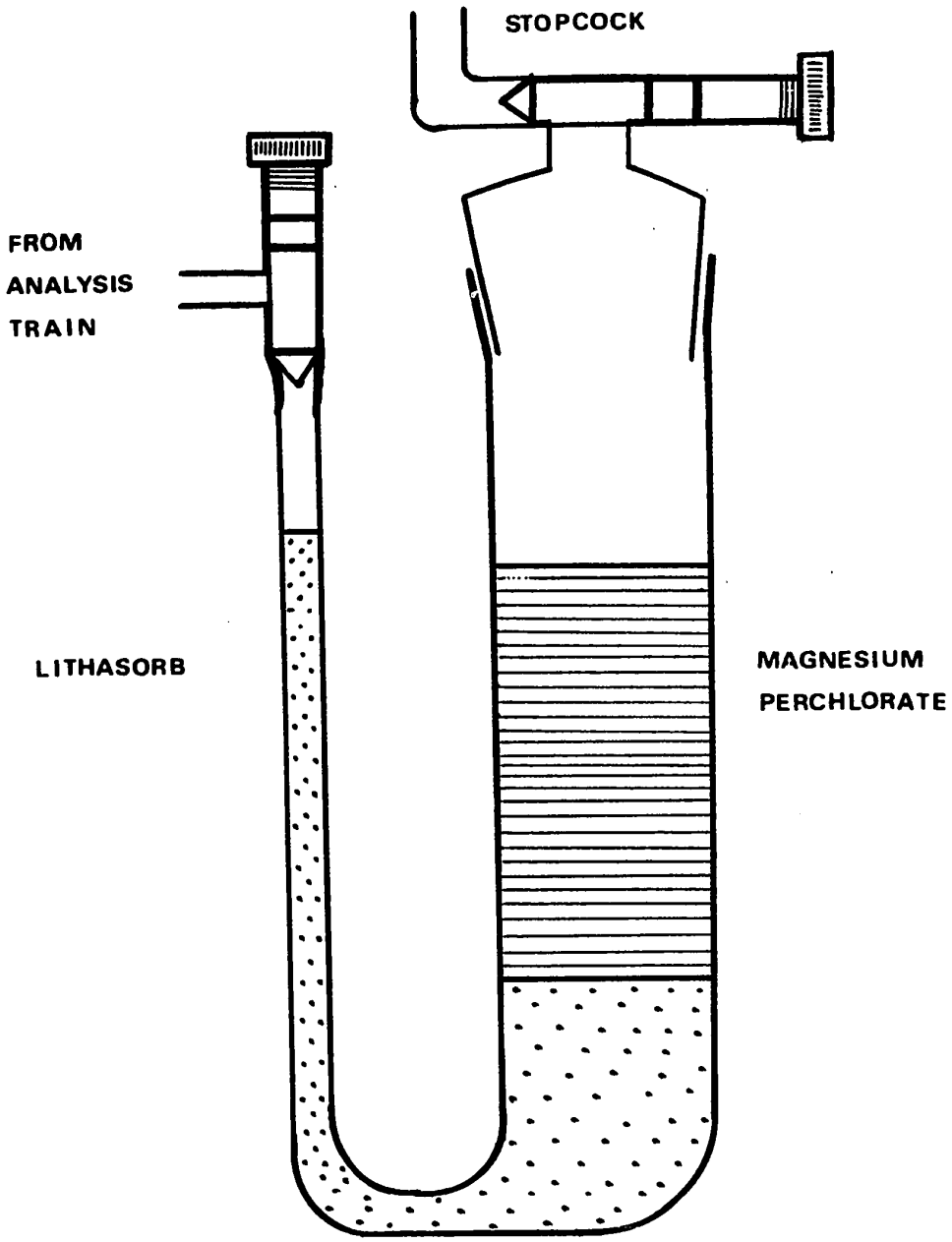


Figure 9: A diagram of the carbon dioxide collection vessel

Table 5: Combustion Data and Calculated Enthalpy of Formation for Hexafluorobenzene

Run	Mass C_6F_6 g	ΔT_{cor} , °C	CO_2/CF_4 [a] by g.c.	CO_2 collected g	F_2 collected g	$\Delta H^\circ_{f\ 298}(C_6F_6,g)$ kcal/mol
1 b	0.983	1.8200				-225.5
2 c	1.423	0.8270				-242.1
3 c	1.282	0.7709				-241.6
4 c	1.402	0.8245				-236.6
5 d	1.423	0.8449				-232.3
6 d	2.034	1.2697				-208.2
7 e	1.437	0.8772	4.48	1.663	0.231	-222.3
8 e	1.465	0.8890	4.52	1.679	0.248	-224.6
9 e	1.404	0.8508	4.59	1.608	0.249	-225.7
10 e	1.427	0.8720	4.56	1.646	0.248	-222.0
11 e	1.467	0.8883	4.54	1.688	0.243	-226.0
12 e	1.418	0.8641	4.52	1.619	0.247	-222.9
13 e	1.432	0.8685	4.55			-225.4
14 e	1.401	0.8489	4.54	1.612		-225.7

Table 5: continued

Run	Mass C_6F_6 g	ΔT_{cor} °C	CO_2/CF_4 [a] by g.c.	CO_2 collected g	F_2 collected g	$\Delta H^\circ_{f\ 298}(C_6F_6,g)$ kcal/mol
15 e	1.418	0.8637	4.54	1.656		-223.2
16 e	1.406	0.8570	4.56		0.226	-222.8
17 e	1.373	0.8368	4.54	1.594		-223.2
18 e	1.430	0.8726	4.52			-223.9
19 e	1.529	0.9360				-222.5
20 e	1.581	0.9679				-222.5
21 e	1.404	0.8580				-223.4
22 e	1.391	0.8415	4.56			-223.5
23 e	1.429	0.8617				-224.8
24 e	1.386	0.8383				-225.0

a ≡ molar ratio

b ≡ open steel crucible, steel bomb; a portion of a total of 6 runs performed in this manner

c ≡ sealed glass ampoules, platinum bomb; a portion of a total of 8 runs performed in this manner

d ≡ platinum bomb sealed in cold room; a portion of a total of 9 runs performed in this manner

e ≡ open platinum crucible, platinum bomb; a portion of a total of 38 runs performed in this manner

Additional typical data (see ref. (6) for notation)
$\varepsilon(-\Delta T_{cor})$ = -3706.8 cal; $\Delta E^\circ_c/M$ = -2628.4 cal/g

Gas chromatographic analysis of the gases contained in the gas collection tube when it was positioned following the Teflon bubbler gave peaks for oxygen, tetrafluoromethane, and carbon dioxide. Analysis of the gases at the exit of the carbon dioxide collection tube (using either Indicarb or Lithasorb) showed only oxygen and tetrafluoromethane. Both gas chromatographic and mass spectrometric tests failed to show even traces of oxygen difluoride.

Gas chromatographic tests for the presence of F_2O were conducted on a Perkin Elmer, Model 154 gas chromatograph, equipped with a thermal conductivity detector. The flow rate of helium, which was used as the carrier gas, was set at 15 cc/m. The column temperature was adjusted to -60°C by immersing the column in a constant temperature acetone-dry ice bath while the column was still connected to the chromatograph. The column used was a 6 ft x 1/4 in. o.d. silical gel column. Donohue and Jones (25) report success in measuring F_2O in the presence of O_2 and further that F_2O may be determined quantitatively to ±2%. They also observed that the relative retention time of oxygen difluoride to oxygen was 3.75 so that if F_2O had been present in the combustion samples in the present work it would be clearly identifiable under the above mentioned conditions.

From Table 5, the average molar ratio of carbon dioxide to tetrafluoromethane is 4.54 ±0.05 and omitting runs 7 and 9 is 4.54 ±0.02. It should be noted here that a change of 0.01 in this CO_2/CF_4 molar ratio gives rise to a change of about 0.25 kcal/mol in $\Delta H^\circ_{f\ 298}(C_6F_6,g)$. Since only relative amounts of CO_2 and CF_4 are important, many of the possible errors normally associated with gas chromatographic calibration are negligible. However, in establishing the relative response of CF_4

it is necessary to use a tetrafluoromethane-oxygen mixture whose composition is similar to that of the samples from the combustion experiment. Use of pure CF_4 yields a response factor that is lower by 4.6% than that obtained with tetrafluoromethane-oxygen mixtures. The carbon dioxide calibration is unaffected by the presence of oxygen. The net result is that if relative response factors which are determined with pure CF_4 and CO_2 are employed, a value for $\Delta H^\circ_{f\ 298}(C_6F_6,g)$ is obtained that is about 5 kcal/mol in excess. With C_6F_6 only approximately 9.3% of the oxygen used in the bomb reacted to produce combustion products.

Based on the observed products and the average CO_2/CF_4 molar ratio, the combustion reaction for hexafluorobenzene may be written

$$C_6F_6 + 4.917\ O_2 \rightarrow 4.917\ CO_2 + 1.083\ CF_4 + 0.834\ F_2 \qquad [3.8]$$

The data for fluorine shown in Table 5 and more particularly in Table 6, average out to within 0.23% of the value predicted from equation [3.8]. If a CO_2/CF_4 molar ratio of 4.53 instead of 4.54 was used in the calculation, exact agreement is obtained.

The data in Table 6 illustrates that, with respect to the carbon dioxide collection, the CO_2 yield is in good agreement with that predicted by equation [3.8]. Runs 9 to 12 inclusive and run 14 indicate a carbon dioxide yield that was 0.78% to 1.82% low, indicating for the majority of these runs a small loss of carbon dioxide, possibly due to surges inflow which sometimes occurred when the outlet valve of the bomb was opened too quickly.

In applying equation [3.8] to the experimental combustion process it must be remembered that the hexafluorobenzene sample is not contained in any way other than in the platinum crucible. The combustion

Table 6: Combustion Products for Hexafluorobenzene

Run	Theoretical CO_2 g	Actual CO_2 g	% CO_2 %	Theoretical F_2 g	Actual F_2 g	% F_2 %
7	1.671	1.663	99.52	0.293	0.236	97.12
8	1.695	1.679	99.06	0.249	0.248	99.60
9	1.632	1.608	98.53	0.240	0.249	103.75
10	1.659	1.646	99.22	0.243	0.248	102.06
11	1.706	1.688	98.94	0.248	0.243	97.98
12	1.649	1.619	98.18	0.241	0.247	102.49
14	1.629	1.612	98.96			
15	1.649	1.656	100.42			
16				0.239	0.226	95.36
17	1.597	1.594	99.81			

occurs in a 0.320 litre bomb with an initial temperature of 23.5°C and and initial pressure of 450 p.s.i. Application of the Gibb's equation in conjunction with the ideal gas law as outlined in equations [3.5], [3.6], and [3.7] and the necessary ancillary data produces a value of w_g = 0.30 g as the amount of hexafluorobenzene which is in the vapour state at the time of combustion. Thus only (W - 0.30) g of liquid hexafluorobenzene are involved in a combustion under the aforementioned conditions where W is the total liquid sample weight initially present in the bomb. This presence of slightly over 20% of the hexafluorobenzene in the vapour state undoubtedly aids combustion and may in fact be responsible for producing complete combustion in the absence of any auxiliary materials.

For the calculation of $\Delta H^\circ_{f\ 298}(C_6F_6,g)$ as shown in Table 5, the standard enthaplies of formation of the combustion products were taken as (26)

$$\Delta H^\circ_{f\ 298}(CO_2,g) = -94.0517 \text{ kcal/mol}$$

$$\Delta H^\circ_{f\ 298}(CF_4,g) = -221.0 \text{ kcal/mol}$$

and the required correction for the hexafluorobenzene in the liquid state

$$[(W - 0.30)/W]\Delta H^\circ_{vap\ 298}(C_6F_6) \qquad [3.9]$$

was based on a heat of vaporization of 8.7 kcal/mol (27). From runs 7 to 24 inclusive in Table 5, the average value of $\Delta H^\circ_{f\ 298}(C_6F_6,g)$ obtained is -223.9 ±1.2 kcal/mol. The previously reported values for this $\Delta H^\circ_{f\ 298}(C_6F_6,g)$ of -220.4 kcal/mol (24) and -228.7 kcal/mol (28) were based on $\Delta H^\circ_{f298}(HF.20H_2O)$ = -75.63 kcal/mol and -76.96 kcal/mol respectively.

The National Bureau of Standards selected value for $\Delta H^\circ_{f\ 298}(HF.20H_2O)$ is -76.28 kcal/mol (26). A recent determination of the heat of solution of HF (29) lends support to this National Bureau of Standards value. If the value of $\Delta H^\circ_{f\ 298}(HF.20H_2O) = -76.28$ kcal/mol is used to recalculate the results of Cox and coworkers (24,28), then a value of $\Delta H^\circ_{f\ 298}(C_6F_6,g) = -224.3$ kcal/mol is obtained. This last figure is in excellent agreement with the value obtained in the present work.

For the present time, the National Bureau of Standards values for the enthalpies of formation of CF_4 and HF are preferred basically since National Bureau of Standards data is internally consistent. Both the present experimental work and that of Cox and coworkers (24,28) can be recalculated using a value $\Delta H^\circ_{f\ 298}(CF_4,g) = -223.$ kcal/mol (30) which was determined directly by the combustion of graphite in fluorine. This leads to a value of -76.35 kcal/mol for $\Delta H^\circ_{f\ 298}(HF.20H_2O)$. Based on these alternate enthalpies of formation, the present work yields $\Delta H^\circ_{f\ 298}(C_6F_6,g) = -225.9$ kcal/mol and the work of Cox and coworkers gives -225.1 kcal/mol.

The Enthalpy of Formation of Octafluorotoluene

As was the case with the hexafluorobenzene, in the determination of the heat of combustion of octafluorotoluene only the compound and oxygen were used in the bomb.

Figure 10 illustrates a typical weight lost from evaporation versus time curve for the octafluorotoluene. The average rate of evaporation for the octafluorotoluene was determined to be 0.11 mg/s. The time between weighing the crucible containing the octafluorotoluene

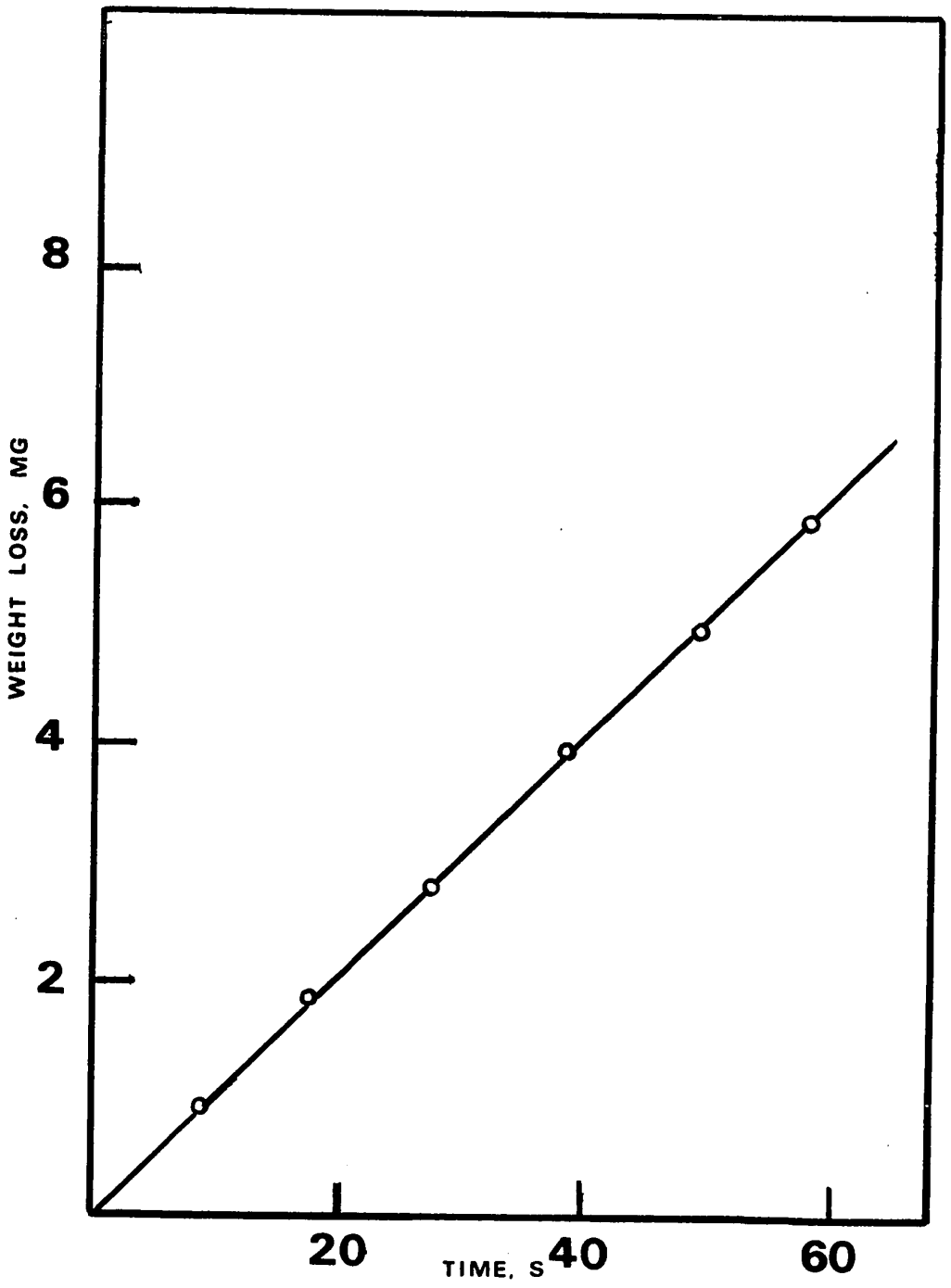


Figure 10: Weight lost from evaporation versus time plot for $C_6F_5CF_3$

and sealing the bomb was such that evaporation of the octafluorotoluene was 0.3% of the total sample weight or less. If the correction for evaporation is estimated to be accurate to within at least ±3%, the error in weight generated by the correction for evaporation should be less than 0.01% of the total sample weight.

