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ABSTRACT

The thermodynamics of positive ions in the gas phase and the techniques employed to measure ionization energies are reviewed. The heat of formation of these ions is shown to be represented by an equation of the form, $\Delta H_f(\text{Ion}) = A - Bn + C/n$, where A, B and C are empirically-determined constants and n is the total number of atoms. Values for A, B and C are presented for linear homologous series including; alkanes, alkenes, alkynes, alkanols, ethers, aldehydes, ketones, carboxylic acids, chloroalkanes, bromoalkanes, iodoalkanes, primary carbonium ions, secondary carbonium ions, tertiary carbonium ions, alkylbenzenes, and cyclic ketones.

It is shown that chain branching, substituent position and cis-trans isomerism can be accommodated in the above model by correction constants. These corrections have been determined for available data in the above homologous series.

It is also shown that a simple plot of log n, where n is again the total number of atoms in the molecule, and the ionic heats of formation is sufficient to yield data correlation up to carbon number 8.

The reciprocal equation, $\Delta H_f(\text{Ion}) = A - Bn + C/n$, is shown to function by a correspondence to the thermodynamic relationship, $\Delta H_f(\text{Ion}) = \Delta H_f(\text{Neutral Molecule}) + \text{Ionization Energy}$. It is shown that the reciprocal term, C/n, corresponds to the ionization energy and that the linear term, Bn, corresponds to the heat of formation of the neutral molecule.

CHAPTER 1

INTRODUCTION

1 INTRODUCTION

1.1 General Survey

Basic thermochemical data such as heats of formation are necessary to understand a number of processes such as the unimolecular fragmentation of ions in mass spectrometers or the reactions in the upper atmosphere or in outer space. These heats of formations are derived from experimental measurements of the ionization energy of a molecule and from the heats of formation of the molecule in its neutral state. Until the publishing of results of this study, it has not been possible to accurately predict the heats of formation of ions nor has it been possible to analyse the ionic heats of formation by means of a mathematical relationship. This thesis describes these heats of formations, how they are measured and introduces a predictive method for obtaining the heats of formation using mathematical relationships.

1.2 THERMOCHEMISTRY

1.2.1 Heat of Formation

The item of interest in this study is the heat of formation of the ion. The heat of formation of a compound is the enthalpy change in the formation of the compound in its standard state from the elements in their standard states. By convention, the heat of formation of an element is assigned the value of zero when it is in its standard state (the stable physical and chemical form at 298 Kelvin and 1 atmosphere pressure). The heat of formation of an ion then includes the heat of formation (enthalpy) of the neutral compound plus the minimum energy required to produce the ion from the compound. This latter energy is referred to as the ionization energy and will be discussed below.

The heats of formation referred to in this paper will be given in Kilocalories per mole at 298 Kelvin and 1 atmosphere.

1.2.2 Ionization Energy

Ionization Energy is defined above. Thus it is the minimum energy required to remove to infinite distance a valence electron from the lowest occupied molecular orbital of the neutral molecule to form the corresponding atomic or molecular ion ie.

$$M \xrightarrow{e \text{ or } h\nu} M^{\cdot +} + e \qquad (1)$$

The process can be performed by the interaction of a molecule with an electron or photon to produce a positive ion and an electron. The heat of formation of the ion then can be written as:

$$\Delta H_f(M^{\cdot +}) = \Delta H_f(M) + IE \qquad (2)$$

Where: $\Delta H_f(M^{\cdot +})$ is the heat of formation of the molecular ion

$\Delta H_f(M)$ is the heat of formation of the neutral molecule

IE is the ionization energy

Note that the heat of formation of the electron is not included since by convention it is zero.

1.2.3 Appearance Energy

Appearance energy is a term analogous to ionization energy and applies to an ion undergoing unimolecular fragmentation. The appearance energy of a given fragment ion is the minimum energy required to produce that fragment ion from a given molecule. The process can be represented as:

$$M \xrightarrow{e \text{ or } h\nu} A^{\cdot +} + B + e \qquad (3)$$

The heat of formation of the fragment ion ($A^{\cdot+}$) can be written as:

$$\Delta H_f(A^{\cdot+}) = \Delta H_f(M) + AE - \Delta H_f(B) \quad \ldots (4)$$

Where: $\Delta H_f(A^{\cdot+})$ is the heat of formation of the fragment ion

$\Delta H_f(M)$ is the heat of formation of the neutral precursor molecule

AE is the appearance energy which is the enthalpy of reaction (3)

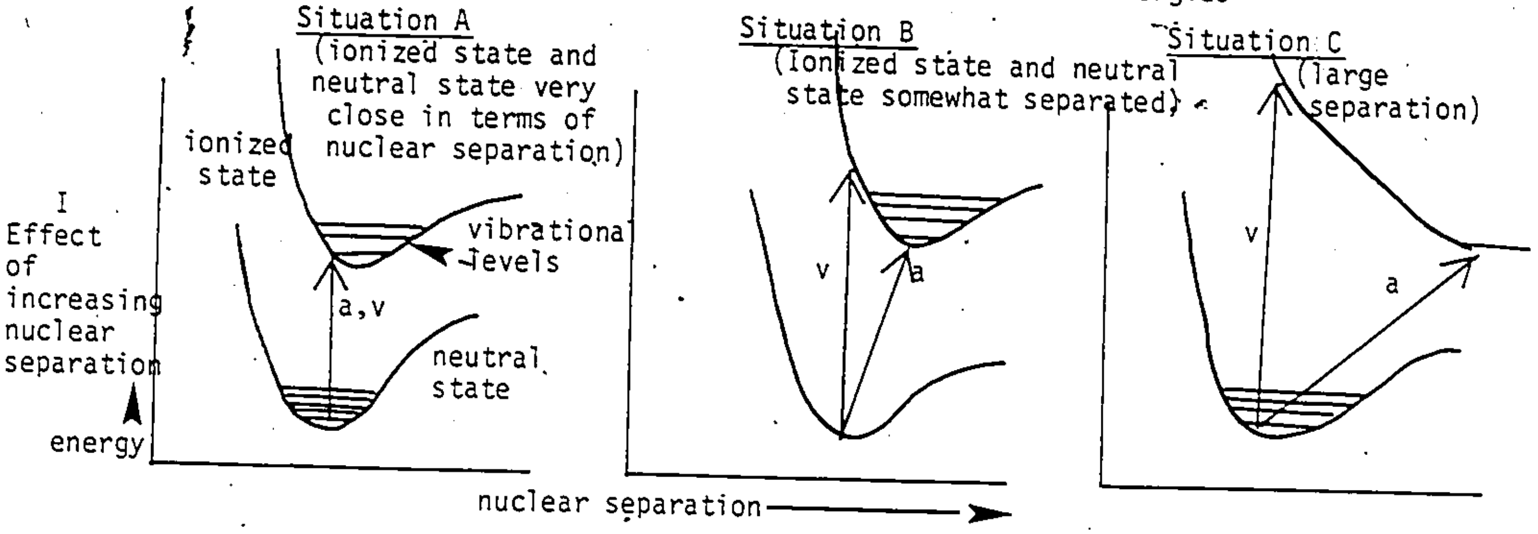
$\Delta H_f(B)$ is the heat of formation of the neutral fragment

1.3 Ionization at Threshold

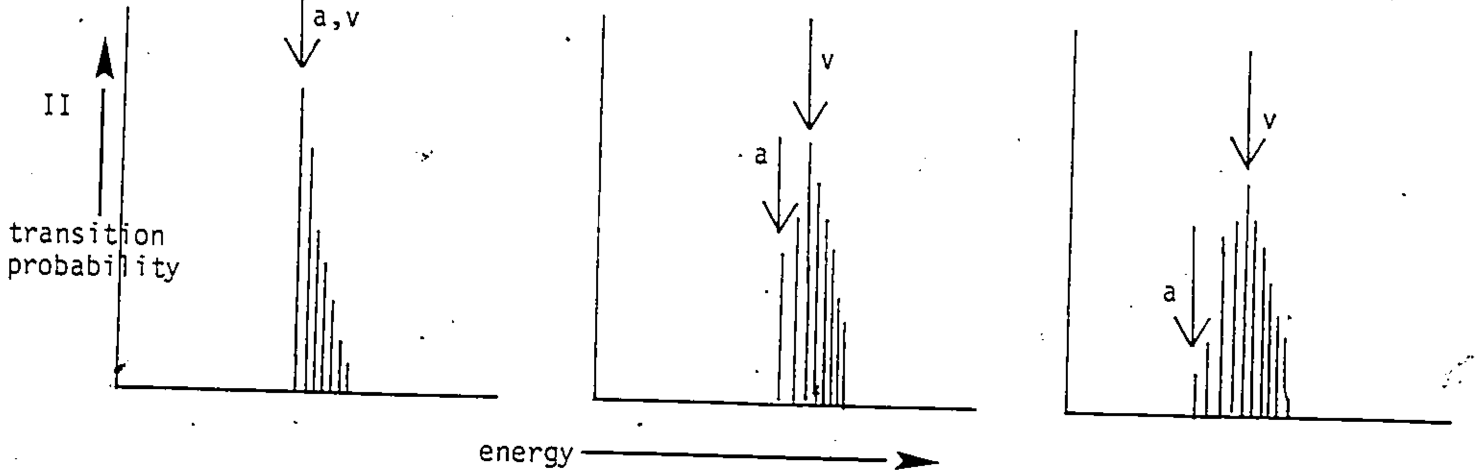
The time for the transfer of energy from an electron beam to a molecule is very short, of the order of 10^{-16} seconds.[1,2] This gives rise to a Franck-Condon type transition where no change occurs in inter-nuclear separations because the transfer time is much shorter than typical vibrational frequencies (10^{-12} to 10^{-13} seconds).[3] Transitions of this type are known as vertical transitions and may involve the energy of one or more vibrational modes. When an electron is removed from a neutral species the equilibrium distances may increase as shown in Figure 1, where I illustrates various equilibrium distances.

It should be noted that a vertical ionization is one in which an unknown amount of vibrational energy is involved. This energy (vertical ionization energy) is then above the minimum or adiabatic ionization energy which includes no vibrational-mode energy. An adiabatic transition is one from the 0,0 (electronic,vibrational) state to the 1,0 state. Thus, in measuring ionization energies it is the adiabatic energy which is of greatest value since since the vertical relates to unidentifiable vibrational levels in the ion depending on nuclear separation as shown in Figure 1.

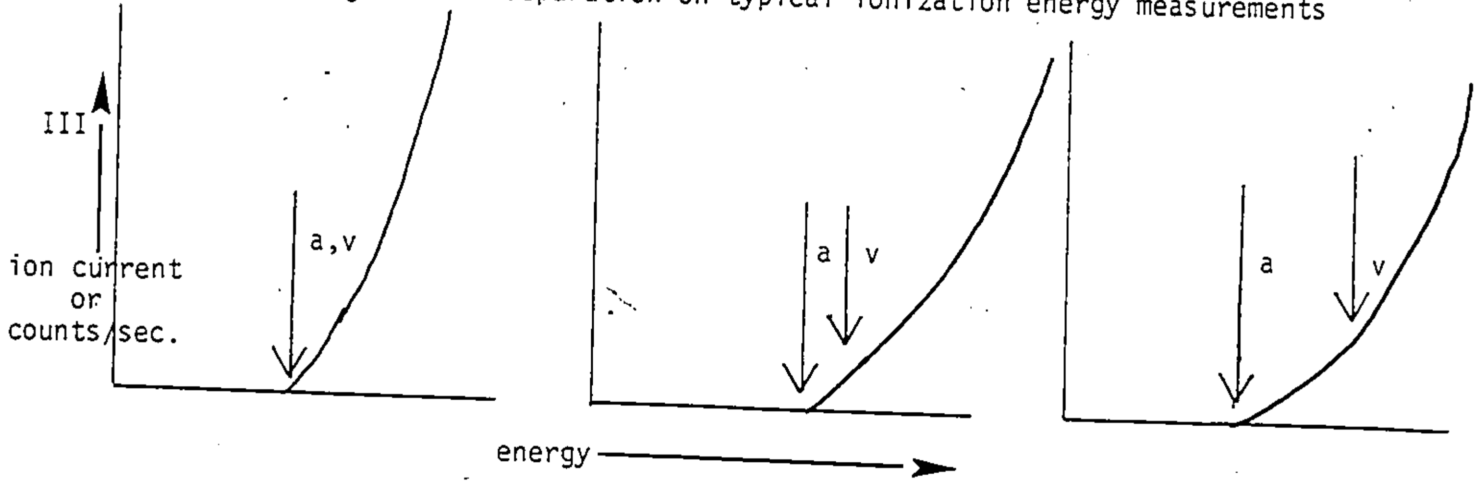
Figure 1 Illustration of Electron Transitions and the Implications on the Positions of the Vertical and Adiabatic Ionization Energies



Effect of increasing nuclear separations on transition probabilities and energies



Effect of increasing nuclear separation on typical ionization energy measurements



a is the adiabatic ionization energy
v is the vertical ionization energy

In situation A where the change of nuclear separation between the two states is small we see that the vertical transition would not involve vibrational-mode transitions and there is a high transition probability for the adiabatic process. Thus the adiabatic and vertical ionization energies are nearly identical and appear at the threshold of the curve shown. When nuclear separation is increased the difference between the vertical and adiabatic energies increases. Note that the adiabatic ionization energy appears at the threshold of the curves shown in III, where the threshold is the point at which the curve departs from the 0-level. This effect then enables experiments to provide an "adiabatic" (threshold) ionization energy or potential in all cases, although the position of the vertical ionization energy would not be known in some experimental methods. In this thesis, only those values which were reported to be adiabatic or threshold values are employed except in a few cases where this will be clearly noted.

In situation B, of Figure 1, the nuclear separation in the ionized state differs from that of the neutral molecule. The transition probabilities are greater for the vertical ionization process than those for the adiabatic process. However, as illustrated in B,III, the adiabatic ionization energy appears at the threshold of the ion current/energy curve. In situation C, the nuclear separation is increased with increasing separation between the adiabatic and vertical ionization energies.

1.4 Measurement Techniques

1.4.1 Spectroscopic Methods

The most precise method for the determination of ionization energies is by spectroscopy. The method involves the measurement of transitions in the vacuum UV spectrum, and assigning the transitions to determine the term value.[4] The atom or molecule with one excited electron can be considered hydrogen-like and accordingly can be described by the Rydberg formula:[5]

$$T_n = IE - \frac{RZ^2}{n^2} \qquad (5)$$

Where: T_n is nth energy value or the term value from the spectrum (cm^{-1})

IE is the ionization energy (here in cm^{-1})

R is the Rydberg constant (cm^{-1})

Z is the net charge of the nucleus and core electrons (dimensionless)

n is the principal quantum number (dimensionless)

Most spectroscopy measurements yield data accurate to 0.001 eV or 0.02 kcal. Polyatomic molecules yield vacuum UV spectra which are obscured by the overlap of several vibrational transitions. Thus it is impossible to perform such measurement on these species.[6] Spectroscopic data exist for a few ions such as CH_3^+ or ions of highly symmetric molecules such as Pyridine. Despite the limitations, the high accuracy of the data has enabled their use in calibrating other methods. For example, spectroscopic data for Ne and Ar, which are accurate to 0.0001 eV are often used ionization energies to calibrate the energy scale of other instrumental methods.[7]

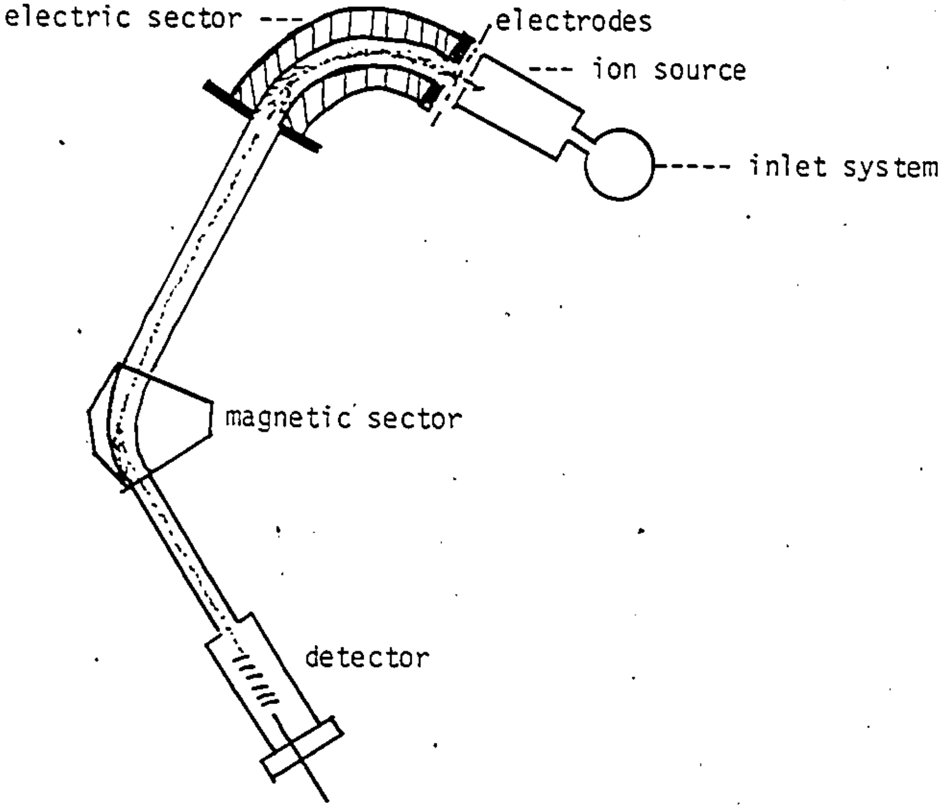
1.4.2 Electron Impact

Much of the currently-available data derives from electron impact studies. The basic method employs a modified mass spectrometer. Figure 2,A, illustrates such an instrument. The procedure by which the ionization energy is measured is straight-forward. The reactant is introduced into the apparatus via a controllable gas leak. For reactants having low vapour pressures, the inlet system can be heated to permit their introduction as a gas. Solids can be admitted to the ionization chamber via a heatable probe which is directly inserted into the ion source.