The same procedures, both in the calorimetric and chemical parts of the thermochemical investigation, were followed for octafluorotoluene as for hexafluorobenzene.

The results of the $C_6F_5CF_3$ investigation are shown by representative experiments in Table 7. Gas chromatographic analysis of the products contained in the gas collection tube, when it was positioned following the Teflon bubbler, gave peaks for oxygen, tetrafluoromethane, and carbon dioxide. Both chromatographic and spectrometric tests failed to show even traces of F_2O.

From Table 7, the average molar ratio of carbon dioxide to tetrafluoromethane is 3.83 ±0.05. In the case of the $C_6F_5CF_3$, approximately 10.5% of the oxygen used in the bomb reacted to form combustion products.

Based on the fact that Table 8 illustrates a product mass balance for runs 1 to 7 inclusive, and using the average CO_2/CF_4 molar ratio, the combustion reaction for octafluorotoluene may be written as

$$C_6F_5CF_3 + 5.552\ O_2 \rightarrow 5.552\ CO_2 + 1.448\ CF_4 + 1.103\ F_2 \qquad [3.10]$$

The data shown for the F_2 and CO_2 yields in Table 8 average out to 0.9% and 0.7% respectively from the values that are predicted from the application of equation [3.10].

In applying equation [3.10] to the combustion process to calculate $\Delta H^\circ_{f\ 298}(C_6F_5CF_3,g)$, allowance must again be made for that portion of the total liquid sample originally placed in the bomb which is in the vapour

Table 7: Combustion Data and Calculated Enthalpy of Formation for Octafluorotoluene

Run	Mass C_7F_8 g	ΔT_{cor} °C	CO_2/CF_4 [a] by g.c.	CO_2 collected g	F_2 collected g	$\Delta H^\circ_{f\ 298}(C_6F_5CF_3,g)$ kcal/mol
1	1.327	0.7091	3.83	1.369	0.233	-297.4
2	1.438	0.7636	3.90	1.439	0.266	-300.6
3	1.450	0.7692	3.85	1.506	0.259	-301.2
4	1.409	0.7506	3.79	1.429	0.239	-299.0
5	1.397	0.7409	3.73	1.440	0.243	-301.6
6	1.451	0.7702	3.88	1.510	0.271	-300.9
7	1.424	0.7534	3.89	1.472	0.259	-302.5
8	1.407	0.7474				-300.6
9	1.400	0.7438				-300.5
10	1.374	0.7297				-300.8
11	1.376	0.7347				-297.6

a ≡ molar ratio

Table 8: Combustion Products for Octafluorotoluene

Run	Theoretical CO_2 g	Actual CO_2 g	% CO_2 %	Theoretical F_2 g	Actual F_2 g	% F_2 %
1	1.373	1.369	99.71	0.236	0.239	101.27
2	1.488	1.439	96.71	0.256	0.266	103.91
3	1.501	1.506	100.33	0.258	0.259	100.39
4	1.458	1.429	98.01	0.250	0.239	95.60
5	1.446	1.440	99.59	0.248	0.243	97.98
6	1.502	1.510	100.53	0.258	0.271	105.04
7	1.473	1.472	99.93	0.253	0.259	102.37

state when combustion occurs. The combustion is carried out at a pressure of 450 p.s.i. of oxygen in a bomb of 0.320 l internal volume and at an initial temperature of 23.5°C.

Application of the Gibb's equation, the ideal gas law, and anciliary data as outlined in equations [3.5], [3.6], and [3.7] gives a value of w_g = 0.125 g as the amount of octafluorotoluene which is in the vapour state when combustion occurs. Therefore only (W - 0.125) g of liquid $C_6F_5CF_3$ are involved in the combustion under the present experimental conditions, where W is the initial total weight of the liquid $C_6F_5CF_3$ prior to combustion. Again, the presence of about 10% of the sample in the vapour state undoubtedly is a reason for obtaining complete combustion without the use of auxiliary materials.

The National Bureau of Standards values (26) for the enthalpies of formation of CO_2 and CF_4 were taken as -94.0517 kcal/mol and -221.0 kcal/mol respectively. The allowance for the amount of octafluorotoluene in the vapour state before combustion, that is,

$$[(W - 0.125)/W]\Delta H^\circ_{vap}(C_6F_5CF_3) \qquad [3.11]$$

was based on an enthalpy of vapourization of 9.47 kcal/mol (31).

The average value of $\Delta H^\circ_{f\ 298}(C_6F_5CF_3,g)$ obtained from the data presented in Table 7 is -300.2 ±1.2 kcal/mol. Employing $\Delta H^\circ_f(CF_4,g)$ = -223. kcal/mol leads to a $\Delta H^\circ_{f298}(C_6F_5CF_3,g)$ = -303.1 kcal/mol (30).

The Enthalpy of Formation of Iodopentafluorobenzene

As was the case in the previous two perfluoroaromatic compound combustions, only iodopentafluorobenzene and oxygen were used in the combustion bomb.

Figure 11 illustrates a typical weight loss from evaporation versus time curve for the C_6F_5I. The rate of evaporation for this compound was determined to be 0.0099 mg/s. The time between weighing the crucible containing the iodopentafluorobenzene and sealing them into the bomb was such that evaporation of the iodopentafluorobenzene was 0.02% of the total sample weight or less. If the correction for evaporation is estimated to be accurate to ±3%, the error generated by such an evaporation loss correction should be less than 0.001%. In the case of the C_6F_5I, the loss due to evaporation of the compound is not likely to be the limiting factor on the accuracy expected since the projected maximum total loss of 0.001% of the total sample weight very closely approximates the limits of accuracy of the balance used.

While the calorimetric part of the investigation of C_6F_5I was similar to that involved with the C_6F_6 and $C_6F_5CF_3$ combustions, the nature of the combustion products necessitated, in this instance, alterations in the chemical part of the investigation.

The products formed by the combustion of iodopentafluorobenzene were identified as carbon dioxide, tetrafluoromethane, iodine, fluorine, and iodine pentafluoride.

CO_2, CF_4, and F_2 were identified in the same manner as was previously used for the combustions of C_6F_6 and $C_6F_5CF_3$.

Ample evidence was available for the presence of I_2 as a combustion product, as the bottom and sides of the bomb were coated with a layer of crystals having the characteristic purple-grey colour of iodine. Titration of a solution formed by the addition of saturated potassium iodide solution to the solid contents of the bomb with a standard solution of 0.1N sodium arsenite and determination of I^- by means of an iodide spec-

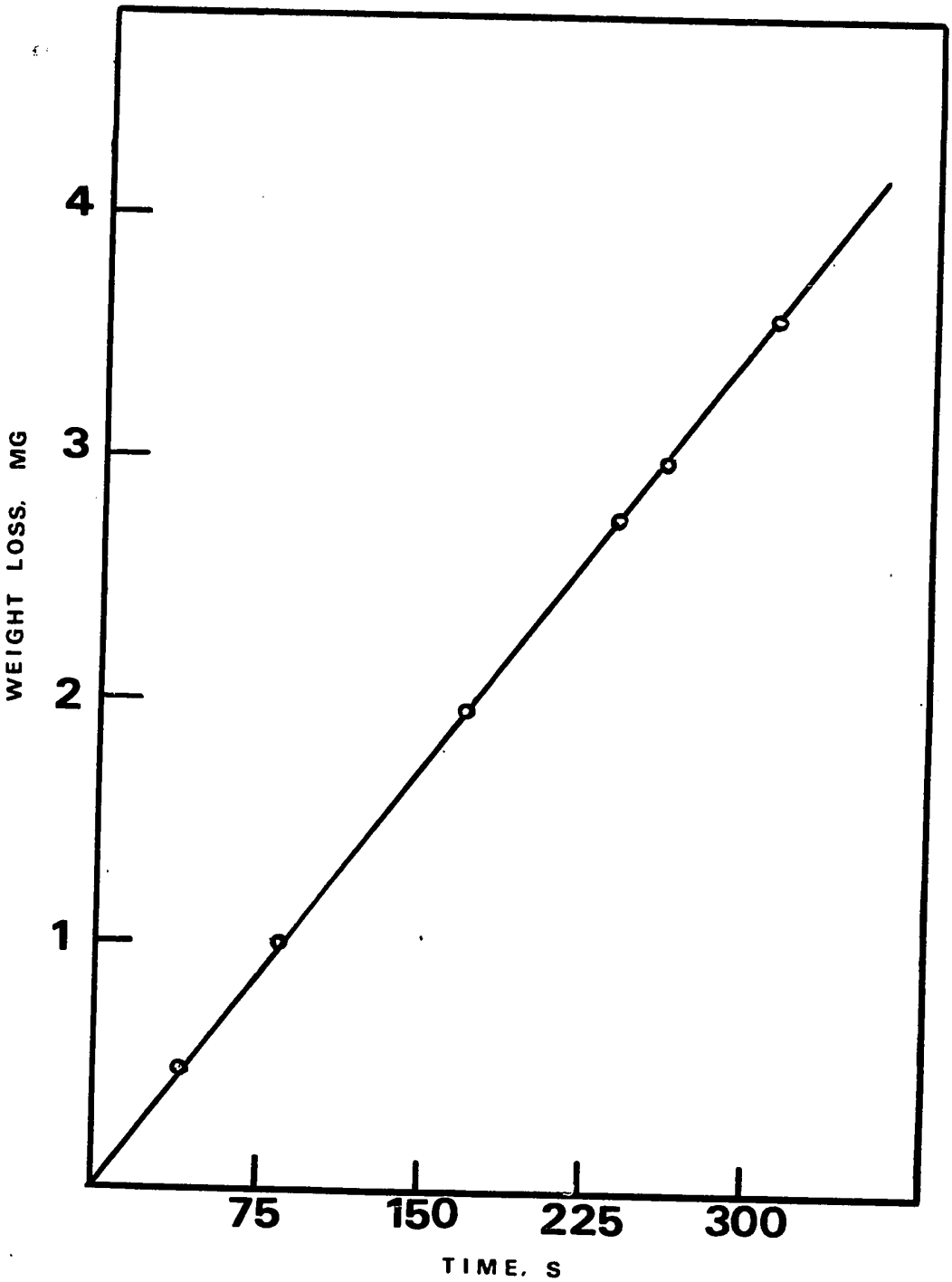


Figure 11: Weight lost from evaporation versus time plot for C_6F_5I

ific ion electrode further confirmed that I_2 was a combustion product.

The confirmation and determination of IF_5 as a combustion product posed some difficulties. In preliminary, non-analytical combustions, the presence of a small amount of a deep red liquid in the platinum crucible and at the bottom of the bomb when it was opened subsequent to a combustion, gave some preliminary indication of the possible formation of an interhalogen compound. During these preliminary combustions, a white smoke was given off from the liquid in the bomb when the bomb was opened in the laboratory. These observations led to a detailed investigation of the liquid compound formed in the combustion of C_6F_5I.

The first step in the identification of the liquid present in the bomb after a combustion was to isolate it from the other combustion products. To accomplish this the bomb, following a combustion, was connected, by means of short pieces of Tygon tubing, to two traps in series followed by a vacuum pump. The first trap contained a small amount of mercury in the bottom and was equipped with two high vacuum stopcocks (with Teflon barrels and Viton O-ringseals), one at each end, so that the trap could be removed and sealed. It was important to take careful precautions that this entire system which was connected to the bomb was moisture free. The first trap containing the mercury was set in a cooled acetone bath adjusted to -45°C. The second trap was placed in a liquid nitrogen bath. The bottom half of the bomb itself was set in an ice-water bath at 0°C in an attempt to prevent excessive amounts of iodine from being deposited in the trapping system once pumping on the bomb was started.

The pump was started and the outlet valve of the bomb was opened and closed intermittently until all the combustion gases had been emptied from the bomb. With the outlet valve now remaining in the open position, pump-

ing was continued for approximately 20 minutes. The outlet valve of the bomb was then closed sealing it off from the trapping system. The first trap containing the mercury was also sealed off by means of the stopcocks at either end and the pumping was terminated. The first trap was then removed from the trapping system and from its cooled acetone bath and warmed slowly to room temperature.

The contents of the trap were in the form of a deep red liquid and this liquid was shaken with the mercury originally placed in the bottom of the trap. When the red liquid in the trap was shaken with the mercury it was decolourized and in a few seconds formed a clear, very slightly blue liquid which rested on the surface of the mercury. This reaction was noted to be similar to that reported by Aynsley (32) for the reaction of IF_5 with mercury.

The trap containing the liquid was then attached to a high vacuum system by means of a ground glass joint using Kel-F brand grease. The liquid was distilled, under vacuum, into a capillary tube suitable for Raman spectroscopy. The capillary, during the distillation, was set in a cooled acetone bath at -45°C. While the compound in the capillary was still frozen, the capillary was sealed under vacuum and removed from the vacuum system for subsequent Raman spectrographic analysis.

98% pureiodine pentafluoride was obtained from Matheson Company. The liquid was distilled under vacuum, making sure that all apparatus was moisture free and that Kel-F brand grease was used on all greased joints, into a vessel containing mercury in the bottom set in a cooled acetone bath adjusted to -45°C. The distilled IF_5, which was a deep red colour, was warmed to room temperature and shaken with the mercury in the bottom of the vessel. In a few seconds, the liquid IF_5 had

changed from a deep red to a clear, almost colourless liquid with a very faint blue tinge, indicating that the excess iodine present in the original sample had reacted with the mercury, leaving a substantially purer sample of IF_5. The once-distilled IF_5 was then distilled again, under vacuum, into a capillary suitable for Raman spectroscopy. The capillary was sealed under vacuum and removed from the high vacuum system for subsequent analysis on a Raman spectrograph.

The Raman spectrum of IF_5 has been reported by Gillespie and Clase (33), Lord (34), and Begun (35). These authors reported response in the Raman spectrum of IF_5 at 275 cm^{-1}, 572 cm^{-1}, 595 cm^{-1}, 694 cm^{-1}, and 705 cm^{-1}. The responses at 694 cm^{-1} and 705 cm^{-1} were in the form of a doublet as previously reported by Gillespie and Clase (33). The Raman spectra of both the liquid removed from the bomb and that of the purified IF_5 were similar producing response at 565 cm^{-1}, 595 cm^{-1}, 692 cm^{-1}, and 706 cm^{-1}.

A crude melting point determination was attempted on the liquid sample collected from the combustion bomb, and the value of 9.6°C which was obtained was in good agreement with the value reported for the melting point of IF_5 of 9.7°C (36).

From the supporting Raman spectra and comparison of physical properties, it was concluded that the liquid formed in the combustion of iodopentafluorobenzene was IF_5.

After the Raman spectra had been run on the pure sample of IF_5 and on the sample obtained from a combustion experiment, the sealed capillaries containing the IF_5 were individually broken under water and tested for iodine and fluorine. The resultant solutions were individually mixed with solutions of sodium arsenite. Two aliquots of each of the re-

sultant solutions were taken and prepared for analysis with an iodide specific ion electrode and a fluoride specific ion electrode. In both instances, the yields of iodine and fluorine were in good agreement with that predicted from a knowledge of the original amount of IF_5 present.

It now became necessary to quantitatively determine the amount of each of the combustion products in order to determine the enthalpy of formation of C_6F_5I. The analysis train used to accomplish this was identical to that used in the C_6F_6 and $C_6F_5CF_3$ combustions. Gas chromatographic analysis of the contents of the gas collection tube, when it was positioned immediately after the Teflon bubbler in the analysis train, gave peaks for CO_2, CF_4, and O_2. From Table 9 the average CO_2/CF_4 molar ratio was determined to be 11.11. The total carbon dioxide produced in the combustion of a sample of iodopentafluorobenzene was again determined using the carbon dioxide collection vessel filled with Lithasorb and magnesium perchlorate. The CO_2 experimental yields are shown in Table 9. Table 10 shows a calculation of the theoretical yield of CO_2, based on the average CO_2/CF_4 molar ratio and the assumption that CO_2 and CF_4 were the only carbon containing combustion products. The average per cent yield of CO_2 was found to be 100.11% as compared to the theoretically determined value, thus producing a carbon mass balance.