The molecules of the reactant are impacted by electrons to produce positive ions. Charged electrodes accelerate the ions into a mass selector, which in Figure 2 is taken as the typical electric sector and then a magnetic sector. The ions then strike a detector from which the ion current is amplified and read. If the energy of the ionizing electron beam is raised from zero the ion current will first be at the noise level; as the energy is increased to the ionization energy, ions are formed and if the mass selector is tuned to the mass

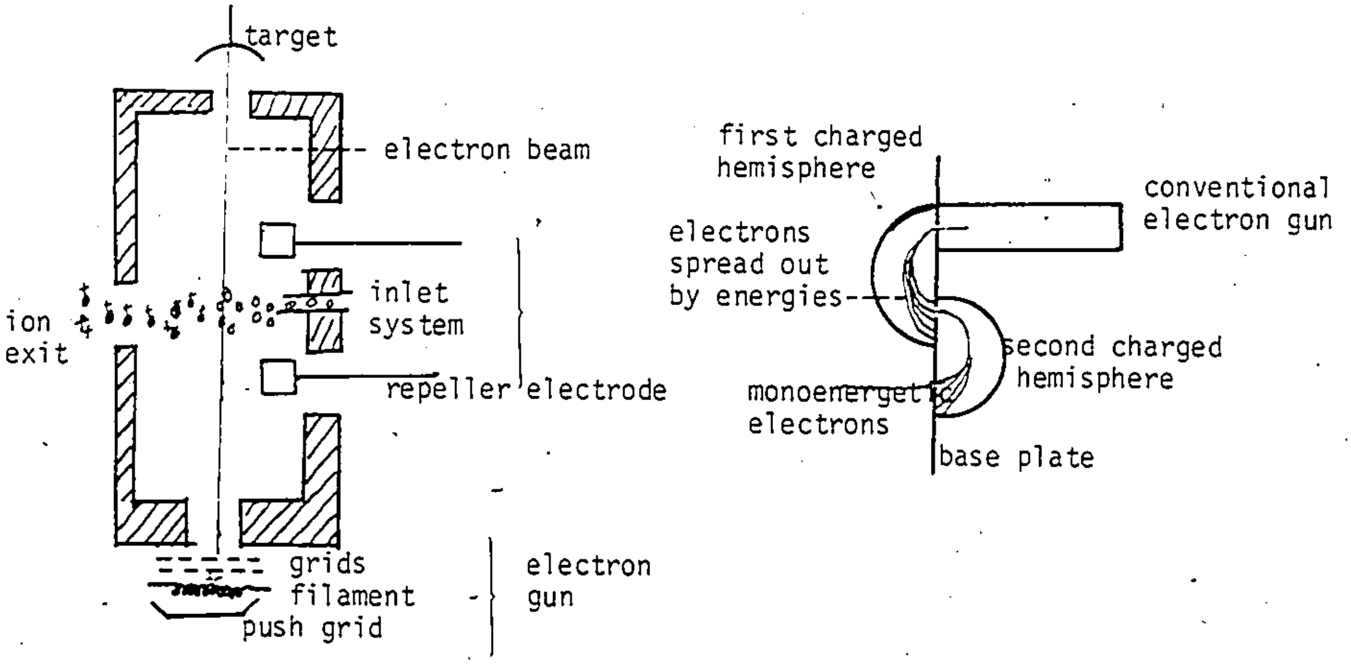
Figure 2 Generalized Schematic of a Mass Spectrometer used to Measure Ionization and Appearance Energies

A Overall Instrument Layout



B Typical Ion Source

C Double Hemisphere Electron Selector



of this ion, the ions will drift to the detector and yield an ion current. The results are plotted to yield an "ionization efficiency curve" similar to those depicted in Figure 1,C. The ionization energy then, is that which just causes the ion current to rise above the noise level.

Because of the difficulty of accurately measuring potentials in a high vacuum, it is necessary to calibrate the energy scale as read by a voltmeter using a "standard" such as Argon of known ionization energy.[9]

The fundamental problem with the basic electron impact method is the broad range of electron energies in a typical electron source. These typically range from 1 to 2 eV at half peak height. The voltmeter will be providing average or RMS (root mean square) readings. Thus, a significant number of electrons have an energy greater than the actual reading. Despite calibration with a "standard" gas, electron impact measurements without correction may be as high as 0.20 eV over measurements by other means. This is accentuated in appearance energy measurements where the values may be as high as 0.50 eV over other measurements.

a. Quasi-Monoenergetic Electron Impact

A number of workers have proposed mathematical means to correct for the large electron energy spread from an electron gun.[10] Many of these assume that the energy distribution of the electrons from the filament is Boltzmann-like. Thus the mathematics becomes an effort to "De-Boltzmannize" the ionization efficiency curves. Other techniques are based on empirical findings that a particular technique will result in an ionization or appearance energy very close to that of spectroscopic or other methods.

One of the methods that was extensively used in the past and still appears on occasion is known as the "semi-log plot" method.[11] The method was based on the finding that plots of the logarithm of the ion current versus electron energy for the molecular ions of many substances gave parallel straight lines in the region of about 1% of the 50 eV ion current. Reproducibility of ionization energy was achieved in the range of 0.05 to 0.25 eV which is an improvement over the uncorrected method.

Another method with a similar history is known as RPD or "Retarding Potential Difference".[12] The method involves the placement of an additional electrode in the electron gun. The potential of this electrode is rapidly varied between two values intended to repel electrons below the energy of these values. Thus the electrons that actually enter the ionization chamber have an energy between that of the two retarding potentials. The reproducability of ionization energy results were generally better but similar to the semi-log plot technique noted above.

b. Mono-Energetic Electron Impact

The excellent solution to the problem of electron-energy spread is to design an electron gun from which the electron beam will be monochromatic. One instrument designed and built by Dr F. P. Lossing of the National Research Council (currently at the University of Ottawa) employs a double-hemisphere electron monochromator.[13] The unit has a beam-width at half height of the order of 50 meV (approximately one kcal/mole) or less.

The double-hemisphere monochromator functions by the principle that an electron beam entering a region of uniform charge (the hemisphere) will be deflected and spread out according to the energies of the electrons. Figure 2,C, illustrates the operation of this monochromator. The electrons of the desired energy are selected by allowing the beam to pass through a hole in the base of the hemisphere. Electrons having other energies will strike the base plate and be lost. Electrons passing through the second stage interact with molecules in the ionization chamber of a mass spectrometer in a manner described above. The energy of the transmitted electrons can be varied by changing the potential of the hemispheres.

1.4.3 Photoionization

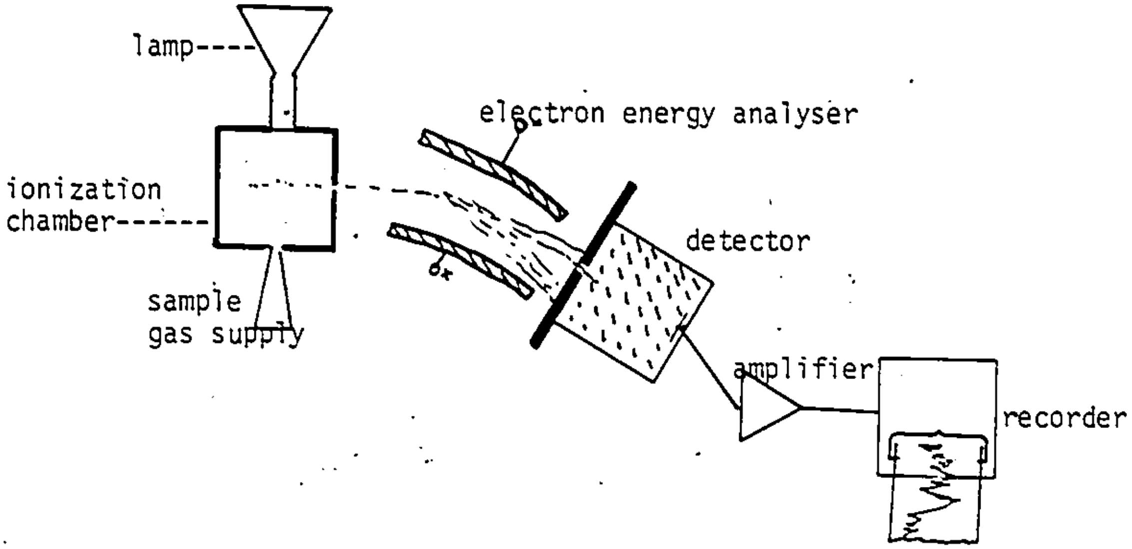
In this method a beam of photons is employed to ionize the molecules.[14] The light sources are typically a hydrogen or helium discharge lamp. The photons are then selected for energy with a Seya-Namioka or near-normal incidence monochromator. The high energy resolution of the incident beam permits an energy resolution of about 5 meV or about 0.1 kcal/mole. Despite the high energy resolution, measurements by photoionization are not as common as those by electron impact or by photoelectron spectroscopy (described below) because of problems with low photon intensity, the greater length of time required to perform an experiment and the high cost and unavailability of the equipment.