Preliminary analytical investigations of combustion products produced difficulty in the quantitative determination of F_2 in the Teflon bubbler, since it was found that a portion of the IF_5 formed in a combustion reached the Teflon bubbler and was detected by the fluoride specific ion electrode. Even when the bomb was cooled to 0°C in an ice-water bath prior to emptying and flushing, some of the IF_5 was

Table 9: Combustion Data and Calculated Enthalpy of Formation for Iodopentafluorobenzene

Run	Mass C_6F_5I g	ΔT_{cor} °C	CO_2/CF_4 [a] by g.c.	CO_2 collected g	IF_5 collected g	Total F_2 [b] collected g	$\Delta H^\circ_{f\ 298}(C_6F_5I,g)$ kcal/mol
1	1.981	0.8804	11.29	1.629			-105.2
2	2.072	0.9235	11.14	1.704			-103.6
3	1.531	0.6799	10.90	1.269		0.298	-105.7
4	1.360	0.6047	11.11	1.115			-105.0
5	1.444	0.6452	11.11	1.187	0.235	0.284	-102.2
6	1.351	0.6017	11.18	1.116	0.208	0.268	-104.2
7	1.328	0.5900	11.06	1.111	0.213	0.256	-105.5
8	1.374	0.6130	10.98	1.129	0.228	0.262	-103.2
9	1.464	0.6518	10.98		0.238	0.290	-104.0
10	1.365	0.6077					-104.2

a ≡ molar ratio

b ≡ from F_2 and IF_5

Table 10: Combustion Products for Iodopentafluorobenzene

Run	Theoretical CO_2 g	Actual CO_2 g	% CO_2 %	Theoretical[a] F_2 g	Actual[a] F_2 g	% F_2 %
1	1.633	1.629	99.76			
2	1.708	1.704	99.77			
3	1.262	1.269	100.55	0.299	0.298	99.67
4	1.121	1.115	99.46			
5	1.190	1.187	99.75	0.282	0.284	100.71
6	1.113	1.116	100.27	0.263	0.268	101.90
7	1.094	1.111	101.55	0.259	0.256	98.84
8	1.132	1.129	99.73	0.268	0.262	97.76
9				0.286	0.290	101.40

a ≡ from F_2 and IF_5

still detected in the Teflon bubbler.

The fluorine yield was determined as total F^-, that is, the F^- produced from F_2 in the bubbler and the F^- produced by the IF_5 both in the Teflon bubbler and that which remained in the bomb. The F^- in the Teflon bubbler was determined as with the C_6F_6 and $C_6F_5CF_3$ combustions using the fluoride specific ion electrode. The combustion products remaining in the bomb after emptying and flushing, were dissolved either in a saturated solution of potassium iodide, as in run 3, Table 9, or in a solution of sodium arsenite, as in runs 5 to 9 inclusive, Table 9. An aliquot of this solution was prepared for analysis with a fluoride specific ion electrode to determine the amount of F^- present in the bomb (and due to IF_5 remaining there). The total fluoride yield due to F_2 and IF_5 is then the sum of the fluoride found in the Teflon bubbler due to F_2 and IF_5 and the fluoride found in the bomb due to IF_5.

Table 9 shows the total fluoride yields due to F_2 and IF_5 expressed as grams of F_2 and Table 10 calculates the theoretical F^- yield due to F_2 and IF_5 based on the average CO_2/CF_4 molar ratio. Comparing the total fluoride yield from F_2 and IF_5, expressed in grams of F_2, with the theoretical yield of fluoride, again expressed as grams of F_2, Table 10 illustrates a recovery of 100.05%. The analytical procedures employed thus produced a mass balance for fluoride.

With a determination of total fluoride due to F_2 and IF_5 accomplished, it became necessary to analytically evaluate the amount of IF_5 produced in a combustion of C_6F_5I. Since IF_5 could be present both in the Teflon bubbler and in the bomb, it was necessary to determine the amount of IF_5 in each of the two locations. The amount of IF_5 present in the bomb after emptying and flushing could be related to the fluoride found in the bomb, which is due entirely to IF_5 and which was determined pre-

viously with the fluoride specific ion electrode. The amount of IF_5 found in the Teflon bubbler could be related to the amount of iodide present in the bubbler.

To insure that the iodide that was detected in the Teflon bubbler was due entirely to the presence of IF_5 and not to any I_2 which might have left the bomb and entered the bubbler, an experiment was performed whereby a weighed amount of iodine was placed in the combustion bomb which was then sealed and pressurized to 450 p.s.i. with oxygen. The bomb was set in an ice-water bath at 0°C and connected, as was the case in a normal combustion experiment, to the analysis train. The bomb was emptied and flushed and an aliquot of the solution in the bubbler was tested with an iodide specific ion electrode for the presence of iodide after it had been properly diluted with sodium arsenite solution and buffered with sodium bicarbonate solution. This testing showed no trace of detectable iodide in the bubbler indicating that it was reasonable to assume that during a combustion analysis all the iodide present in the bubbler was due to IF_5.

The analysis of the solution in the bubbler to determine IF_5 during a combustion experiment was accomplished with an iodide specific ion electrode which had previously been calibrated with standard iodide solutions obtained from Orion Company. Before analysis with the iodide specific ion electrode, the aliquot used was buffered with an aqueous solution of sodium bicarbonate to adjust the pH to between 5 and 9. Care was taken to insure that effervescence was not so vigorous as to carry away any iodine.

The total moles of IF_5 were then determined as the sum of one-fifth of the moles of fluoride found in the bomb and the total moles of iodide

found in the Teflon bubbler. The IF_5 produced by the combustion of C_6F_5I and determined in the previously described manner, expressed in grams, is shown in Table 9 and verified by a mass balance of total F^- from both F_2 and IF_5.

The determination of the total iodide yield remained to be performed so as to arrive at a complete mass balance. The iodide yield determined by the sum of the iodide produced from I_2 and IF_5 was determined by the iodide present in the bomb and in the Teflon bubbler. The iodide in the bomb is due to the I_2 and IF_5 present there. The iodide in the Teflon bubbler is due to the IF_5 in the bubbler, a value for which has already been determined.

In the event that one of the other two reported interhalogen compounds, that is, IF or IF_7 was formed in the combustion of C_6F_5I, an experiment had to be devised whereby their presence could be detected.

Sidgwick reports (37) with regard to IF_7 that "it seems to be curiously stable to water" and Ruff (38) says "the gas can even be blown through the liquid (water) with the formation of clouds, but with only very slight decomposition". In light of the preceeding statements, a combustion was performed and the bomb was connected to an analysis train in which there were two Teflon bubblers placed in series, identical in all respects except that the first bubbler contained 100 ml of distilled water and the second bubbler contained the usual solution of 5 ml of concentrated hydrochloric acid in 95 ml of distilled water. It was postulated that if IF_7 were present it would pass through the first bubbler containing the distilled water without reaction and be collected in the second bubbler containing the acidified solution. When tested for fluoride in the usual manner, the second bubbler containing the acidified

solution showed a negligible amount of fluoride, while the total fluoride yield, computed from the fluoride found in the distilled water bubbler and the fluoride found in the bomb was 99.80% of the total fluoride yield predicted from theoretical considerations.

The presence of IF as a reaction product was discounted in that neither the isolation of IF nor the determination of its physical properties have been reported. Durie and Gaydon (39) confirm that IF has been identified only by spectra and indicate that IF_5 is the most stable of this group of three interhalogen compounds, exhibiting stability at temperatures up to 400°C.

Several methods were attempted to determine the total iodide present in the bomb as the sum of I_2 and IF_5. These included dissolving the contents of the bomb, after emptying and flushing, with a saturated potassium iodide solution followed by titration with standard 0.1N sodium arsenite solution and determining the total iodide by means of an iodide specific ion electrode. Determination of iodide by these methods, when expressed in grams of iodine, yielded a value which was between 65% and 73% of the total theoretically determined yield.

It should be noted here that after the bomb had been emptied and flushed and was opened in the laboratory for analysis, the presence of a white smoke was immediately observed. In an effort to eliminate this smoke and improve the per cent recovery of iodide, the bomb was opened in a dry box under a nitrogen atmosphere. Under these conditions no smoke was observed when the bomb was opened. However, when the sodium arsenite solution was added to the contents of the bomb to prepare them for iodide analysis, the white smoke appeared and again the iodide yield was approximately 70% of the theoretical amount.

At this juncture several experiments were attempted using U.S.P. iodine from Fisher Scientific Company and IF_5 obtained from Matheson Company. The IF_5 was distilled under vacuum as previously described and was then distilled again under vacuum into a preweighed detachable finger. The finger and distilled IF_5 were then weighed in order to calculate the amount of IF_5 present. This finger containing the IF_5 was then attached, by means of a ground glass joint, to a vessel containing a weighed amount of iodine set in a cooled acetone bath at -45°C. The IF_5 was subsequently distilled under vacuum into the vessel containing the iodine. The vessel now containing the I_2 and IF_5 was sealed, removed from the vacuum system, and warmed to room temperature. The contents were shaken and then one of the three methods previously employed for the analysis of iodide in a combustion sample was carried out on the sample of pure I_2 and IF_5; that is, addition of a saturated solution of potassium iodide and titration with 0.1N sodium arsenite solution, or addition of sodium arsenite solution and determination of iodide with an iodide specific ion electrode, or opening the vessel in a dry box under a nitrogen atmosphere, adding sodium arsenite solution and determining iodide with an iodide specific ion electrode. Each of these methods produced the same results on the mixed samples of I_2 and IF_5 as it did on the combustion sample taken from the bomb. The per cent recovery expressed in grams of iodine varied from 68% to 73% relative to the total iodine that was originally present plus the contribution of the IF_5 added.

The following equations were postulated to account for the observed shortfall in recoverable iodide in the combustion samples and in the comparison experiments.

$$2\ I_2 + IF_5 + 5\ O_2 \xrightarrow[air]{moist} 5\ IO_2F \qquad [3.12]$$

and

$$IO_2F + H_2O \rightarrow IO_2(OH) + HF \qquad [3.13]$$

These reactions are supported by Aynsley and coworkers (32) and the work of Schmeisser and Lang (40) confirms the formation of $IO_2(OH)$ in the form $[IO_2^+.OH^-]$.

The IO_2F, iodyl fluoride, is a white solid which is stable in dry air but evolves HF on exposure to moist air. The product $IO_2(OH)$ shown in reaction [3.13] is not in the form of iodic acid, HIO_3, but is reported by Schmeisser and Lang (40) to be in the form $[IO_2^+.OH^-]$ which must be undetectable as iodide in either titration with sodium arsenite solution or determination with the iodide specific ion electrode. The reactions [3.12] and [3.13] still predict a theoretical yield for fluoride from IF_5 that is unchanged from that determined earlier and in good agreement with the experimentally determined yield shown in Table 10.

It was thought that if the I_2 and IF_5 in the bomb could be separated before exposure either to moist air or aqueous solutions, there might be a possibility of determining total iodide. To accomplish this the bomb, after a combustion, was emptied and opened in a dry box under a nitrogen atmosphere. Dry carbon tetrachloride was then added to the contents of the bomb. The colourless carbon tetrachloride became pink and the contents of the bomb readily dissolved in the solvent. Iodine pentafluoride is reported to react with carbon tetrachloride, at room temperature, to produce CCl_3F,ICl, ICl_3 and traces of CCl_2F_2 (38). The solution, originally containing I_2, IF_5 and CCl_4 was vigourously shaken and sodium arsenite solution was added to it in a separatory funnel until all the pink colour had been removed from the non-aqueous layer. When

an aliquot of the aqueous layer of the solution was tested with an iodide specific ion electrode, a 63% yield, as compared with that expected from theoretical considerations, was obtained for the iodide. The procedure was repeated using a weighed amount of iodine and a weighed amount of purified IF_5, as described in earlier test experiments, and a 65% yield of iodide was obtained.

Faced with a similar apparent iodide shortfall both in the combustion analyses and test experiments with IF_5 and I_2, and having obtained a material balance for both the total fluoride and total carbon in combustion experiments, it was assumed that all the iodide not found as IF_5 was present as I_2. The CO_2/CF_4 average molar ratio can then be used with the CO_2 and IF_5 yields to give the required combustion equation.

The data for the IF_5 produced in runs 5 to 9 inclusive in Table 9 along with the average CO_2/CF_4 molar ratio were employed to calculate the following equation which is representative of the combustion of iodopentafluorobenzene

$$C_6F_5I + 5.504\ O_2 \rightarrow 5.504\ CO_2 + 0.496\ CF_4 + 0.213\ IF_5 + 0.394\ I_2 + 0.975\ F_2 \qquad [3.14]$$

Before applying equation [3.14] to the combustion process, it was necessary to calculate the heat of association of the liquid IF_5 with the I_2 in the bomb. This experiment was carried out in a reaction calorimeter which had previously been calibrated and whose energy equivalent was found to be 157.2 cal/°C. A measured amount of IF_5 contained in a sealed vessel with a stopcock at the bottom was added to a measured amount of I_2 in the reaction vessel in the calorimeter. The IF_5 was treated as the limiting reagent. From this experiment, the heat of association of IF_5 and I_2 was found to be -10.4 kcal/mol of IF_5. A

sample of 0.8625 g of IF_5 produced a temperature rise of 0.2573°C in the reaction calorimeter used. A similar experiment was performed in the rotating bomb calorimeter. Initially the iodine was sublimed on to the bottom and walls of the bomb and a weighed amount of IF_5 was sealed in a thin-walled glass ampoule. The ampoule was then broken by means of a hot platinum fuse wire and the rotation of the bomb was started. This method for the determination of the heat of association of IF_5 and I_2 produced a value that was in good agreement with that determined previously in the reaction calorimeter.

In applying equation [3.14] to the combustion process to calculate $\Delta H^\circ_{f\ 298}(C_6F_5I,g)$, allowance was made for that portion of the total liquid sample originally placed in the bomb which was in the vapour state when combustion occurred. Again the combustion occurs under 450 p.s.i. of oxygen in a bomb of 0.320 l internal volume and at an initial temperature of 23.5°C.

Application of the Gibb's equation, the ideal gas law, and anciliary data as outlined in equations [3.5], [3.6], and [3.7] gives a value of $w_g = 0.0091$ g as the amount of iodopentafluorobenzene that is in the vapour state when combustion occurs. Therefore only (W - 0.0091) g of liquid iodopentafluorobenzene are involved in the combustion under the present experimental conditions, where W is the initial total weight of the liquid iodopentafluorobenzene prior to combustion.

The National Bureau of Standards values for the enthalpies of formation of CO_2 and CF_4 were taken as -94.0517 kcal/mol and -221.0 kcal/mol respectively (26). The standard enthalpy of formation of IF_5 was taken as -210.437 (47). The allowance for C_6F_5I in the vapour state,

$$[(W - 0.0091)/W]\Delta H^\circ_{vap}(C_6F_5I) \qquad [3.15].$$

was based on an enthalpy of vapourization of 13.97 kcal/mol (31). From the experimental results in Table 9, the average value of $\Delta H^\circ_{f\ 298}$ (C_6F_5I,g) obtained is -104.3 ±0.9 kcal/mol.

Discussion of Thermochemical Results

A method has been developed which permits the determination of enthapies of formation of perfluoroaromatic and halogen substituted perfluoroaromatic compounds that requires no auxiliary substances whatsoever to achieve complete combustion. No published values exist for the enthalpies of formation of octafluorotoluene and iodopentafluorobenzene. The value which has been reported by Cox and coworkers (28) for the enthalpy of formation of hexafluorobenzene is in good agreement with the present work, lending credence to the method which was devised in this work.

The present work calculates the enthalpies of formation of the compounds studied as follows

$$\Delta H^\circ_{f\ 298}(C_6F_6,g) = -223.9 \pm 1.2 \text{ kcal/mol}$$

$$\Delta H^\circ_{f\ 298}(C_6F_5CF_3,g) = -300.2 \pm 1.2 \text{ kcal/mol}$$

$$\Delta H^\circ_{f\ 298}(C_6F_5I,g) = -104.3 \pm 0.9 \text{ kcal/mol}$$

For the convenience of those persons using the joule as the unit of energy, the enthalpies of formation have been recalculated on that scale. Using 1 calorie = 4.1840 absolute joule, the enthalpies of formation are as follows

$$\Delta H^\circ_{f\ 298}(C_6F_6,g) = -936.8 \text{ kJ/mol}$$

$$\Delta H^\circ_{f\ 298}(C_6F_5CF_3,g) = -1256.0 \text{ kJ/mol}$$

$$\Delta H^\circ_{f\ 298}(C_6F_5I,g) = -436.4 \text{ kJ/mol}$$

If the bond energy term for the C-F bond in fluoroaromatic compounds is constant, that is, transferable from one molecular structure to another, then enthalpies of formation can be calculated based on the relation

$$\Delta H_f^\circ(C_6F_5X,g) = \Delta H_f^\circ(C_6H_5X,g) + 5\Delta H_f^\circ(C_6H_5F,g) - 5\Delta H_f^\circ(C_6H_6,g) \quad [3.16]$$

The following values of $\Delta H_f^\circ(g)$ were used in the calculations of $\Delta H_f^\circ(C_6F_5X,g)$, all being referred to 298°K

$$\Delta H_f^\circ(C_6H_5I,g) = 38.35 \text{ kcal/mol (41,42)}$$

$$\Delta H_f^\circ(C_6H_5F,g) = -27.76 \text{ kcal/mol (19)}$$

$$\Delta H_f^\circ(C_6H_6,g) = 19.83 \text{ kcal/mol (26)}$$

They give rise to the following calculated enthalpies of formation.

$$\Delta H_f^\circ(C_6F_6,g) = -265.7 \text{ kcal/mol}$$

$$\Delta H_f^\circ(C_6F_5I,g) = -199.6 \text{ kcal/mol}$$

The experimentally determined values of $\Delta H_f^\circ(C_6F_6,g)$ and $\Delta H_f^\circ(C_6F_5I,g)$ at 298°K are -223.9 kcal/mol and -104.3 kcal/mol respectively. They differ from the values obtained via equation [3.16] by 41.8 kcal/mol and 95.3 kcal/mol respectively. These differences are far greater than can be explained by all the uncertainties involved in obtaining the experimental number. It can thus be concluded that the assumption made about the constancy of the difference between the C-F bond energy and C-H bond energy terms is not justified. The value of $\Delta H_f^\circ(g)$(experimental) - $\Delta H_f^\circ(g)$(calculated) can be referred to as $\Delta H_{destabilization}$ and is calculated to be 41.8 kcal/mol and 95,3 kcal/mol for hexafluorobenzene and iodopentafluorobenzene respectively. The ΔH_{destab} of octafluorotoluene can not, at present, be determined since the value of $\Delta H_f^\circ(C_6H_5CF_3,g)$ is lacking.

There is an alternate approach to the problem of calculating destabilization energies in molecules of the type C_6F_5X. Calculation of the energy of interaction between dipoles in C_6X_6 indicate that two-thirds of the total interaction energy arises from interactions with the C_6X_5 group and one-third from interaction between the C_6X_5 group and the remaining C-X dipole (24). This enables a very approximate estimate of the destabilization energy in C_6F_5X to be made by the relation

$$\Delta H_{destab}(C_6F_5X) = 2/3\Delta H_{destab}(C_6F_6) + 1/3\Delta H_{destab}(C_6X_6) \qquad [3.17]$$

This calculation can not be performed at present for the iodopentafluorobenzene since a value for $\Delta H^\circ_{f\ 298}(C_6I_6,g)$ and hence $\Delta H_{destab}(C_6I_6)$ is not available.

CHAPTER IV

THE PYROLYSIS OF IODOPENTAFLUOROBENZENE

Apparatus and Procedure

A schematic diagram of the toluene carrier flow system used in the pyrolysis of iodopentafluorobenzene is shown in Figure 12.

The vacuum source of the system was a two-stage mercury diffusion pump backed by a two stage oil-sealed rotary vane fore pump, Balzers Duo 5. All ground glass joints were lubricated with Dow Corning High Vacuum Silicone Stopcock Grease. Any heated taps were lubricated with Apiezon T grease, while Apiezon N grease was used for lubrication of the unheated taps. Due to the fact that toluene tends to attack grease, high vacuum stopcocks obtained from Ace Glass Company, equipped with a Teflon barrel and three Viton O-ring seals, were used in the carrier inlet system.

An electric furnace was used to heat the reaction vessel. The furnace was constructed from a quartz cylinder three inches in diameter and twenty-four inches long with a wall thickness of one-quarter inch. The quartz cylinder was wound with Chromel-A resistance ribbon, 2 mm wide and 0.2 mm thick, having a resistance of 0.603 ohm/ft. The windings were cemented into place with Sauereisen Cement, Number 31. The spacing of the windings is shown in Figure 13. The heating element was tapped at seven points so that the temperature profile could be adjusted by shunt resistances. An inconel liner 2.5 in. in diameter, 12 in long, and 0.25 in thick was centred inside the quartz cylinder to even out the temperature profile.

The quartz tube was centred horizontally in a box of dimensions

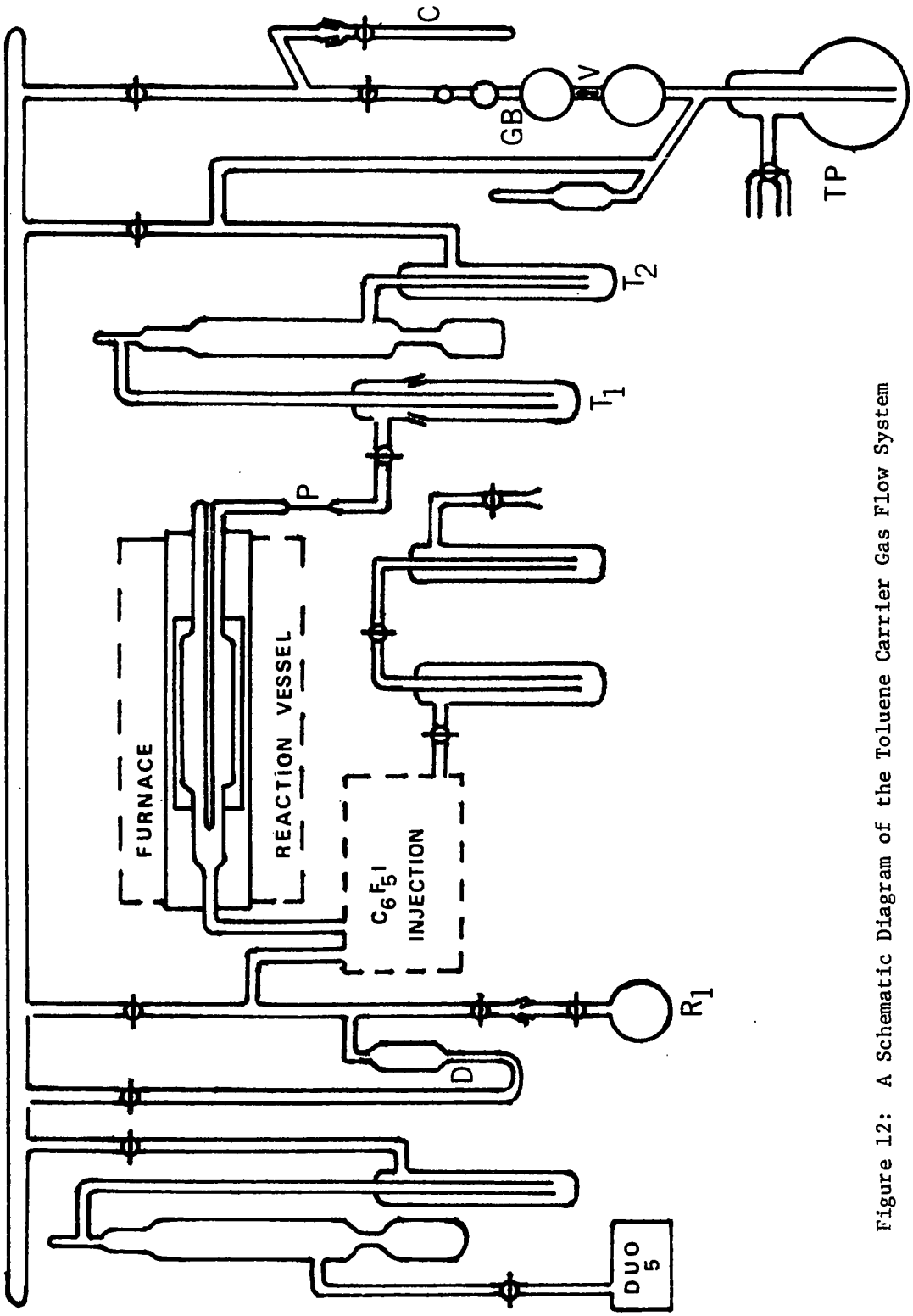


Figure 12: A Schematic Diagram of the Toluene Carrier Gas Flow System

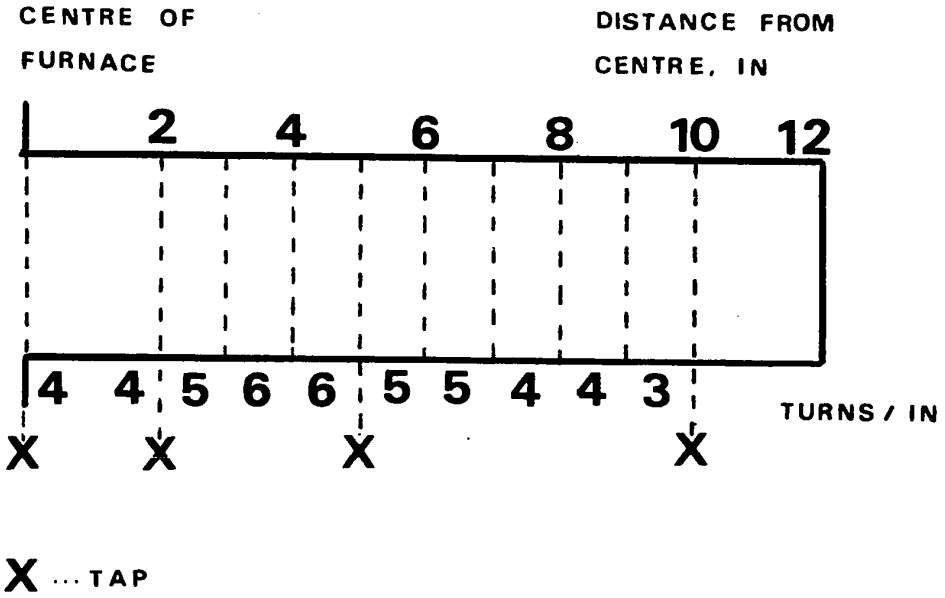


Figure 13: The furnace block showing the windings and the taps for changing the temperature profile

12 in X 12 in X 24 in. and constructed of 0.25 in. asbestos sheeting with a 0.75 in. angle iron frame. The ends of the asbestos box had 3 in diameter holes to accomodate the quartz tube. A mixture of powdered alumina and Fibrefrax ceramic fibre from Carborundum Company filled the remainder of the box to provide insulation. The furnace was connected through a Type W 20 HM Variac (Autotransformer) to a 220 V alternating current laboratory power source. The maximum operating temperature of the furnace was 1200°C.

A 10 ohm platinum resistance thermometer was mounted along the inside wall of the quartz tube to act as the sensing element for a Sunvic Resistance Thermometer Controller, Type RT 2. The measurement of the voltage across a movable Chromel - P - Alumel thermocouple, which was inserted in the axial thermocouple well of the reaction vessel, provided a means of monitoring the temperature in the vessel. A Leeds and Northrup Millivolt Potentiometer, Model 8691 was used in the measurement of this voltage. With the inconel liner extending over the length of the reaction zone, the temperature was maintained within ±2°C with a steep fall-off of temperature at the ends as shown in Figure 14.

The reaction vessel was made of fused quartz with graded quartz to Pyrex seals a few inches beyond the ends of the furnace. The vessels were 40 mm o.d. and 6 to 8 inches in length, sealed to 20 mm o.d. ends. An axial thermocouple well constructed of 10 mm o.d. tubing ran the length of the reaction vessel as illustrated in Figure 12. The shape of the reaction vessel was designed to minimize turbulence and channelling. The reaction vessel employed in this work was treated with hot fuming nitric acid before use. The residual acid was baked out under vacuum after the vessel was installed in the system. The bake-out pro-

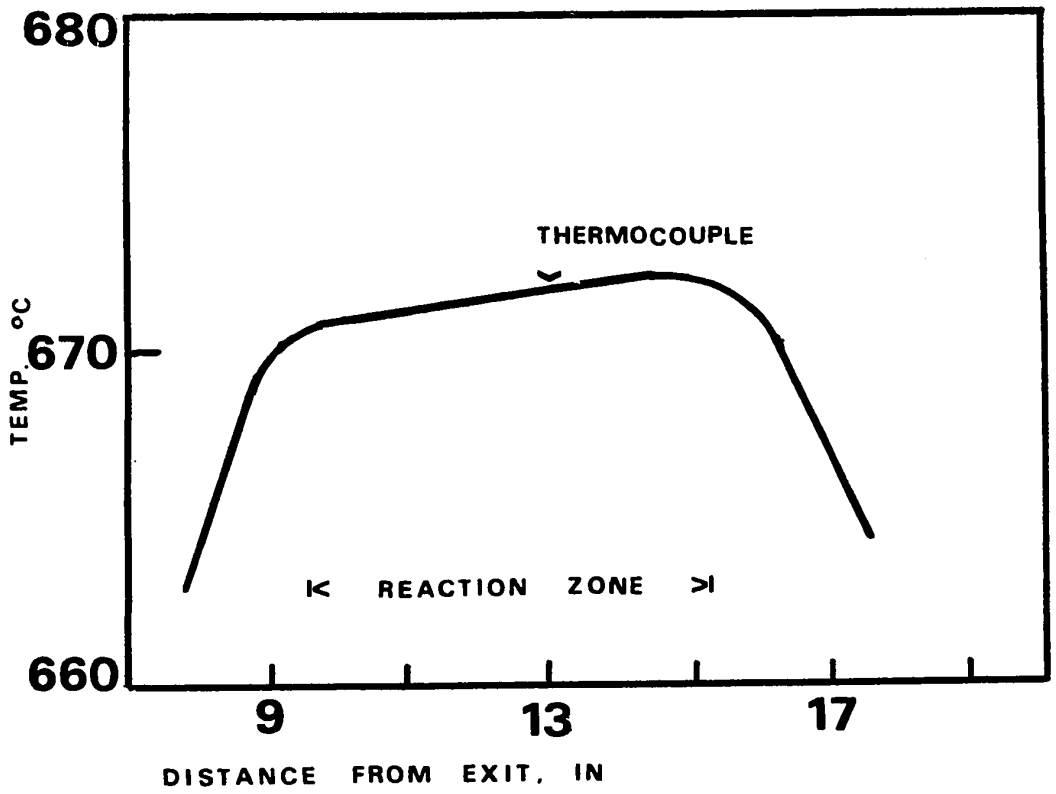


Figure 14: A typical temperature profile

cedure was carried out at 100°C to 200°C higher than the temperature used in the experimental work.

The flow rate through the reaction zone was controlled by the length and inside diameter of the sealed in capillaries at the outlet of the furnace as illustrated in Figure 12.

The tubing on the inlet side of the reaction vessel was wound with Chromel-A asbestos covered heating wire connected to a Variac. This allowed the tubing to be heated up to approximately 90°C when necessary.

After the furnace was steady at a particular temperature and the vacuum had reached 10^{-4} mm Hg or better, a run could begin. The toluene used was stored in a detachable vessel, R_1, Figure 12, so that it could be weighed before and after each run. A constant temperature water bath maintained the required toluene carrier pressure. The pressure of the toluene carrier was read on a dioctylphthalate-mercury differential manometer, represented by D in Figure 12, having a 10.4 magnification factor as compared to a mercury manometer.

A small amount of the iodopentafluorobenzene was distilled from its detachable vessel, R_2, to the finger F_1 under vacuum as shown in Figure 15. A fixed temperature bath in a Dewar flask was placed around F_1 to obtain the desired iodopentafluorobenzene pressure. The vapour pressure of iodopentafluorobenzene was, at all times, greater than the toluene carrier pressure to prohibit any back diffusion of toluene vapour into the iodopentafluorobenzene injection system. The magnitude of the difference in vapour pressures determined the concentration of iodopentafluorobenzene in the toluene stream.