1.4.4 Photoelectron Spectroscopy

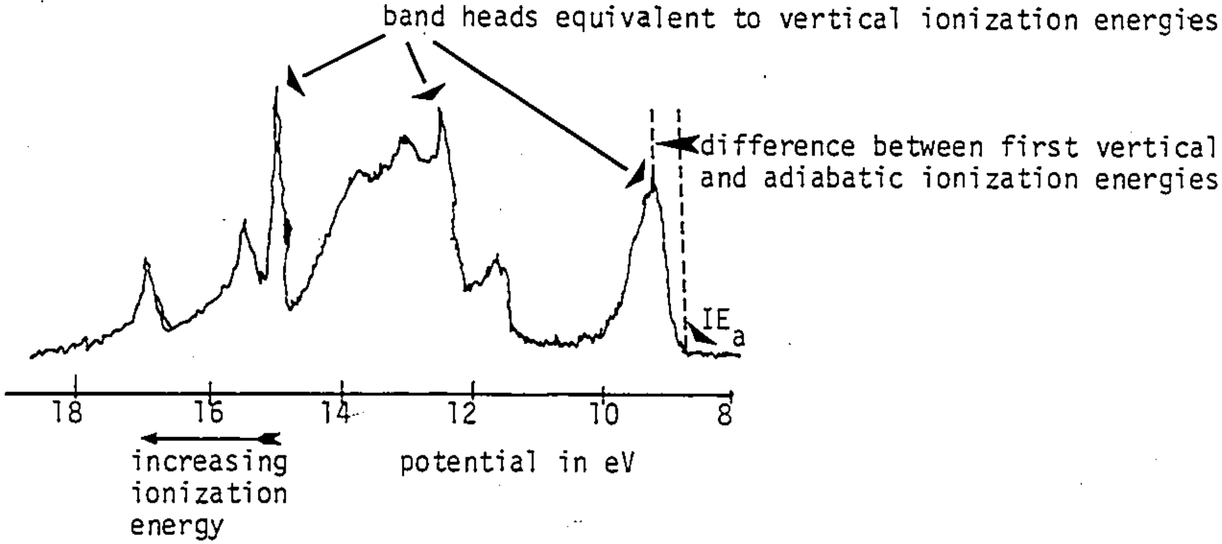
Photoelectron spectroscopic data are becoming a very common source of ionization energies. Several instruments of sufficient precision are available commercially and with their ease of operation, a large amount of data is being generated. Photoelectron spectroscopy is different from both the photoionization and electron impact methods in that ionization at threshold is not the directly-observed phenomenon, rather the energy of ejected electrons (the photoelectron effect) is measured.[15,16] The electrons from molecules are ejected with monochromatic light, almost always the helium resonance line, HeI, at 584 A°(21.22 eV). A generalized photoelectron spectrometer is presented in Figure 3. The principle of operation is as follows; a reactant gas is admitted to the ionization chamber and photons from the helium I source cause photoelectrons to be ejected. the ejected photoelectrons pass into an energy selector which is scanned across the range of interest. Those photoelectrons of the "correct" energy pass into the detector and the counts/second (comparable to ion current in electron impact and photoionization methods) are recorded as a function of the electron energy. A typical photoelectron spectrum is shown in Figure 3B. Threshold behaviour is analogous to other methods and the minimum energy is taken as the adiabatic ionization energy.

Figure 3 Generalized Schematic of a Photoelectron Spectrometer and a Typical Photoelectron Spectrum

(after Eland, ref. 15)



Photoelectron Spectrum of Dimethyl Mercury



The energy of the ejected electrons is not directly the energy of the molecular orbitals. The kinetic energy of the electrons is given by:

$$KE = h\nu - I_j - E_{vib,rot} \qquad (6)$$

Where: KE is the kinetic energy of the photoelectron

$h\nu$ is the energy of the exciting photon which is 21.22 eV for a HeI lamp

I_j is the energy of the molecular orbital from which the photoelectron is ejected

$E_{vib,rot}$ is the vibrational and/or rotational energy above threshold

For adiabatic or threshold ionization energy measurements this expression becomes:

$$IE_a = h\nu(21.22 \text{ eV}) - KE \qquad (7)$$

Where: IE_a is the adiabatic or threshold ionization energy

The accuracy of photoelectron measurements varies from 0.05 eV to 0.50 eV (the same difference between photoionization and monochromatic electron impact respectively). Thus the data represents a good source of ionization energies. One problem has been that many experimenters do not provide the threshold data but only provide the bandhead potentials (equivalent to vertical ionization energies). Another problem with the data from photoelectron spectroscopy is that there is no mass analysis. Thus one must be careful with data on molecules that fragment at internal energies at or very close to their ionization energies. In these cases the spectrum although presumed to be that of the molecular ion, may in actual fact be that of a fragment ion or even a combined spectrum of both species.

1.4.5 Proton Affinity Methods

Proton affinity methods for measuring heats of formation of ions are relatively new; published results began to appear in the early 70's. These methods rely on the use of mass spectrometers to measure the equilibria of proton transfer between two bases and then by performing standard thermochemical calculations derive a "proton affinity" value and subsequently a heat of formation.[17-21] The procedure is simple; two reactant gases, B_1 and B_2, are admitted into a mass spectrometer and the proton exchange between them is measured at various reactant concentrations.

The reaction can be written:[21]

$$B_1H^+ + B_2 \Leftrightarrow B_2H^+ + B_1 \quad (8)$$

or can be considered to be the sum of the two half-reactions where B_1 is the reference base:

$$B_1 + H^+ \Leftrightarrow B_1H^+ \quad (9)$$

$$B_2 + H^+ \Leftrightarrow B_2H^+ \quad (10)$$

The equilibrium constant for reaction (8) is given by:

$$K_{eq} = \left[\frac{(B_1)\ (B_2H^+)}{(B_2)\ (B_1H^+)}\right]$$

and all terms are measured in the experiment provided that equilibrium is reached.

Then the Gibbs free energy change can be given by standard thermochemical procedures as follows:

$$\Delta G_{reac} = -RT \ln K = \Delta H_{reac} - T\,\Delta S_{reac}$$

To obtain the heat of the reaction (8) one can correct for entropy as follows:

$$\Delta S_{reac} = R \ln \left\{\frac{\sigma(B_1H)\ \sigma(B_2)}{\sigma(B_2H^+)\ \sigma(B_1)}\right\} \quad (13)$$

Where σ is the rotational entropy number

Thus we have the heat of reaction (8) and by definition the heat of reaction (ΔH_{reac}) is the negative of the proton affinity of Base 2 ($-PA(B_2)$) relative to Base 1 (by considering (8) to be made up of the half-reactions (9) and (10)). Thus if we have the proton affinity of Base 1 (relative to the heat of formation of hydrogen) it can be used to obtain the heat of formation of the protonated Base 2 (B_2H^+):

$$\Delta H_f(B_2H^+) = \Delta H_f(B_2) + \Delta H_f(H^+) - PA(B_2) \qquad (14)$$

The major problem with this method is that it depends upon the availability of an accurate absolute proton affinity of one base. Historically the proton affinity of ammonia was used as the standard.[22] The proton affinity of ammonia was taken to be 207 kcal/mole until about 1975 when 202 kcal/mole was suggested.[22] Several other values have also been proposed in recent years. The difference of 5 kcal/mole as noted has increased the uncertainty of the data.

The method does have some advantage in that species which cannot be examined by other means can now be studied, examples of these being protonated alkanes and saturated alkanols.

1.4.6 The Heats of Formation of Neutral Species

As noted in section 1.2 above, heats of formation of the neutral species are required to calculate ionic heats of formation. Fortunately, this is a well-established field and several extensive collections of reliable data exist - such as that by Cox and Pilcher [24] and that by Pedley and Rylance.[25]

In addition to collections of experimental values, an additivity scheme has been devised by S.W. Benson.[26] This scheme allows the calculation of a very large number of heats of formation which have not been experimentally measured - as well as providing confirmation where only one experimental determination has been performed. The agreement between "selected" experimental values and "Benson" values is good - usually differences do not exceed 0.20 kcal/mole. This value is well within the generally-accepted experimental errors for the ion heat of formation, ± 1 kcal/mole at best or more generally ±2 kcal/mole. Thus the heat of formation of the neutral would not in most cases contribute a significant error. Table 1 illustrates the use and accuracy of the Benson scheme as applied to the homologous alkane series.

TABLE I USE OF THE BENSON ADDITIVITY SCHEME TO CALCULATE THE HEAT OF FORMATION OF THE n-ALKANES

Compound	Benson Calculation[a]	ΔH_f(Neutral)[b]	Selected Experimental Value[c]
Methane CH_4	cannot be done	----------	-17.89
Ethane H_3CCH_3	(-10.08)+(-10.08)	-20.16	-20.24
Propane $H_3CCH_2CH_3$	(-10.08)+(-4.95)+(-10.08)	-25.11	-24.83
Butane $H_3C(CH_2)_2CH_3$	2(-10.08)+2(-4.95)	-30.06	-30.36
Pentane $H_3C(CH_2)_3CH_3$	2(-10.08)+3(-4.95)	-35.01	-35.10
Hexane $H_3C(CH_2)_4CH_3$	2(-10.08)+4(-4.95)	-39.96	-39.92
Heptane $H_3C(CH_2)_5CH_3$	2(-10.08)+5(-4.95)	-44.91	-44.85

[a] Ref. 28, The additivity factors which are applicable here are:

$C-(H)_3(C) = -10.08$

$C-(H)_2(C)_2 = -4.95$

[b] Values in kcal/mole throughout this table.

[c] Ref. 24, The Cox and Pilcher Collection, it should be noted that the values for Ethane, Propane and Butane are not selected values.

CHAPTER 2

STUDY METHODOLOGY

Chapter 2 Study Methodology

The central aim of the study was to find a correlative and/or predictive scheme for evaluating the heats of formation of positive ions in the gas phase. Initial work in this study using a compilation of data showed them to be insufficient to yield any type of correlation; these data were published as a National Bureau of Standards collection.[27] This collection contains approximately 1,500 data points, yielding reliable data on about 150 different ions. Since the above-noted data collection covered literature published up to the end of 1971, work was therefore begun on collecting data from this time onwards. At the time of writing, this new data collection has yielded approximately 8,000 data points, yielding acceptable data on approximately 800 ions - all in addition to that noted for the NBS data collection above.

In many cases more than one data point was available for an ionization energy of a particular molecule. In these cases the following criteria were applied in the given order of priority:

a. Only adiabatic or threshold values were used except in one or two cases and this fact will be noted in the tables. As noted above, vertical ionization energies include an unspecified vibrational energy and thus can not be used to provide a consistent scheme.

b. The concensus of values was used where such a concensus exists. In many cases there is generally good agreement among available values and the most recent value was quoted.

c. The accuracy of each experimental method was considered in the selection of data. Photoionization, spectroscopic, monoenergetic electron impact and photoelectron spectroscopic methods were considered to be of equivalent precision for this study. This criterion leads to no significant choice-problem. "Normal" electron impact data, for reasons noted in the experimental section, are significantly less accurate than the above methods and no results from this method were adopted.

d. Where values do not agree well (for no apparent reason), the average was taken.

CHAPTER 3

RESULTS

Chapter 3 Results

3.1 Review of Earlier Methods

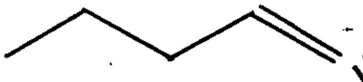
Only two correlation schemes for ions in the gas phase have been found in the literature and both of these are additive schemes. The one method known as "isodesmic substitution" was first suggested by Pople and coworkers [30] and later extended by Williams and coworkers.[31] The method is based on the hypothesis that the heat of formation of an ion can be determined from the known heat of formation of one ion, which is used as the comparison point, and the difference between the heats of formation of the neutrals. The method was claimed to be applicable only to those ions where the charge and the substituent group were widely separated (greater than 5 methylene groups) along the molecule. Figure 4 shows examples of the use of the method. The immediate problem with this method is that it is not widely applicable. In the examples shown in Figure 4, the predicted values are from 1 to 35 kcal/mole different from the experimental values. This difference would be considered to be unacceptable for use in any quantitative manner.

The other scheme for the prediction of heats of formation of ions was proposed by J.L. Franklin in 1953.[35] This method used the hypothesis that the charge on an ion is localised and therefore the heat of formation of any ion can be determined by additivity as in the neutral molecules except that the charge-bearing substituent required a value particular to that group. Table 2 illustrates the use of this prediction system. As can be seen from this table, the difference between the predicted value and the experimental value can be as large as 17 kcal/mole. It is not surprising that this system did not become widely used.

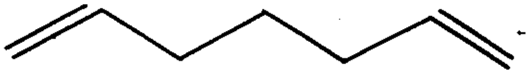
FIGURE 4 ILLUSTRATION OF THE USE OF THE "ISODESMIC SUBSTITUTION" METHOD

REFERENCE ION

ION WHOSE HEAT OF FORMATION IS DESIRED

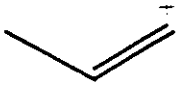


ΔH_f(Ion) = 213 kcal/mole[a]
ΔH_f(neutral)= −4.94[b]

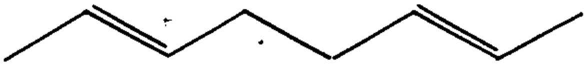


predicted ΔH_f(Ion)=233 kcal
= 213 + (15.2-(-4.94))
ΔH_f(neutral) = 15.2[b]
Whereas experimental value is 234 kcal/mole[c]
In this case the method works because both double bonds are external and thus have the same ionization energy.

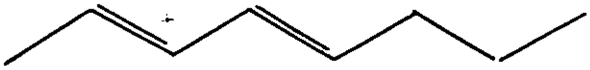
predicted ΔH_f(Ion)=225 kcal/mole
= 213 + (7.67 -(-4.94))
ΔH_f(neutral) = 7.67[b]
whereas the experimental value is 221 kcal/mole[d]
The methodology does not work as in the previous example because there are now two functional groups, one of which, the 3-ene, has a lower ionization energy.



ΔH_f(Ion)=229 kcal/mole[a]
ΔH_f(neutral)=4.77[b]



predicted ΔH_f(Ion)=229 kcal/mole
= 229 + (4.7 -(4.77))
ΔH_f(neutral) = 4.7[b]
whereas the experimental value is 206 kcal/mole[e]
The large difference is due to the larger ionization of the terminal double bond than those of the example above.



Predicted ΔH_f(Ion)=229 kcal/mole
= 229 + (4.5 -(4.77))
ΔH_f(neutral) = 4.5[b]
Whereas the experimental value is 194 kcal/mole[e]
The same problem as noted in the above example is also observed here, but the difference is larger because of the conjugation which the isodesmic substitution method ignores.

a Reference 32
b Reference 26
c Reference 33
d Reference 34
e F.P. Lossing, unpublished results

TABLE 2 ILLUSTRATION OF THE USE OF THE FRANKLIN ADDITIVITY SCHEME

EXAMPLE ION	RELEVANT FRANKLIN ADDITIVITY TERMS (values in kcal/mole)[a]		ΔH_f(ION) BY ADDITIVITY (kcal/mole)	ΔH_f(Ion) FROM EXPER. DATA (kcal/mole)	DIFFERENCE
$CH_3\overset{+}{C}H_2$	$-\overset{+}{C}H_2$	212	202	219[b]	-17
	$-CH_3$	-10.1			
$CH_3CH_2CH_2\overset{+}{C}H_2$	$-\overset{+}{C}H_2$	212	192	201[c]	-9
	$-CH_3$	-10.1			
	$-CH_2-$	-5.0			
$(CH_3)_3\overset{+}{C}$	$-CH_3$	-10.1	165	167[d]	-2
	$-C-+$	195			
$CH_3\overset{+}{C}=CH_2$	$-CH_3$	-10.1	230	226[e]	+4
	$-\overset{+}{C}=CH_2$	240			

[a] Reference 35

[b] Reference 36

[c] Reference 36

[d] Reference 36

[e] Reference 37

The failure of both systems, both of which are additivity schemes, indicates that additivity is not a promising method. Table 3 illustrates the ΔH_f differences between homologs in the alkane ion series. It is interesting to note that in the neutral, the ΔH_f difference between each successive homolog is -4.95 kcal/mole. Clearly then, an additivity scheme will fail.

3.2 Principal Findings

The principal finding of this study is that the heats of formation for homologous series of ions can be represented by an equation of the form (hereafter referred to as the reciprocal equation):

$$\Delta H_f(M^{\cdot +}) = A - Bn + C/n \qquad (15)$$

Where: $\Delta H_f(M^{\cdot +})$ is the heat of formation of an ion in the homologous series

A,B and C are empirically-determined constants

n is the total number of atoms in the ion

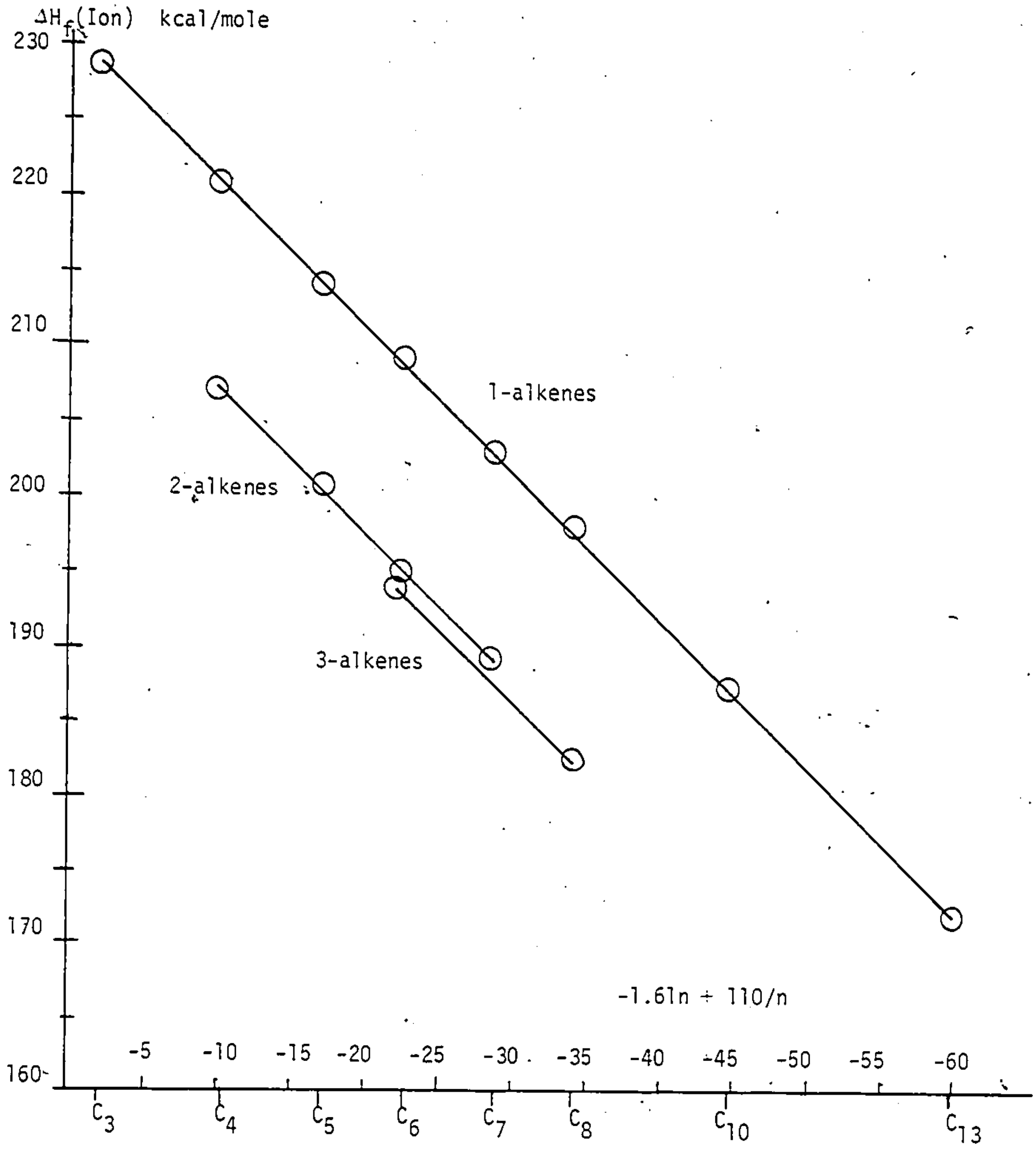
This finding is illustrated by Figure 5. The heats of formation of the 1-alkenes are plotted against the multiple parameter, 1.61n + 110/n, which was derived empirically by regression. Initial regressions were performed using a Hewlett-Packard programmable calculator and standard regression packages as supplied.[28] Regressions presented later in this thesis were performed using the University of Ottawa computer and the SPSS standard package.[29] The latter package was employed to perform calculations according to a standard multiple-linear regression method.