To begin a run, the flow of toluene was commenced and the pressure, as recorded on the differential manometer, was noted. A prerun flow of toluene which extended for five minutes was performed to help stabilize

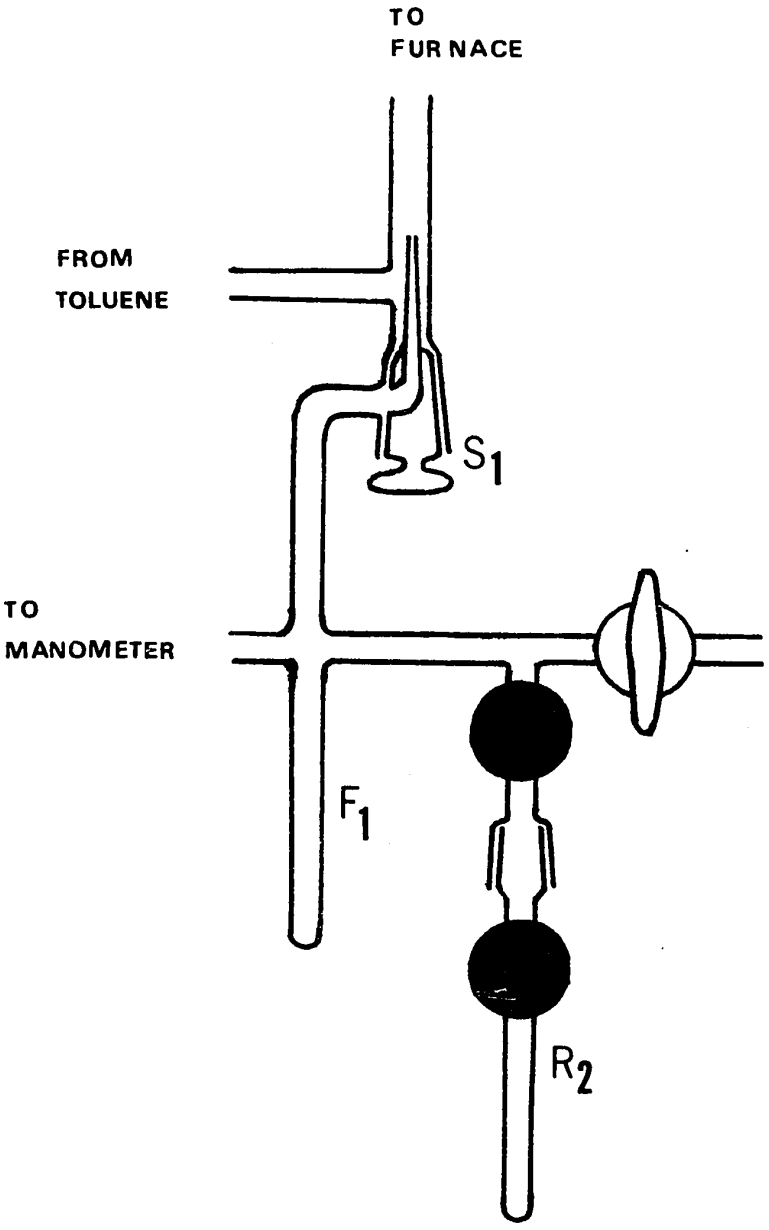


Figure 15: The iodopentafluorobenzene injection system

the flow conditions. After the prerun period, tap S_1 as shown in Figure 15, was opened and the iodopentafluorobenzene was admitted into the toluene stream. The flow of iodopentafluorobenzene continued from 25 m to 30 m depending on the reaction conditions used. This period was followed by a fiveminute postrun with the toluene alone. The iodopentafluorobenzene remaining in F_1 was redistilled into R_2 and then both R_1 and R_2 were weighed. The weights of R_1 and R_2 after the run had been performed were compared to their respective weights taken prior to the run and the respective amounts of toluene and iodopentafluorobenzene used in the run were determined.

Trap T_1, Figure 12, thermostated at -80°C with an acetone-dry ice bath, collected the liquid products. In the event that some of the liquid products passed by T_1 and were not trapped, T_2 was maintained at liquid nitrogen temperatures for insurance. The remaining gaseous mixture, if it passed by T_2, could be transferred by means of a Toepler pump past a non-return valve to a calibrated gas burette. A sample of the gaseous products could then be sealed into the collection vessel, C, after the pressure, volume, and temperature data of the mixture had been obtained.

During a run the total pressure and the iodopentafluorobenzene temperature were checked and recorded every two minutes. The furnace temperature was recorded every two minutes and then averaged. The variation was never more than 1.5°C over the period of the run.

The gaseous products were analyzed using a Perkin Elmer, Model 154 gas chromatograph equipped with a thermal conductivity detector. A 6 ft X 1/4 in. o.d. silica gel column was used. The column was maintained at 80°C and a helium carrier flow rate of 20 cc/m was used.

The liquid sample collected in T_1 was removed from the trap and sealed in an airtight, amber coloured sample bottle. The liquid products were analyzed on a Perkin Elmer 900 gas chromatograph equipped with a flame ionization and electron capture detector. A 6 ft X 1/8 in. o.d. Silicone Oil DC-710 column was used in the analysis and operated at 105°C.

Synthetic mixtures containing the components present in the liquid sample, that is pentafluorobenzene, toluene, and iodopentafluorobenzene were made by weighing each component into a 100 ml amber volumetric of known weight. From these calibration mixtures, calibration curves were constructed.

Materials

Toluene

The toluene used was from sulfonic acid and was purchased from Eastman Organic. It was dried by refluxing over sodium ribbon under vacuum and then degassed by bulb to bulb distillation.

Iodopentafluorobenzene

The iodopentafluorobenzene used in the kinetic work was from the same batch as that used in the thermochemical investigation of the compound by bomb calorimetry. A description of pertinent physical properties may be found in Chapter III.

Experimental Results and Discussion

The pyrolysis of iodopentafluorobenzene was undertaken in conj-

unction with Dr. M. Krech (43) who is presently continuing with detailed analytical work on this subject with Dr. J. Kominar to give further confirmation to the mechanism proposed by Krech and Price (44). The object of this present experimental work was to investigate the Arrhenius equation proposed by Krech for the pyrolysis of iodopentafluorobenzene and either substantiate or alter his proposed values for the activation energy and the pre-exponential factor.

The data obtained for the present work on the pyrolysis of iodopentafluorobenzene is found in Table 11. The present work studied the thermal decomposition of C_6F_5I from 900.2°K to 978.2°K and pressures of 11.21 mm to 19.05 mm with contact times ranging from 0.397 s to 2.010 s.

The rate constants were calculated using the first order rate equation in the form

$$k = (2.303/t_c) \log [100/(100 - x)] \qquad [4.1]$$

where x represents the per cent of reactant decomposed. The contact time, t_c, was evaluated from the expression

$$t_c = (V/22416.)(P/760)(273/T)(1/F) \qquad [4.2]$$

where V in cc represents the volume of the reaction vessel, P is the overall pressure during the run in mm, T is the temperature in °K, and F in moles/s is the molar flow rate through the reaction zone. The per cent decomposition was calculated from the residual C_6F_5I remaining after pyrolysis and determined by chromatographic analysis of the liquid products collected from a run, that is

$$x = \frac{(\text{g of } C_6F_5I \text{ used}) - (\text{g of } C_6F_5I \text{ recovered})}{\text{g of } C_6F_5I \text{ used}} \qquad [4.3]$$

It is interesting to note that both in the analysis of the liquid

products and in the construction of calibration curves for their analysis, ratios of peak areas served as the basis for comparison. Areas were calculated by means of a Perkin Elmer printing integrator and comparison between the calibration mixtures and the liquid sample obtained from a run was on the basis of relative areas of pentafluorobenzene to toluene and iodopentafluorobenzene to toluene. This method was employed because it gave excellent reproducibility in the aforementioned ratios.

The presence of HI as the only detectable major gaseous product was confirmed by gas chromatographic analysis of the collectable gas products. Quantitative determination of the HI present was not attempted since the HI was found to react both with the mercury in the Toepler pump on the pyrolysis system and with the mercury in the gas chromatographic injection system.

Mulcahy and Pethard (45) recommend that $3.0 > \frac{t_c, s}{P, cm} > 0.5$ to avoid significant thermal equilibrium problems. Approximately 70% of the runs in Table 11 fall within these recommendations and there appears to be no problem with those remaining runs whose value of (t_c/P) falls below the recommended limit. The results calculated for runs 4 and 5, runs 6, 7, and 8, and runs 9 and 10 support this conclusion. The negligible effect on k of a variation by a factor of 3.1 in molar toluene to iodopentafluorobenzene ratio (3.7 in iodopentafluorobenzene concentration) at 927°K and by a factor of 2.8 in molar toluene to iodopentafluorobenzene ratio at 900°K coupled with the investigations on this aspect by Krech indicates that the decomposition is first order.

Relating the fact that the parent C_6F_5I has approximately eighteen effective oscillators to the work of Pritchard, Sowden, and Trotman-

Table 11: Fundamental Data for the Pyrolysis of Iodopentafluorobenzene

Run	Pressure mm	Furnace Temp.°K	Time[a] m	Toluene Used g	C_6F_5I Used g	Toluene/C_6F_5I Molar Ratio
1	11.21	966.9	5,30,5	3.6132	0.0337	342.
2	19.05	952.7	5,30,5	7.6828	0.0516	475.
3	15.25	932.8	5,30,5	20.7281	0.1285	515.5
4	14.72	949.4	5.25,5	17.2833	0.2054	268.8
5	18.64	949.9	5.30,5	5.0692	0.0416	389.4
6	15.13	927.9	5,30,5	5.0145	0.2556	62.7
7	13.55	927.4	5,30,5	4.3565	0.0871	159.8
8	11.67	926.9	5,25,5	12.5936	0.2096	191.9
9	11.49	9]2.2	5,25,5	12.4284	0.1946	204.1
10	14.55	9]2.2	5,30,5	4.8481	0.1003	154.4
11	14.62	900.2	5,30,5	4.8284	0.0850	181.5
12	14.45	900.2	5,30,5	4.7548	0.1943	78.3
13	11.82	978.2	5,25,6	13.3740	0.1891	225.9

a ≡ the times representing the prerun, run, and postrun respectively

Dickenson (46) indicates that all the studies performed in the present work are essentially producing the high pressure limiting value of the rate constant, k.

The agreement in Figure 16 with the experiments conducted in unpacked vessels and those in packed vessels which were performed by Krech, shows that no detectable surface reactions are occurring.

The mechanism used in the determination of the first order rate constant is postulated by Krech and Price (44) to be

$$C_6F_5I \rightarrow C_6F_5 + I \qquad [4.4]$$

$$C_6F_5 + C_6H_5CH_3 \rightarrow C_6F_5H + C_6H_5CH_2 \qquad [4.5]$$

$$I + C_6H_5CH_3 \rightarrow HI + C_6H_5CH_2 \qquad [4.6]$$

$$I + I + M \rightarrow I_2 + M \qquad [4.7]$$

$$2\ C_6H_5CH_2 \rightarrow (C_6H_5CH_2)_2 \qquad [4.8]$$

$$C_6H_5CH_2 + I \rightarrow C_6H_5CH_2I \qquad [4.9]$$

$$2\ C_6F_5 \rightarrow C_6F_5\text{-}C_6F_5 \qquad [4.10]$$

$$C_6F_5 + C_6H_5CH_2 \rightarrow C_6H_5CH_2\text{-}C_6F_5 \qquad [4.11]$$

The present calculation of the rate constant is based on the fact that equation [4.4] is the rate determining step and that the pyrolytic decomposition of C_6F_5I is the initial rupture of a C-I bond rather than a C-F bond. It may be concluded from a cursory examination of the C-F and C-I bond strengths that it is very favourable energetically to rupture the C-I bond rather than the C-F bond.

What must now be examined to add credence to the mechanism proposed is evidence that other forms of attack on the parent C_6F_5I do not play a part in the determination of the rate constant. Attack on the parent

C_6F_5I could conceivably come in the following manner

$$C_6F_5 + C_6F_5I \rightarrow C_6F_5 + C_6F_5I \quad [4.12]$$

$$I + C_6F_5I \rightarrow C_6F_5 + I_2 \quad [4.13]$$

$$I + C_6F_5I \rightarrow C_6F_4I + IF \quad [4.14]$$

$$C_6H_5CH_2 + C_6F_5I \rightarrow C_6H_5CH_2F + C_6F_4I \quad [4.15]$$

$$C_6H_5CH_2 + C_6F_5I \rightarrow C_6H_5CH_2I + C_6F_5 \quad [4.16]$$

Reaction [4.12] does not affect the rate constant since it is a thermoneutral reaction which, if it occurred, would produce the parent C_6F_5I as a product. It has further been shown through the pentafluorobenzene yield in Table 12, that approximately 80% to 100% of the C_6F_5 produced reacts via reaction [4.5] to form C_6F_5H.

When the toluene to iodopentafluorobenzene molar ratio was relatively low, as in runs 6 and 12, Table 11, the C_6F_5H produced accounted for only about 65% of the C_6F_5 produced, but no effect was observed on the value of the rate constant, k. These facts lend support to the conclusion that k_{-1} is insignificant.

The relative roles of reactions [4.13] and [4.6] depend upon the toluene to iodopentafluorobenzene molar ratios. No observable change in $k_{[4.4]}$ occurs even with a ratio change from 62.7:1 to 475:1. It seems unlikely therefore that reaction [4.13] plays any significant role. Reaction [4.6] exhibits an endothermicity of approximately 13 kcal/mol. Based on $D[C_6F_5\text{-}I]$ = 69 kcal/mol, reaction [4.13] has an endothermicity of 17 kcal/mol. It therefore seems reasonable to assume that the rate constant of reaction [4.6] is greater than that of reaction [4.13]. Based on a molar ratio of 150:1, reaction [4.13] should account for a maximum of 0.07% of the I removal (0.07% of reaction [4.6], not taking into account

Table 12: Rate Constant Data for the Pyrolysis of Iodopentafluorobenzene

Run	t_c s	% decomposition %	Moles C_6F_5H x 10^{-4}	log k (s^{-1})	$10^3/T$ $°K^{-1}$
1	2.010	97.74		0.275	1.034
2	1.521	78.81	1.222	0.008	1.050
3	0.445	18.81	0.306	-0.330	1.072
4	0.459	27.70	1.599	-0.051	1.053
5	1.891	84.29	0.710	-0.010	1.053
6	1.588	47.89	2.557	-0.387	1.078
7	1.639	46.28	1.307	-0.422	1.078
8	0.427	15.17	0.872	-0.415	1.079
9	0.433	8.59	0.590	-0.684	1.096
10	1.607	27.97	1.383	-0.691	1.096
11	1.643	19.81		-0.873	1.111
12	1.650	18.30		-0.912	1.111
13	0.397	65.80	3.815	0.437	1.022

reactions [4.7] and [4.9]).

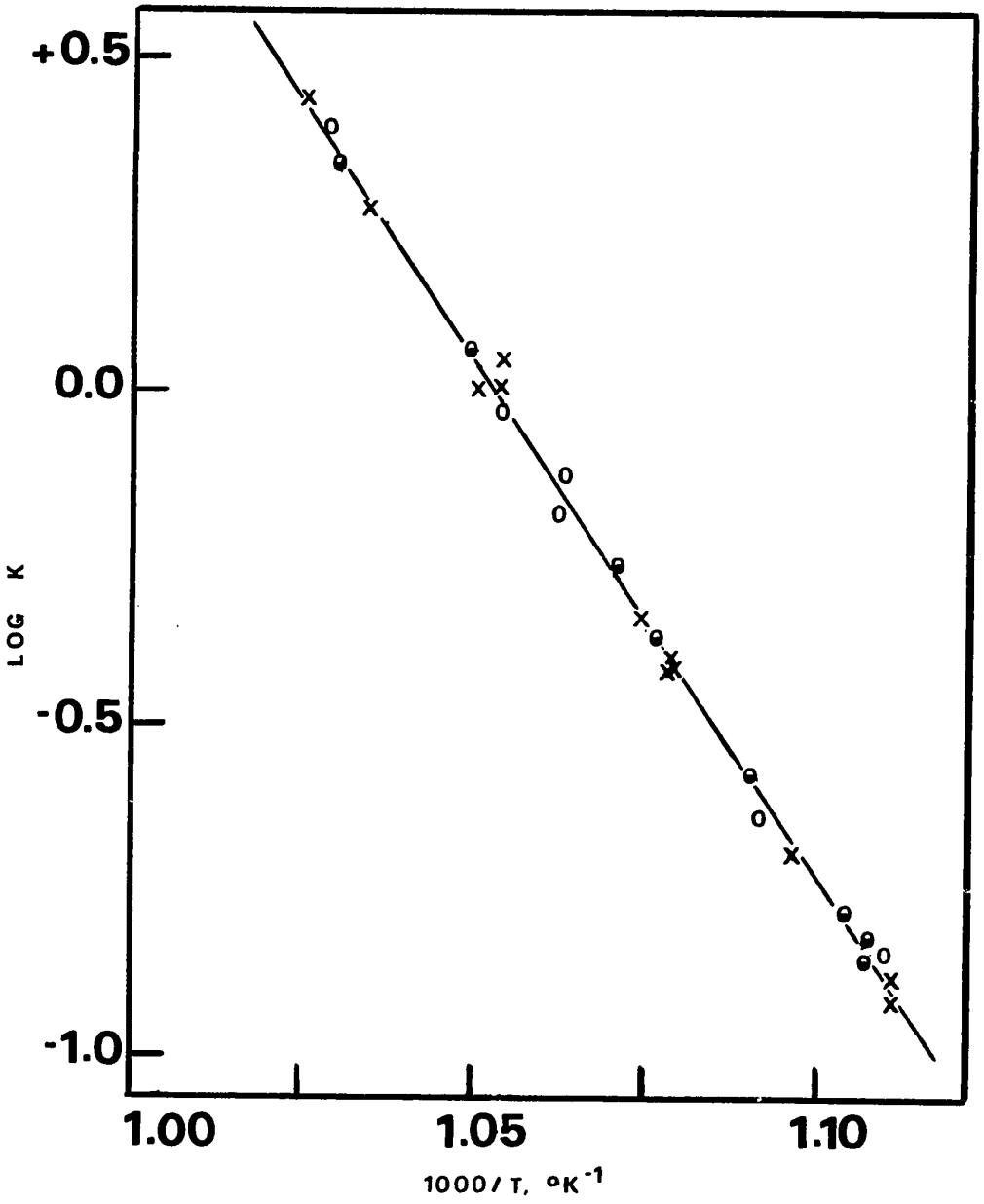
It is probably valid to assume that in C_6F_5I, D[C-F]>>110 kcal/mol. Using $\Delta H^\circ_{f\ 298}(IF,g)$ = -22.86 kcal/mol (47), D[I-F] ≈ 67 kcal/mol. Reaction [4.14] is therefore endothermic by at least 43 kcal/mol, making it an unlikely possibility for attack on the parent C_6F_5I.