TABLE 3 HEATS OF FORMATION OF THE IONIZED n-ALKANES

ION	HEAT OF FORMATION(kcal/mole)[a]	DIFFERENCE BETWEEN ADJACENT HOMOLOGS
$CH_4^{\cdot+}$	273	
$C_2H_6^{\cdot+}$	245	28
$C_3H_8^{\cdot+}$	228	17
$C_4H_{10}^{\cdot+}$	213	15
$C_5H_{12}^{\cdot+}$	204	9
$C_6H_{14}^{\cdot+}$	195	9
$C_7H_{16}^{\cdot+}$	186	9

[a] Heats of formation from Reference 27

Figure 5 Plot of Ionic Heats of Formation of the 1-, 2- and 3-alkenes versus -1.61n + 110/n, where n is the Total Number of Atoms *



*data from Table 6

In Figure 5, the heats of formation of ions of 2- and 3-alkenes are also plotted on the same scale. The figure illustrates that the ΔH_f for a given homologous series, such as the 1-alkenes, can be described accurately using a relationship of the type (15). Verification of this finding appears in subsequent chapters of this thesis by application to a large number of homologous series.

It is proposed that when one examines the components of the heat of formation by the relationship presented earlier in this thesis:

$$\Delta H_f(\text{Ion}) = \Delta H_f(\text{Neutral}) + \text{Ionization Energy} \quad (16)$$

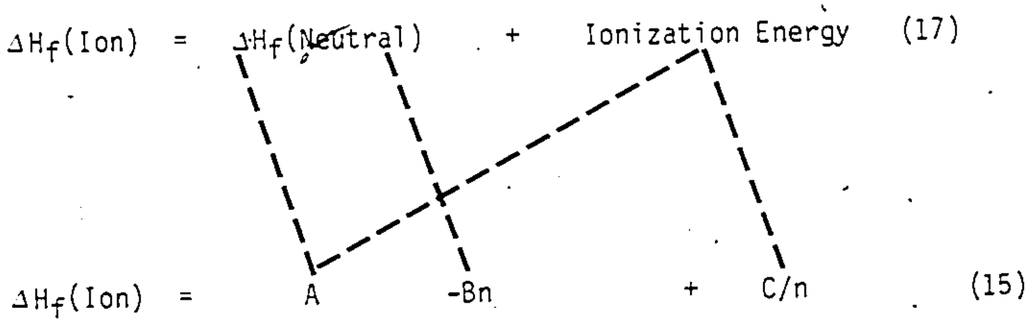
that this corresponds to the 3-term reciprocal formula.

It has been noted that the heat of formation of the neutral molecule can be accurately predicted by a linear or additive relationship as shown by Benson and coworkers.[26] Also, in this study, it has been found that the ionization potential can be accurately represented using a relationship of the type:

$$IP = A + B/n \quad (17)$$

This is shown in Figure 6.

Thus it is proposed that the following correspondence applies:



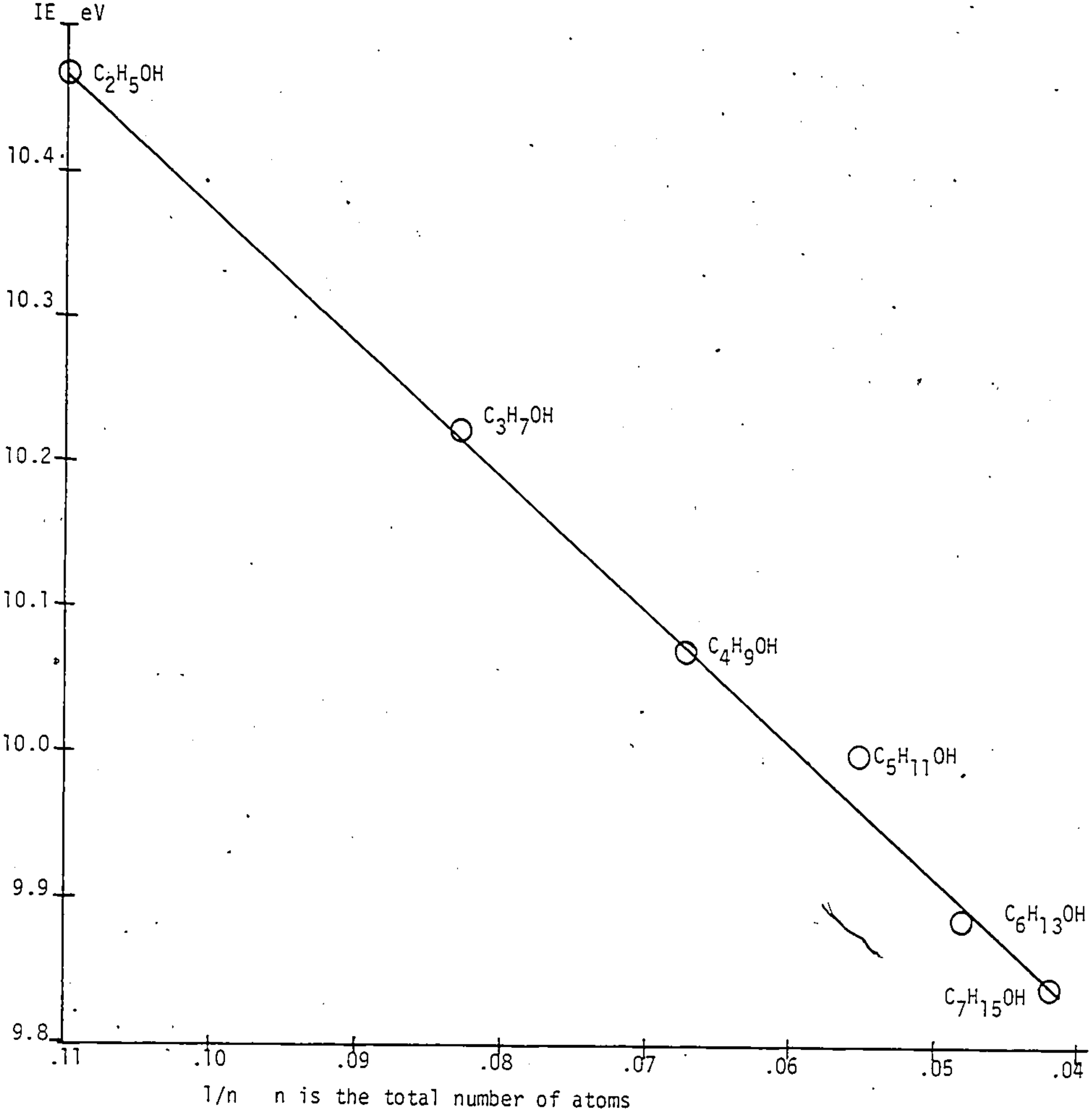
$$\Delta H_f(\text{Ion}) = \Delta H_f(\text{Neutral}) + \text{Ionization Energy} \quad (17)$$

(19)

$$\Delta H_f(\text{Ion}) = A \quad -Bn \quad + \quad C/n \quad (15)$$

That is, the constant over n term (reciprocal term) corresponds to the ionization energy. The -Bn term corresponds to the linear prediction of the heat of formation of the neutral.

Figure 6 Ionization Energies of the n-alkanols *

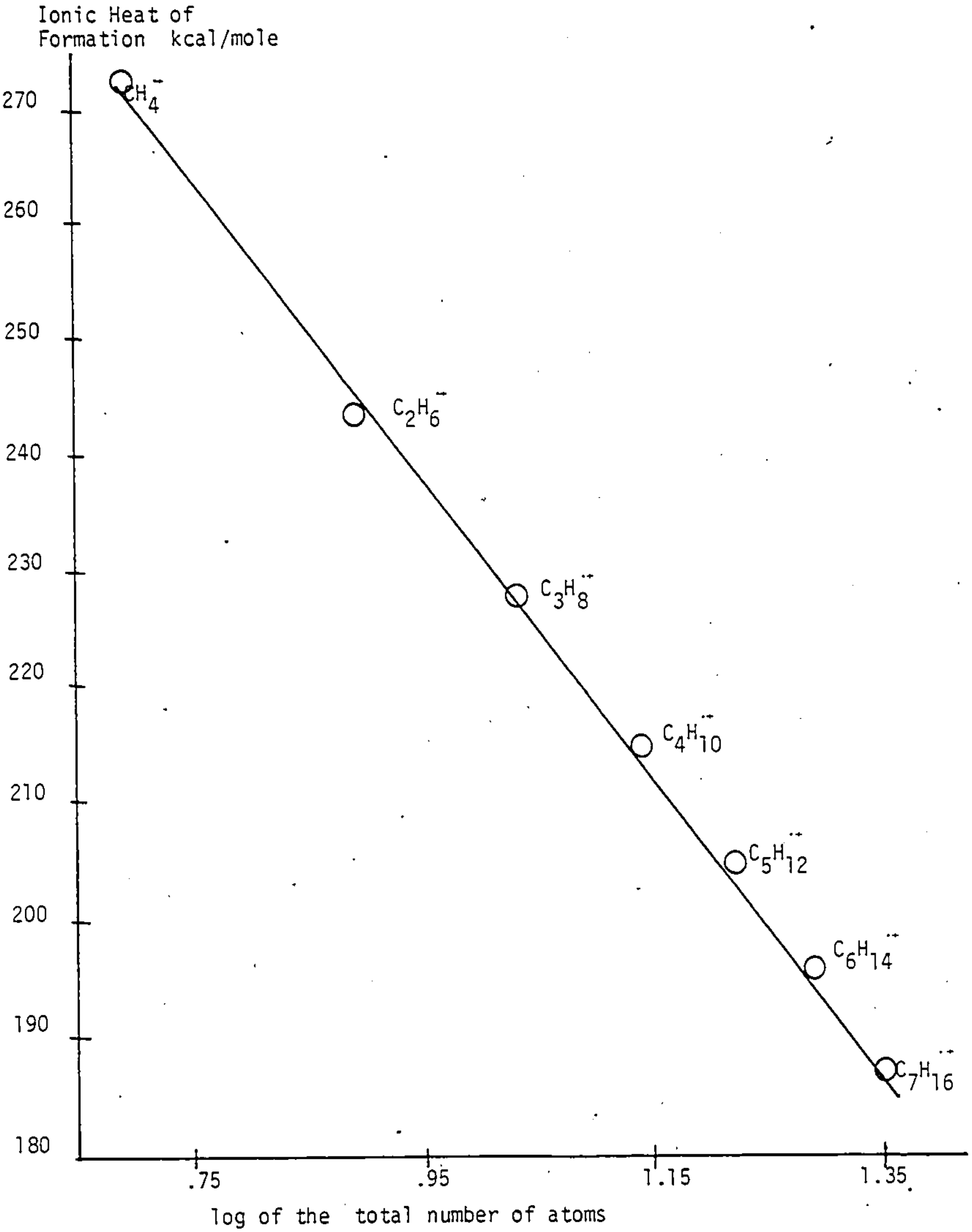


* Ionization energy data from Table 8

3.3 Anciliary Finding

As can be seen in Figure 5, the graphical analysis of heats of formation by equation 15 is difficult, in that the x-axis is a composite scale, -Bn + C/n. A simpler distribution was sought to allow for graphical presentation. The finding is that a simple plot of the heat of formation of an ion versus the logarithm (base 10) of the total number of atoms yields good linear plots up to about carbon number 8. An illustration of the "log-plot" appears in Figure 7, where the accuracy achieved is well within the limits of experimental error, ± 2 kcal/mole, for the size of the molecules presented here.

Figure 7 Plot of the Heat of Formation of the n-alkane Molecular Ions Versus the Log of the Total Number of Atoms *



* data from Table 5

3.4 Comparison of The 3-term Reciprocal Determination and The Log-Plot Determination

As noted in the above sections, two schemes have been proposed to correlate and predict the heats of formation of ions. The 3-term reciprocal equation (15) reproduces accurately the experimental data on all molecules found in the present data collection. The simpler log-plot method is useful for graphical analysis and applies up to about carbon number 8. Figure 8 presents a comparison of the prediction capability of both systems for the n-alkanes up to C_{14}. The log-plot system provides predictions within experimental error (± 2 kcal/mole) up to about carbon number 8 whereafter it produces values progressively below the experimental value as the size of the ion increases.

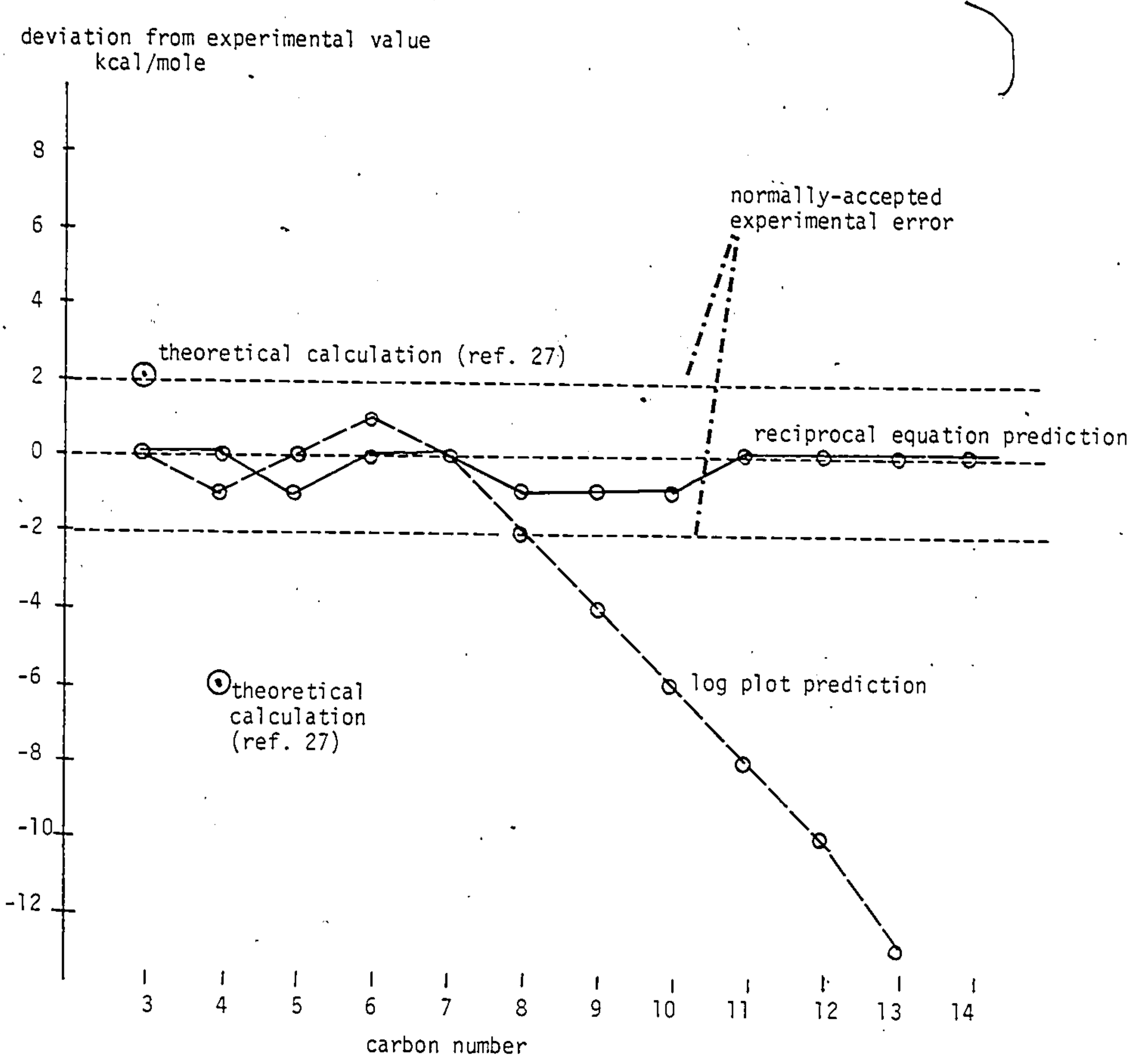
Two values derived from quantum mechanical calculations (referred to as theoretical calculations in Figure 8) have also been plotted. It is interesting to note that these particular calculations do not fall within the generally-accepted experimental error.

The reason for the fall-off of the log-plot can be found in the behaviour of the ionization energy. This can be illustrated by examining the ionization energies of the 1-alkynes, as shown in Table 4. Despite the data gap at C_7, one can see that the ionization energy has essentially become stationary at carbon number 8, whereas a formula of the type:

$$\Delta H_f(\text{Ion}) = A - B\ \text{Logn} \qquad (18)$$

predicts that the heat of formation will continue changing as the logarithm of n, the total number of atoms.