For reaction [4.15] to proceed a C-F bond must be ruptured. Again setting D[C-F]>>110 kcal/mol in C_6F_5I, the endothermicity of the reaction can be examined. Benson (48) estimated $D[C_6H_5CH_2\text{-}Br]$ = 57 kcal/mol and $D[C_6H_5CH_2\text{-}Cl]$ ≈ 68 kcal/mol. From this it is reasonable to assume that $D[C_6H_5CH_2\text{-}F]$>68 kcal/mol and possibly in the area of 90 kcal/mol. This gives reaction [4.15] a minimum endothermicity of 20 kcal/mol and makes it unfavoured for attack on the parent C_6F_5I. It is also probable that $C_6H_5CH_2F$ would be seen in the analysis of the liquid pyrolysis products at a retention time between that of toluene and C_6F_5I if it was present as a product of reaction [4.15].

In the same manner as the endothermicity was determined for reaction [4.15], reaction [4.16] can be examined. If $D[C_6F_5\text{-}I]$ is set at 69 kcal/mol and with the knowledge that $D[C_6H_5CH_2\text{-}I]$<57 kcal/mol (48) and is probably close to 50 kcal/mol, reaction [4.16] exhibits an endothermicity of approximately 20 kcal/mol making it unfavoured compared to reactions [4.8] and [4.11] which exhibit thermoneutrality and reaction [4.9] which is exothermic.

This discussion then leads to the conclusion that reaction [4.4], as the originally proposed rate determining step, is the only favoured reaction of parent C_6F_5I.

A least squares analysis of the points used to obtain the plot in Figure 16 gives



X ≡ present work, unpacked vessel
O ≡ Krech, unpacked vessel
Θ ≡ Krech, packed vessel

Figure 16: Arhennius plot for the pyrolysis of iodopentafluorobenzene

$$\log k\ (s^{-1}) = 15.9 - 69200/2.3RT \qquad [4.17]$$

The observed activation energy of 69.2 kcal/mol should then be a reasonable measure of $D[C_6F_5\text{-}I]$.

CHAPTER V

THE CALCULATION OF BOND ENERGIES

The present work has produced the following data

$$D[C_6F_5\text{-}I] = 69.2 \text{ kcal/mol}$$

$$\Delta H^\circ_{f\ 298}(C_6F_6,g) = -223.9 \text{ kcal/mol}$$

$$\Delta H^\circ_{f\ 298}(C_6F_5CF_3,g] = -300.2 \text{ kcal/mol}$$

$$\Delta H^\circ_{f\ 298}(C_6F_5I,g] = -104.3 \text{ kcal/mol}$$

Using the relationship, referred to 298°K and in the gaseous state

$$D[C_6F_5\text{-}I] = \Delta H^\circ_f(C_6F_5) + \Delta H^\circ_f(I) - \Delta H^\circ_f(C_6F_5I) \qquad [5.1]$$

and the value

$$\Delta H^\circ_f(I) = 25.5 \text{ kcal/mol} \quad (47)$$

in conjunction with the aforementioned enthalpies of formation, produces

$$\Delta H^\circ_f(C_6F_5) = -60.6 \text{ kcal/mol}$$

The values of $D[C_6F_5\text{-}X]$ calculated from

$$D[C_6F_5\text{-}X] = \Delta H^\circ_f(C_6F_5) + \Delta H^\circ_f(X) - \Delta H^\circ_f(C_6F_5X) \qquad [5.2]$$

are shown in Table 13.

In work done by Dibeler (49), the observed ionization potential of C_6F_6 was approximately 0.7 eV greater than that of C_6H_6 which was determined to be 9.2 eV. Kandel (50) reports $I(C_6H_5) = 9.9$ eV which is 0.7 eV greater than $I(C_6H_6)$. Based on a similarilty of structure and of ionization processes, Dibeler (49) therefore estimates $I(C_6F_5) = 10.6$ eV. The appearance potential of $C_6F_5^+$ from C_6F_6 is 16.9 eV (49, 51). This leads to $D[C_6F_5\text{-}F] = 6.3$ eV or 145 kcal/mol. This varies from the value obtain-

Table 13: Calculation of $D[C_6F_5\text{-}X]$

C_6F_5X X=	$\Delta H^\circ_{f\ 298}(X,g)$ kcal/mol	$\Delta H^\circ_{f\ 298}(C_6F_5X,g)$ kcal/mol	$D[C_6F_5\text{-}X]^a$ kcal/mol	$D[C_6F_5\text{-}X]^b$ kcal/mol
F	18.9 (47)	-223.9	182.2	175.3
H	52.1 (26)	-201.3 (28)	192.8	185.9
CF_3	-114.0 (26)	-300.2	125.6	118.7
CH_3	33.2 (26)	-211.4 (28)	184.0	177.1
Cl	29.0 (47)	-203.3 (28)	171.7	164.8
OH	9.3 (26)	-244.9 (28)	193.6	186.7
I	25.5 (47)	-104.3	69.2[c]	62.3

a ≡ Based on $\Delta H^\circ_{f\ 298}(C_6F_5I)$ and the kinetic value for $D[C_6F_5\text{-}I]$

b ≡ Based on the ionization potential of C_6F_5 = 9.3 ±0.4 eV and $\Delta H^\circ_{f\ 298}(C_6F_6,g)$ (see Appendix B)

c ≡ Direct kinetic measurement

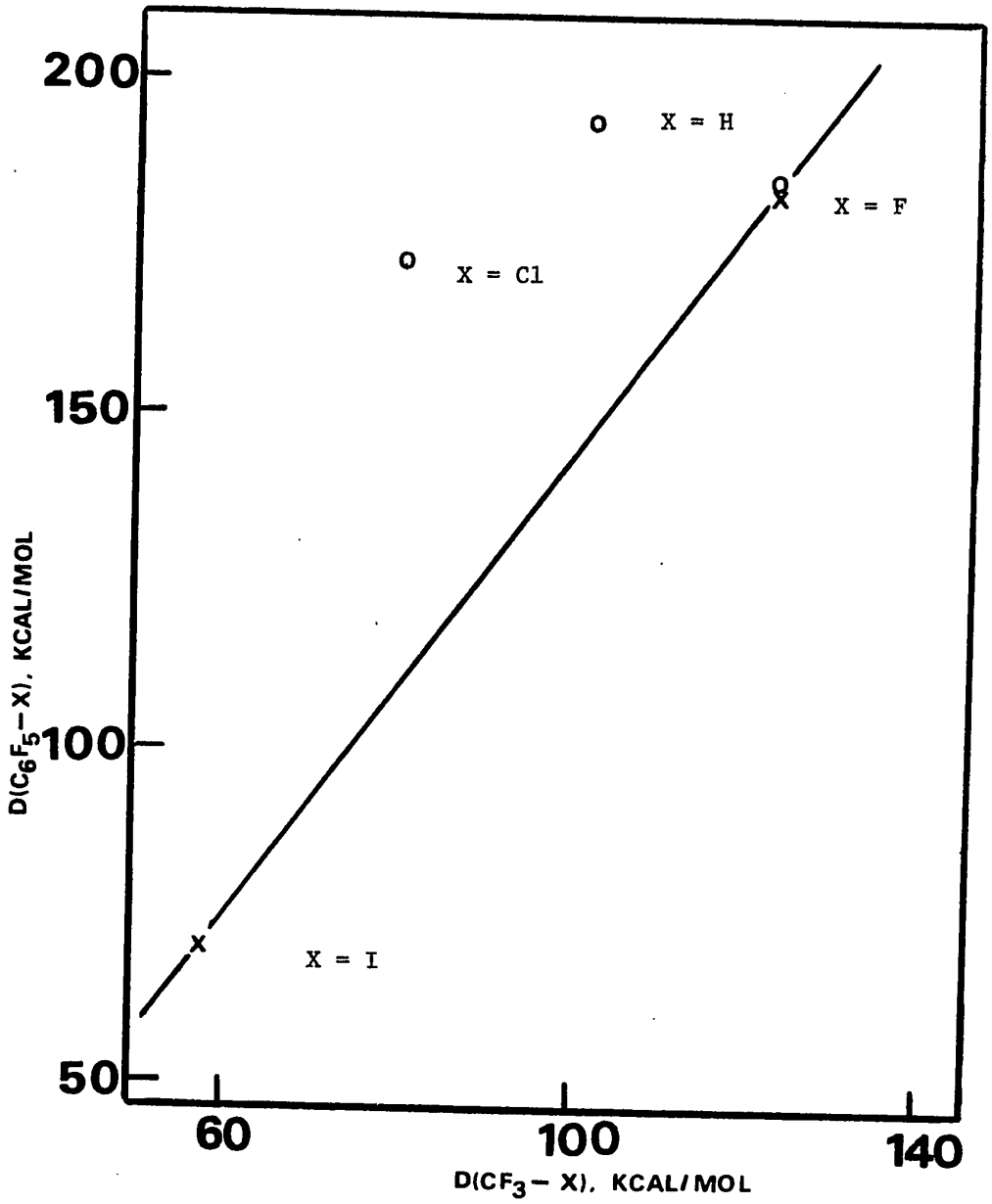
ed in this work based on $\Delta H^{\circ}_{f\ 298}(C_6F_5I,g)$ and the kinetically determined $D[C_6F_5\text{-}I]$ by 37.2 kcal/mol.

An approximate direct measurement of the ionization potential of C_6F_5 was performed in the present work (see Appendix B), and produced a value of $I(C_6F_5)$ = 9.3 ±0.4 eV. Using this value with the appearance potential of $C_6F_5^+$ = 16.9 eV (49, 51) gives rise to a value of $D[C_6F_5\text{-}F]$ = 175.3 kcal/mol and allows the second set of $D[C_6F_5\text{-}X]$ values shown in Table 13 to be calculated. From Table 13, is can be seen that the bond dissociation energies determined by thermochemical methods vary by 6.9 kcal/mol from those calculated from electron impact considerations. It should be noted that this difference is within the limits of experimental error placed on the ionization potential of C_6F_5.

Table 13 shows that $D[C_6F_5\text{-}CH_3] > D[C_6F_5\text{-}CF_3]$ by 58.4 kcal/mol. It is postulated that this large difference in bond dissociation energy may be due to the fact that the fluorine in CF_3 tends to be strongly electron withdrawing, thus weakening the $C_6F_5\text{-}CF_3$ bond.

Figure 17 is a plot of $D[C_6F_5\text{-}X]$ (where X = F, Cl, I, and H) versus $D[CF_3\text{-}X]$ as reported by Semenov (52). Figure 17 indicates those values of $D[C_6F_5\text{-}X]$ which were determined in the present work and those which were calculated from the enthalpies of formation determined by Cox (28). It can be seen that the values of $D[C_6F_5\text{-}F]$ obtained in the present work and calculated from the work of Cox (28) agree.

It is expected that Figure 17 might produce a linear plot. Provided the bond dissociation energy for C_6F_5I (kinetically determined) is correct, the possibility seems to exist that $D[C_6F_5\text{-}Cl]$ and $D[C_6F_5\text{-}H]$, as determined from their respective enthalpies of formation, are incorrect. The enthalpies of formation of both these compounds were determined by



X Present work

O Cox and coworkers (28)

Figure 17: A plot of $D[C_6F_5\text{-}X]$ versus $D[CF_3\text{-}X]$

Cox and coworkers (28).

It is possible that, since the system used by Cox in these determinations was relatively complex, significant errors could be present in the determination of their enthalpies of formation. To achieve linearity in Figure 17, $D[C_6F_5\text{-}H]$ and $D[C_6F_5\text{-}Cl]$ would have to be set at approximately 147 kcal/mol and 108 kcal/mol respectively. These alterations require $\Delta H^\circ_{f\ 298}(C_6F_5H,g)$ = -155 kcal/mol and $\Delta H^\circ_{f\ 298}(C_6F_5Cl,g)$ = -140 kcal/mol representing changes of approximately -46 kcal/mol and -63 kcal/mol respectively. A further study of these compounds is obviously warranted.

APPENDIX A

SUGGESTIONS FOR FURTHER WORK

Since only limited thermochemical data is presently available for perfluoroaromatic and halogen substituted perfluoroaromatic compounds, it would be useful to continue in the determination of heats of combustion of such compounds as chloropentafluorobenzene and bromopentafluorobenzene, both of which are now available, by the method developed in this work. The heat of formation of chloropentafluorobenzene has recently been determined by Cox (28) and a determination of this enthalpy of formation by the method outlined in the present work would prove an interesting check on the procedures used to determine it.

If both kinetic investigations leading to the calculation of $D[C_6F_5\text{-}X]$ and thermochemical investigations leading to $\Delta H^\circ_{f\ 298}(C_6F_5X,g)$ were performed on the same compounds, useful information which could serve as a basis for comparison of values calculated in the present work, would become available.

Some limited work has already been undertaken on the pyrolysis of $C_6F_5CF_3$. The elevated temperatures that were required to achieve a reasonable degree of decomposition did not permit the use of toluene as a carrier gas and radical scavenger. No particularly useful chemical information was produced in the brief study of $C_6F_5CF_3$ except that the gaseous products included F_2 and C_2F_6. It would seem to be instructive to devise a system which could readily study the pyrolysis of $C_6F_5CF_3$ and hence serve as a comparison for some of the data calculated in the present work.

Naturally, additional analytical work on the confirmation of the

mechanism proposed for the pyrolytic decomposition of iodopentafluorobenzene would reinforce the values of the parameters of the Arrhenius equation as determined in this present work and in the work undertaken by Krech.

Very generally then, investigations of any sort on the series of perfluoroaromatic and halogen substituted perfluoroaromatic compounds would seem to be a most fruitful exercise since only a limited number of these compounds has received any chemical attention whatsoever.

APPENDIX B

DETERMINATION OF IONIZATION POTENTIAL

Figure 18 is a plot of ion current versus electron energy to determine the appearance potential of $C_6F_5^+$ from C_6F_5I. The data was treated by the linear extrapolation method which produces an upper limit value for the appearance potential (53). From Figure 18 the appearance potential of $C_6F_5^+$ from C_6F_5I is determined to be 12.6 ±0.2 eV.

Based on a comparison of appearance potentials obtained by the linear extrapolation method and two more exact procedures (53) for ten sets of data, the linear extrapolation method generally produces an appearance potential that is about 0.3 ±0.2 eV too high. The actual appearance potential for $C_6F_5^+$ from C_6F_5I is therefore probably about 12.3 ±0.4 eV.

Provided the fragments are not formed with any appreciable excess kinetic energy

$$I(R_1) = A(R_1^+) - D[R_1\text{-}R_2] \qquad [B.1]$$

where $I(R_1)$ is the ionization potential of a fragment ion, R_1, and $A(R_1^+)$ is its appearance potential.

For C_6F_5I the present work has determined $D[C_6F_5\text{-}I]$ = 69.2 kcal/mol = 3.0 eV by kinetic experiments. Using this value along with $A(C_6F_5^+)$ = 12.3 ±0.4 eV in conjunction with equation [B.1] yields $I(C_6F_5)$ = 9.3 ±0.4 eV. The value of 9.3 ±0.4 eV obtained in the present work differs by 1.3 eV from a value of 10.6 eV estimated for the same quantity by Dibeler (49) from structural considerations.

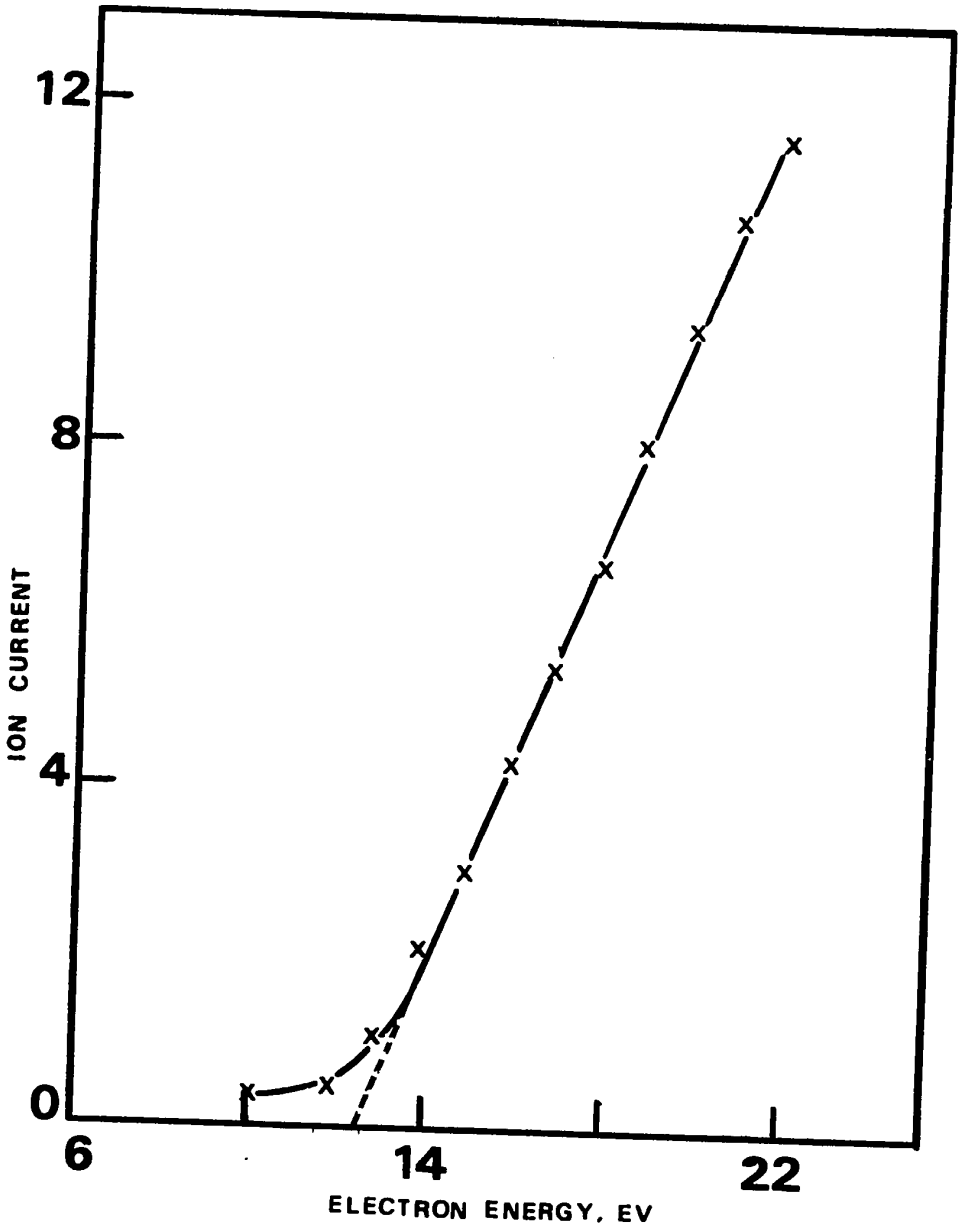


Figure 18: A plot of ion current versus electron energy

APPENDIX C

COMPUTER PROGRAMS USED IN THE

ANALYSIS OF THERMOCHEMICAL DATA

Program to calibrate the calorimeter and calculate ΔT_{cor}

```
      $JOB    WATFIV  S79603F064,KP#26 LSQ.  S.J.PRICE
      C       PROGRAM FOR CALIBRATING THE CALORIMETER
      C       NOTE MM, IC, ID MUST BE ODD NUMBERS
      C       WAYNE YARED    CHEMISTRY DEPARTMENT
      C       MAIN PROGRAM FOR CALIBRATING THE CALORIMETER
  1           COMMON TEMP,TIME,QE,NO,MO
  2           DIMENSION TEMP(500),TIME(500),QE(5,5)
  3           READ, INO
  4           DO 66 NIJ=1,INO
  5           A=4.025
  6           B=-5.77328
  7           NO=2
  8           MO=3
  9           VBOM=.32
 10           EBENZ=6318.
 11           EFUSE=2.3
 12           READ, DH2O,CH2O,CO2,CCO2,CPT,BASEN
 13           READ,     IRUN,MM,IC,ID,WBENZ,WFUSE,WCRUC,WWIRE,VH2O,V1,PO2,VBASE,T
             1JACK
 14           READ,     (TIME(I),TEMP(I),I=1,MM)
 15       125 CALL G05COP(TEMP,MM)
 16           TMP=TEMP(1)
 17           DO 97 I=1,MM
 18        97 TEMP(I)=TEMP(I)-TMP
 19           DO 230 L=1,40
 20           JA=1
 21           IA=IC
 22           DO 120 I=1,2
 23           SLOPE=0.
 24           YINT=0.
 25           TAVE=0.
 26           CALL G05LSQ(TEMP,TIME,JA,IA,SLOPE,YINT,TAVE)
```

```
      QE(I,1)=1.
      QE(I,2)=TAVE
      QE(I,3)=SLOPE
      JA=ID
      IA=MM
  120 CONTINUE
      CALL G05SIM(QE,NO,MO)
      DELT=QE(1,1)*(TIME(ID)-TIME(IC))+QE(2,2)*G05ARD(TEMP,TIME,IC,ID)
      DELTC=TEMP(ID)-TEMP(IC)-DELT
      PPO2=(14.7+PO2)/14.7
      WH2O=DH2O*VH2O
      F=1.+(20.*(PPO2-30.)+42.*((WBENZ/VBOM)-3.)+30.*((WH2O/VBOM)-3.)-45
     1.*(TEMP(MM)-(8.0-TMP)))/(10.**6)
      EBENZC=EBENZ*F
      EIGN=(500.*V1*V1)/(4.184*10.**6)
      EACID=VBASE*BASEN*13.8
      DQ=WBENZ*EBENZC+EIGN+EACID+WFUSE*EFUSE
  130 CMEAS=DQ/DELTC
      BEN=WBENZ/122.12
      O2NI=(PPO2*VBOM)/(0.082*(TEMP(IC)+290.))
      O2NF=O2NI-7.5*BEN
      CO2N=7.0*BEN
      H2ON=WH2O/18.016+3.*BEN
      PTN=(WCRUC+WWIRE)/195.09
      CSYS=CMEAS-CH2O*H2ON-CO2*O2NF-CCO2*CO2N-CPT*PTN
      PRINT 250,IRUN,CSYS,QE(1,1),QE(2,2),DELTC,DELT,CMEAS
      ID=ID+2
      IF(ID.EQ.MM) GO TO 3
  230 CONTINUE
   66 CONTINUE
  250 FORMAT (1X,I4,6E20.8)
    3 CALL EXIT
      END
```

```
      SUBROUTINE G05LSQ(YYY,XXX,IH,II,SLP,YNT,YAVE)
C     SUBROUTINE TO DO LEAST SQUARES ANALYSIS ON LINEAR RELATIONSHIP
      DIMENSION YYY(200),XXX(200)
      SUMX=0.
      SUMY=0.
      DO 8 IG=IH,II
      SUMY=SUMY+YYY(IG)
      SUMX=SUMX+XXX(IG)
    8 CONTINUE
      XII=II+1-IH
      YAVE=SUMY/XII
      SX=0.
      SY=0.
      SXY=0.
      SXSQ=0.
      DO 7 IE=IH,II
      SX=SX+XXX(IE)
      SY=SY+YYY(IE)
      SXY=SXY+XXX(IE)*YYY(IE)
      SXSQ=SXSQ+XXX(IE)*XXX(IE)
    7 CONTINUE
      XII=II+1-IH
      SLP=(SX*SY-XII*SXY)/(SX*SX-XII*SXSQ)
      YNT=(SX*SXY-SXSQ*SY)/(SX*SX-XII*SXSQ)
      RETURN
      END
```

```
      SUBROUTINE G05SIM(Q,NP,MP)
C     SUBROUTINE FOR SOLUTION OF SIMULTANEOUS LINEAR EQUATIONS
      DIMENSION TX(200),TY(200),Q(5,5)
      Q(2,2)=(Q(2,3)*Q(1,1)-Q(1,3)*Q(2,1))/(Q(2,2)*Q(1,1)-Q(1,2)*Q(2,1))
      Q(1,1)=(Q(1,3)-Q(1,2)*Q(2,2))/Q(1,1)
      RETURN
      END
```

```
      FUNCTION G05ARA(TE,TI,N,NM)
      DIMENSION TE(200),TI(200)
C     SUBPROGRAM FOR FINDING AREA UNDER CURVE USING LAGRANGIAN FORMULA
      MM=NM-2
      G05ARA=0.0
      DO 40 J=N,MM,2
      D=(TE(J)*(3.*TI(J+1)-2.*TI(J)-TI(J+2)))/((TI(J)-TI(J+1))*(TI(J)-TI
     1(J+2)))
      E=(TE(J+1)*(TI(J)-TI(J+2)))/((TI(J+1)-TI(J))*(TI(J+1)-TI(J+2)))
      F=(TE(J+2)*(2.*TI(J+2)+TI(J)-3.*TI(J+1)))/((TI(J+2)-TI(J))*(TI(J+2
     1)-TI(J+1)))
      TDT=(TI(J+2)-TI(J))*(TI(J+2)-TI(J))*(D+E+F)/6.
      G05ARA=G05ARA+TDT
   40 CONTINUE
      RETURN
      END
```

```
103           SUBROUTINE G05CUP(TEM,MM)
      C       SUBPROGRAM FOR CONVERSION OF RESISTANCE TO T EMPERATURE
104           DIMENSION TEM(200)
105           NN=MM
106           DO 22 I=1 .NN
107           XC=(ALUG(TEM(I))*10.)-77.8
108           TEM(I)=1 .6578123+2 .5536824*XC+.0011885630*XC*XC
109           TEM(I)=((10.**5)/(TEM(I)+335.))-290.
110        22 CONTINUE
111           RETURN
112           END
```

Program to calculate the theoretical yields of CO_2 and F_2 in a combustion of $C_6F_5CF_3$

```
      $JOB   WATFIV  S79603F064,KP#26 LSQ.  S.J.PRICE
      $IBSYS
      $NAME     WAYNE YARED  --  CHEMISTRY
      C      PROGRAM TO CALCULATE THE THEORETICAL YIELDS OF CO2 AND F2
 1           READ,INO
 2           DO 15 I=1.INO
 3           READ, IRUN,WC7F8,RAT1
      C      RAT1 IS THE CO2/CF4 RATIO
 4           DATA FWCO2,FWF2,FWC7F8/44.01,37.996,236.07/
 5           RAT2=(RAT1+1.)/7.
 6           WCO2=(WC7F8*RAT1*FWCO2)/(FWC7F8*RAT2)
 7           COEF2=(((RAT1+1.)*(8./7.))-4.)/2.
 8           WF2=(WC7F8*COEF2*FWF2)/(FWC7F8*RAT2)
 9           PRINT 7, IRUN,WC7F8,RAT1,WCO2,WF2
10         7  FORMAT (1X,10HRUN NUMBER,I4,/,1X,22HWEIGHT OF C7F8 USED IS,F10.6,/
           2,1X,10HCO2/CF4 IS,F10.6,/,1X,25HWEIGHT OF CO2 PRODUCED IS,F10.6,/
           3,1X,24HWEIGHT OF F2 PRODUCED IS,F10.6,///)
11         15 CONTINUE
12            STOP
13            END
```

Program to find the CO_2/CF_4 molar ratio given the weight of CO_2 produced in a combustion of $C_6F_5CF_3$

```
      $JOB    WATFIV  S79603F064,KP#26 LSQ.  S.J.PRICE
      C       PROGRAM TO FIND THE RATIO OF CO2/CF4 GIVEN THE WEIGHT OF CO2
 1            READ, INO
 2            DO 15 I=1,INO
 3            READ, IRUN,WCO2,WC7F8
 4            DATA FWCO2,FWC7F8/44.01,236.07/
      C       RAT1 IS THE CO2/CF4 RATIO
 5            RAT1=(WCO2*FWC7F8)/((7*FWCO2*WC7F8)-(WCO2*FWC7F8))
 6            PRINT 7,IRUN,WC7F8,WCO2,RAT1
 7          7 FORMAT (1X,10HRUN NUMBER,I4,/,1X,23HWEIGHT OF C6F5I USED IS,F10.6,
             2/,1X,25HWEIGHT OF CO2 PRODUCED IS,F10.6,/,1X,16HCO2/CF4 RATIO IS
             3,F10.6,///□
 8         15 CONTINUE
 9            STOP
10            END
```

Program to find the CO_2/CF_4 molar ratio given the weight of F_2 produced in a combustion of $C_6F_5CF_3$

```
     $JOB   WATFIV  S79603F064.KP#26 LSQ.  S.J.PRICE
     C      PROGRAM TO FIND THE RATIO OF CO2/CF4 GIVEN THE WEIGHT OF F2
1            READ, INU
2            DO 15 I=1,INU
3            READ, IRUN,WF2,WC7F8
4            DATA FWF2,FWC7F8/37.996,236.07/
     C       RAT1 IS THE CO2/CF4 RATIO
5            RAT1=((WF2*FWC7F8)+(10*WC7F8*FWF2))/((4*FWF2*WC7F8)-(FWC7F8*WF2))
6            PRINT 7, IRUN,WC7F8,WF2,RAT1
7          7 FORMAT (1X,10HRUN NUMBER,I4,/,1X,22HWEIGHT OF C7F8 USED IS,F10.6,
           2/,1X,24HWEIGHT OF F2 PRODUCED IS,F10.6,/,1X,16HCO2/CF4 RATIO IS
           3,F10.6,///□
8         15 CONTINUE
9            STOP
10           END
```

Program to calculate the heat of combustion of $C_6F_5CF_3$ given the CO_2/CF_4 molar ratio

```
      $JOB   WATFIV  S79603F064,KP#26 LSQ.  S.J.PRICE
      C      PROGRAM FOR CALCULATING THE HEAT OF COMBUSTION OF C7F8 FROM
      C      THE CO2/CF4 RATIO
    1         READ,INU
    2         DO 10 I=1,INU
    3         READ, IRUN,RATIO,DW
    4         DATA FCO2,FCF4/-94.0517,-221.0000/
    5         RAT2 = (RATIO + 1.)/7.
    6         FC7F8=(((RATIO*FCO2)+FCF4)/RAT2)-DW
    7         PRINT 5, IRUN,FC7F8,RATIO
    8       5 FORMAT (1X,10HRUN NUMBER,I4,/,1X,29HHEAT OF COMBUSTION OF C7F8 IS,
             2F10.4,/,1X,22HFOR A CO2/CF4 RATIO OF,F6.3,///)
    9      10 CONTINUE
   10         STOP
   11         END
```

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Primary Schools:
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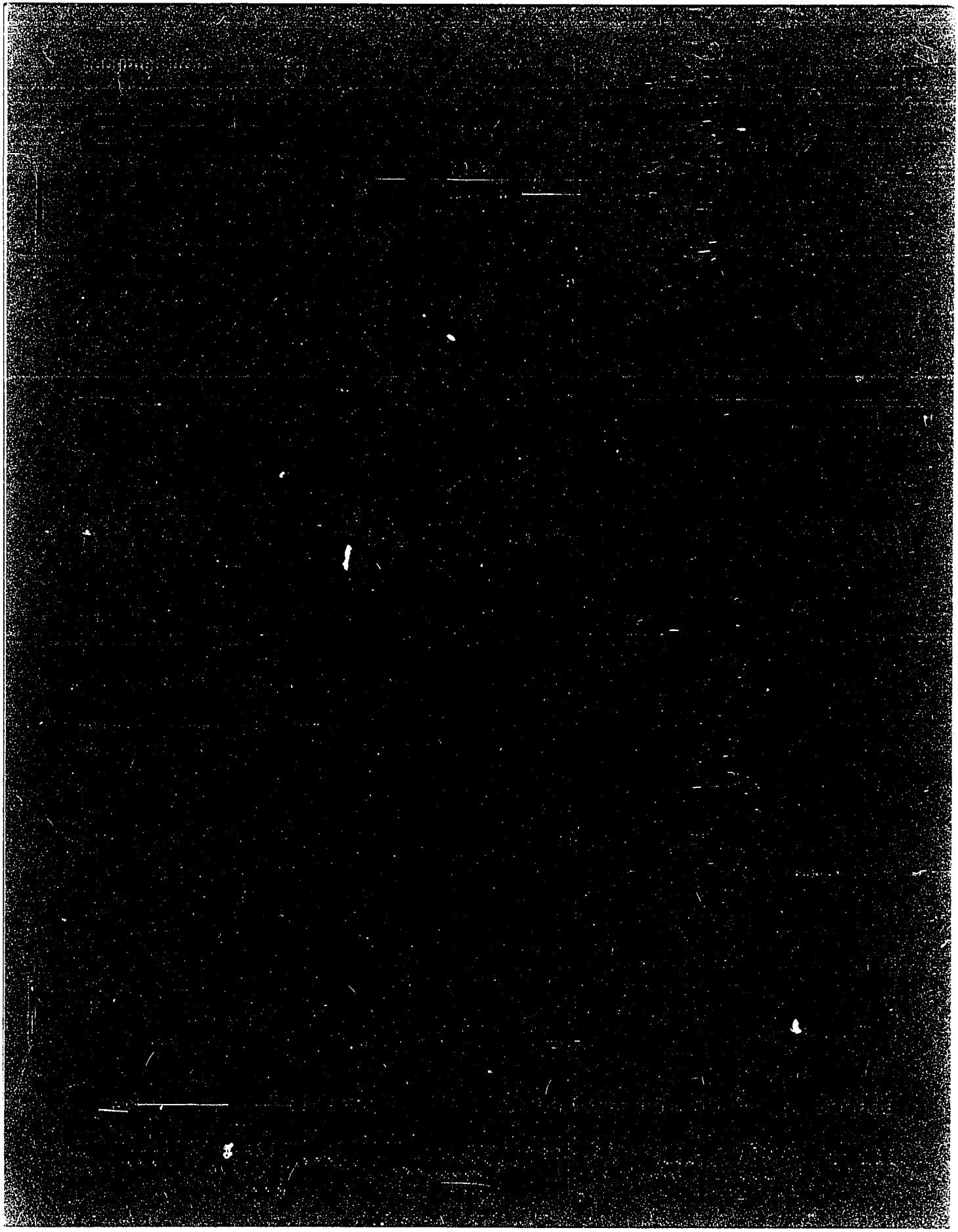

Determination of the Heat of Formation of Hexafluorobenzene

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A new method has been developed for determining the heat of combustion of perfluoro aromatic compounds. The basic differences from previous methods are that no auxiliary substance is used and no water is present in the bomb. The combustion of hexafluorobenzene in a platinum lined bomb yields CO_2, CF_4, and F_2. Visual inspection and the material balance indicate that complete combustion is obtained. The value of $\Delta H^0_{f\,298}(C_6F_6,g)$ obtained by this method is -224.0 ± 2.0 kcal/mol. Recalculation of the result of Cox *et al.* (1, 2) obtained from combustion of C_6F_6 in mylar bags in the presence of hydrocarbon oil and water leads to $\Delta H^0_{f\,298}(C_6F_6,g) = -224.3$ kcal/mol.

Une nouvelle méthode a été développée pour déterminer la chaleur de combustion des composés aromatiques perfluorés. Les différences de base par rapport aux méthodes précédentes, sont l'absence de toute substance auxiliaire et d'eau dans la bombe. La combustion de l'hexafluorobenzène dans une bombe à revêtement de platine, conduit au CO_2, CF_4, et F_2. L'examen visuel et la balance pondérale indiquent une combustion complète. La valeur de $\Delta H^0_{f\,298}(C_6F_6,g)$ obtenue par cette méthode est -224.0 ± 2.0 kcal/mol. Le résultat de Cox *et al.* (1, 2) recalculé, donne $\Delta H^0_{f\,298}(C_6F_6,g) = -224.3$ kcal/mol, à partir de la combustion de C_6F_6 dans une enceinte étanche en présence d'huile d'hydrocarbure et d'eau.

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Introduction

The determination of the heats of combustion of perfluoro aromatic compounds has received relatively little attention. Cox and co-workers (1) determined the heat of combustion of hexafluorobenzene in a platinum lined rotating bomb calorimeter using hydrogen-containing organic auxiliary substances. The value determined by Cox and co-workers for the heat of combustion of hexafluorobenzene in the ideal gas state was -220.4 kcal/mol. Based on a new value for $\Delta H_{f298}(HF.2OH_2O)$, this value was later revised to -228.4 kcal/mol (2).

The present paper describes the measurement of the heat of combustion of hexafluorobenzene in a platinum lined rotating bomb calorimeter without the use of any auxiliary substances. This work determines that complete combustion, substantiated by a product mass balance, makes it unnecessary to use any auxiliary substance and that the liquid hexafluorobenzene need not be contained in any manner but simply weighed into the platinum crucible.

Experimental

Hexafluorobenzene

The hexafluorobenzene used was obtained from Imperial Smelting Corporation and was analyzed by means of a thermal conductivity gas chromatograph using 6 ft × 1/4 in. o.d., polypropylene glycol column (110 °C, 60 cc/min He). The only detectable impurity was approximately 0.02% pentafluorobenzene.

Index of refraction at 25 °C, 1.3762 ($n_D^{25} = 1.3761$ (3)). Boiling point, 80.1 °C; freezing point, 5.2 °C (published values, 80 °C and 5.2 °C, respectively (3)).

A modified Ramsay–Young system was used to measure the vapor pressure of C_6F_6 over the range 8 to 62 °C. Approximately 80 vapor pressure measurements were made in four separate runs. The conventional plot of log p *vs.* $10^3/T$ was very slightly curved. The data are adequately represented by

$$[1] \quad \log P\,(\text{cm}) = 27.498 - 2{,}797.2/T - 6.945 \log_{10} T$$

The resulting heat of vaporization and average heat capacity difference (vapor − liquid) are $\Delta H^0_{298} = 8.69 \pm 0.02$ kcal/mol and $\langle \Delta C_p \rangle_{8-62\,^\circ C} = -13.8 \pm 2.0$ cal deg^{-1} mol^{-1}. The error limits on ΔH are representative of the uncertainty in the precision only. The value of ΔH^0_{298} is in good agreement with the previously reported value (1), 8.65 kcal/mol. It is interesting to note that the boiling point of C_6F_6 is virtually identical to that of C_6H_6 and that the $\langle \Delta C_p \rangle$ value

over 8–62 °C is close to $\langle \Delta C_p \rangle_{25\,°C}$ for benzene, −13.0 cal deg^{-1} mol^{-1} (4).

Apparatus and Calorimetric Procedure

The rotating bomb calorimeter used was similar to that used in the Bureau of Mines Laboratory, Bartlesville (5). The combustion bomb was a platinum lined Parr Model 1004C bomb, 320 cc in volume. It was equipped with a geared rotating mechanism which rotated the bomb axially and end-over-end beneath the water in the calorimeter bucket.

The calorimetric jacket was maintained at 25.000 °C by using a Thermotrol Proportional Temperature Controller Model 1053 to balance the output of small heaters against cooling by a cooling coil supplied from a bath regulated to 16 ± 0.01 °C.

The rotating bomb calorimeter was used only as a matter of convenience. A static system of the same precision would have worked equally well provided it was equipped with a platinum lined bomb. A limited number of combustions was done in a static steel bomb but these combustions produced a green coloration on the inside of the bomb which was visual indication of the formation of compounds presumed to be iron fluorides.

The temperature of the water in the bucket was monitored by a 2000 ohm thermistor in conjunction with a Honeywell Wheatstone Bridge Model 1081 and a Leeds and Northrup D.C. Null Detector with variable sensitivity. The thermistor was calibrated against a Parr certified thermometer capable of being read to 0.001 °C. The resistance of the thermistor could be estimated to 0.01 ohm (about 0.0001 °C) with the null detector at low to moderate sensitivity. Time was measured and recorded on a Simplex timer capable of recording time to 0.01 min.

In a determination of the heat of combustion of hexafluorobenzene only the compound and oxygen were used in the bomb. Care was taken to insure that the interior of the bomb and the inner portion of the bomb lid were clean and moisture free. The sample of hexafluorobenzene to be combusted was weighed in a platinum crucible which was then placed in the gimbal which had previously been fitted with a weighed platinum fuse wire (12 cm long, 36 gauge) fixed to the terminals of the ignition circuit. The lid containing the crucible, compound, and fuse wire was then fitted into the bomb which was in an inverted position and the bomb was sealed by means of the screw cap and sealing bolts.

The length of time from taking the weight of the crucible and hexafluorobenzene to the insertion of the lid into the bomb was measured by means of a stopwatch to the nearest 0.1 s. The amount of hexafluorobenzene lost by evaporation could then be calculated from the rate of evaporation which was determined prior to each experiment. The time between weighing the crucible and compound and the closing of the bomb was such that evaporation of the compound was 0.5% of the total sample weight or less. The correction for evaporation is estimated to be accurate to within at least ±3%. The error in weight generated by the correction procedure therefore should be less than ±0.02% of the sample weight.

After a 15 min period during which the bomb achieved thermal equilibrium with the water in the calorimeter bucket, time and temperature readings were taken every 10–15 s for about 10 min. After this pre-run period, ignition was affected by discharging a pair of 250 mF capacitors charged to a measured voltage (approximately 140 V) and time and temperature readings were taken as often as every 0.05 min for the ensuing 25 min. Rotation of the bomb was started 3 min after ignition and was continued throughout the remainder of the calorimetric experiment.

A computer program was used to calculate the corrected temperature rise (6). The procedure used was based essentially on Dickinson's method (7, 8). The correction to standard states followed the method of Good and Scott (9). The energy equivalent of the calorimeter as determined using standard benzoic acid was 4250.9 ± 0.2 cal/deg.

Analysis of Reaction Products

Before analysis the lid of the bomb was thoroughly dried with special attention being given to the inlet and outlet valves so that no moisture was present. The bomb was then connected by means of Tygon tubing to an analysis train consisting of a Teflon bubbler, a drying tube containing magnesium perchlorate, a gas sample collection tube and a carbon dioxide collection vessel. The bomb outlet valve was opened and the gases were allowed to pass through the analysis train until all the gases had been emptied from the bomb. Analytical grade oxygen was then passed through the inlet valve of the bomb and into the analysis train for about 1½ h to flush the bomb of any remaining combustion products. The entire process of emptying the bomb and flushing with oxygen lasted approximately 16 h.

The solution from the bubbler was analyzed for F^- using a fluoride specific ion electrode in conjunction with an Orion Model 701 digital p*H* meter capable of reading relative millivolts to the nearest 0.1 mV. The 4 cc gas collection tube was removed periodically for analysis on a Perkin–Elmer 154D thermal conductivity gas chromatograph (6 ft × 1/4 in. o.d., silical gel column, 25 °C, He carrier 15 cc/min). When the gas collection tube was removed from the analysis train it was replaced with a short length of Tygon tubing. The chromatographic conditions used gave separation of the tetrafluoromethane peak from the massive oxygen peak and thus permitted a determination of the ratio of carbon dioxide to tetrafluoromethane. The carbon dioxide collection tube contained Lithasorb and magnesium perchlorate. It was evacuated to a constant weight prior to use in the analysis train and was again evacuated to a constant weight subsequent to the flushing procedure (through the magnesium perchlorate end to prevent loss of liberated water). Allowance was made for the small amount of carbon dioxide removed in the gas chromatography samples. Analysis of the gases at the exit of the carbon dioxide collection tube by gas chromatography did not show any carbon dioxide.

Results and Discussion

Gas chromatographic analysis of the gases contained in the gas collection tube gave peaks for CO_2, CF_4, and O_2. Both gas chromatographic and mass spectromatic tests failed to show even traces of F_2O. From Table 1 the average molar ratio of CO_2 to CF_4 is 4.54 ± 0.05 (omitting runs 1 and 3, ±0.02). It should be noted that a change of 0.01 in this ratio leads

TABLE 1. Combustion data and calculated heat of formation for hexafluorobenzene

Run	Mass C_6F_6 (g)	ΔT corr. (°C)	CO_2/CF_4* (by g.c.)	CO_2 collected (g)	F_2 collected (g)	$\Delta H^0_{f\,298}(C_6F_6,g)$ (kcal/mol)
1	1.437	0.8772	4.48	1.663	0.236	−222.3
2	1.465	0.8890	4.52	1.679	0.248	−224.6
3	1.404	0.8508	4.59	1.608	0.249	−225.7
4	1.427	0.8720	4.56	1.646	0.248	−222.0
5	1.467	0.8883	4.54	1.688	0.243	−226.0
6	1.418	0.8641	4.52	1.619	0.247	−222.9
7	1.432	0.8685	4.55			−225.4
8	1.401	0.8489	4.54	1.612		−225.7
9	1.418	0.8637	4.54	1.656		−223.2
10	1.406	0.8570	4.56		0.226	−222.8
11	1.373	0.8368	4.54	1.594		−223.2

*Molar ratio. Additional typical data (see ref. 7 for notation): ΔE, ign/cal = 2.41, ε(cal)$(-\Delta t_c)$/cal = −3706.79, $\Delta E^0_c/M$ (compound)/cal g^{-1} = −2628.36.

to a change in $\Delta H^0_{f\,298}(C_6F_6,g)$ of about 0.25 kcal/mol. Since only the relative amounts of CO_2 and CF_4 are important many of the possible errors normally associated with absolute gas chromatographic calibration are unimportant. However, in establishing the relative response of CF_4 it is important to use a CF_4–O_2 mixture whose composition is similar to that of the samples from the combustion experiment. Use of pure CF_4 leads to a response factor that is lower by 4.6%. The CO_2 calibration is unaffected. The net result is that if relative response factors determined with pure CF_4 and CO_2 are used a value for $\Delta H^0_{f\,298}(C_6F_6,g)$ is obtained that is about 5 kcal/mol too high.

Based on the observed products and the CO_2/CF_4 ratio the combustion reaction may be written

[2] $C_6F_6 + 4.917O_2 \rightarrow 4.917\,CO_2 + 1.083\,CF_4 + 0.834\,F_2$

The F_2 data in Table 1 average out to within 0.4% of the value predicted from this equation (if $CO_2/CF_4 = 4.53$ rather than 4.54, then exact agreement is obtained). In three of the nine runs in which CO_2 analyses were done the CO_2 yield is also in good agreement. In the other six runs the CO_2 yield was 0.8 to 1.6% low indicating a small loss of CO_2, possibly due to surges in flow which sometimes occurred when the bomb valve was opened too quickly.

In applying eq. 2 to the experimental combustion process it must be remembered that the C_6F_6 sample is not contained in any way and that combustion occurs in a 320 cc bomb with an initial temperature of 23.5 °C and an initial pressure of 450 p.s.i. The experimental procedure therefore involves the combustion of 0.30 g C_6F_6 vapor and $(W - 0.30)$ g C_6F_6 liquid where W = weight C_6F_6 sample in grams. This presence of just over 20% of the samples in the vapor state undoubtedly aids combustion and in fact is probably responsible for the fact that complete combustion is obtained in the absence of any auxiliary compound.

For calculation of $\Delta H^0_{f\,298}(C_6F_6,g)$ the standard heat of formation of the combustion products were taken as (10)

$$\Delta H^0_{f\,298}(CO_2,g) = -94.0517 \text{ kcal/mol}$$

$$\Delta H^0_{f\,298}(CF_4,g) = -221.0 \text{ kcal/mol}$$

and the required correction for the C_6F_6 in the liquid state, $[(W - 0.30)/W]\Delta H^0_{f\,298}$(vap) was based on a heat of vaporization of 8.7 kcal/mol.

The average value of $\Delta H^0_{f\,298}(C_6F_6,g)$ obtained is -224.0 ± 2.0 kcal/mol. The previously reported values −220.4 (1) and −228.7 kcal/mol (2) were based on $\Delta H^0_{f\,298}(HF.2OH_2O) = -75.63$ and −76.96 kcal/mol, respectively. The NBS selected value (10) is −76.28 kcal/mol. A recent determination of the heat of solution of HF (11) lends strong support to this value. If the NBS value is used to recalculate the result of Cox *et al.* (1, 2) then a value of $\Delta H^0_{f\,298}(C_6F_6, g) = -224.3$ kcal/mol is obtained, a result in excellent agreement with the present work.

Although for the present, the NBS values for the heat of formation of CF_4 and HF are preferred, if for no other reason than the check for internal consistency made on all NBS data, both the present result and that of Cox *et al.* can also

be calculated using the slightly more recent value $\Delta H^0_{f\,298}(CF_4,g) = -223$ kcal mol^{-1} (12). This result leads to a value of about -76.35 kcal mol^{-1} for $\Delta H^0_{f\,298}(HF.2OH_2O)$. Based on these values the present value for $\Delta H^0_{f\,298}(C_6F_6, g)$ becomes -226.0 kcal mol^{-1} and that of Cox *et al.* -225.1 kcal mol^{-1}.

In conclusion the present experimental method seems to provide a simpler and more direct method for determining the heat of formation of perfluoroaromatic compounds. Complete combustion is easily obtained without the aid of heat shields, auxiliary oils, etc. and a simple static bomb calorimeter should produce just as good a result as a rotating bomb system. With slight modification the procedure should be suitable for compounds of the type C_6F_5X where X is another halogen and also possibly for other related compounds.

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