Figure 8 Comparison of Prediction Methods: the Log Plot and Reciprocal Methods applied to the 1-alkynes *



* data from Table 7

TABLE 4 BEHAVIOUR OF THE IONIZATION ENERGIES OF THE 1-ALKYNES

MEMBER	CARBON NUMBER	IP(ev)[a]	DIFFERENCE BETWEEN HOMOLOGS(ev)
1-Propyne	3	10.36	
1-Butyne	4	10.18	0.18
1-Pentyne	5	10.05	0.13
1-Hexyne	6	9.95	0.10
1-Heptyne	7	?	---
1-Octyne	8	9.95	
1-Nonyne	9	9.93	0.02
1-Decyne	10	9.91	0.02
1-Undecyne	11	9.90	0.01
1-Dodecyne	12	9.90	0.00
1-Tridecyne	13	9.90	0.00
1-Tetradecyne	14	9.89	0.01

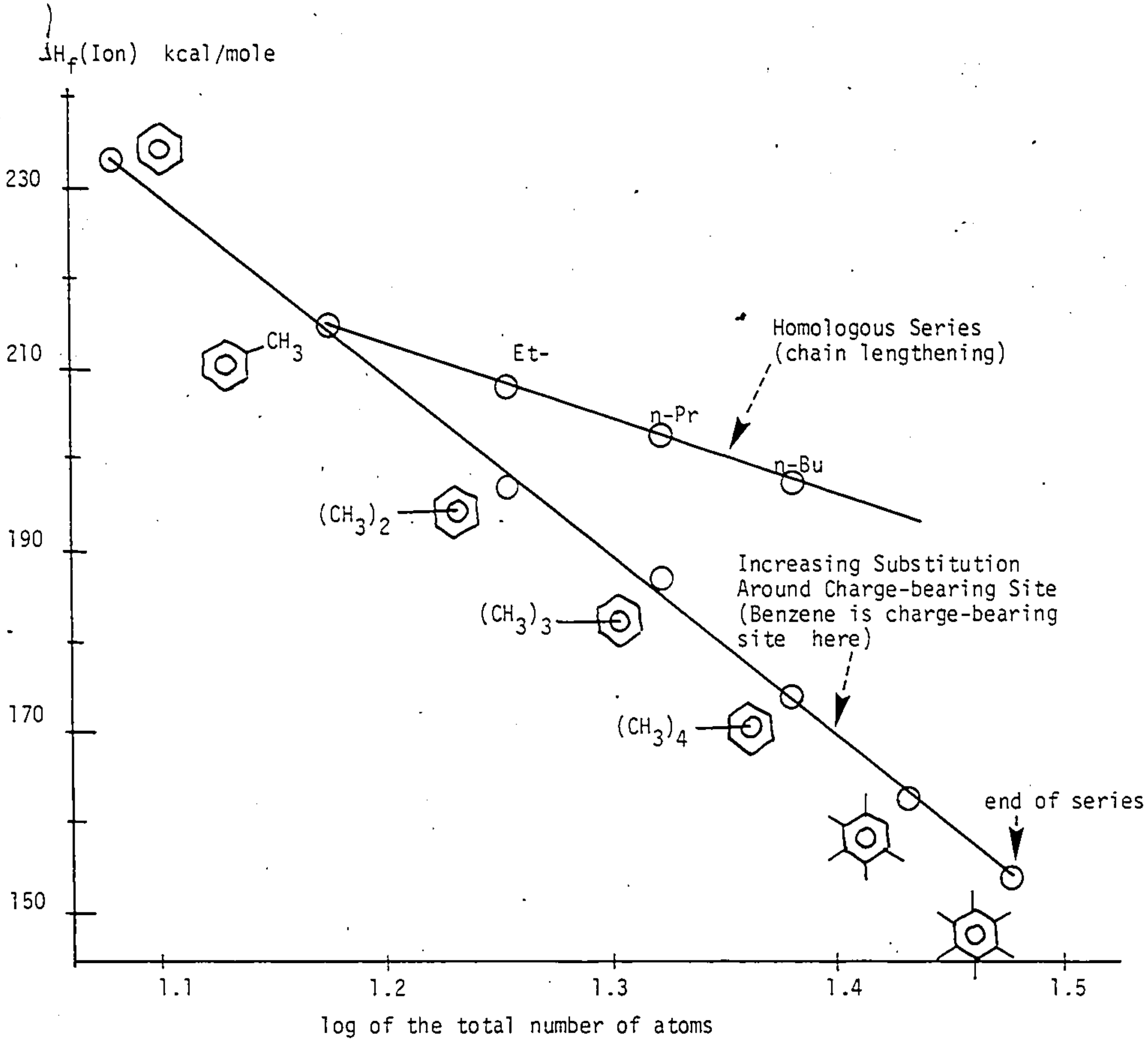
[a] Ionization energies from Table 7

It is noted that the term, logn, must correspond to both the heat of formation of the neutral and the ionization energy. We have also seen in Table 1 that the difference between homologs in the neutral is a constant difference. We have also seen in Table 4 and Figure 8 that the ionization energy decreases as a reciprocal,1/n, where n is the total number of atoms. It is then obvious that the logarithm of n will be unable to predict both of these behaviours over the full range of possible values of n.

3.5 Definition of Homologous Series and Increasing Substitution Around A Charge-bearing Site

In the above sections, it has been noted that the proposed equations are applicable to homologous series of ions. For this study and the schemes proposed herein, a homologous series of ions is one in which the adjacent members are characterized by increasing methylene substitution to form an increasingly-longer chain. For example, the following series of alkanol ions; methanol, ethanol, propanol, butanol, pentanol, etc., is a homologous series. The series; benzene, toluene, xylene, tri-methyl benzene, etc., is not a homologous series, whereas the series; toluene, ethylbenzene, propylbenzene, butylbenzene, etc., is a homologous series. The former is considered to be an example of "increasing substitution around a charge-bearing site" (benzene is the charge-bearing site in the example given above). The former can also be predicted by the methods described in this study, however, because these series end rapidly (one can only insert 3 methylene groups around a charge-bearing carbon, eg. in CH_3^{+}), they were not considered as part of this study. Examples of the difference between these two types of series is illustrated in Figure 9.

Figure 9 Illustration of the Difference between a "Homologous Series" and "Increasing Substitution Around a Charge-bearing Site" ; Alkyl-substituted Benzene *

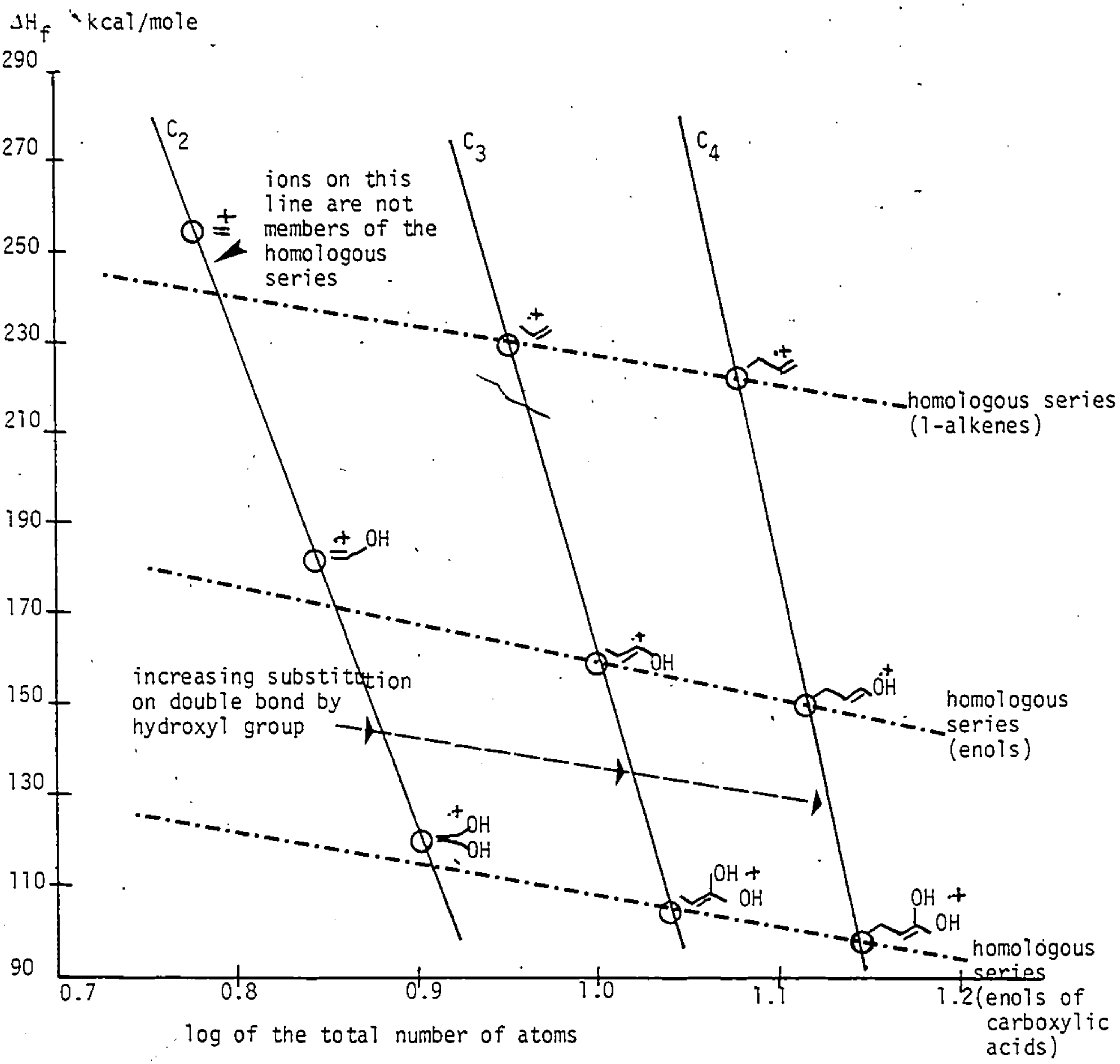


* data is from Table 20

Another reason for making the above distinction between the two types of series is illustrated by Figure 9. This is the effect that the slopes of the homologous series are always less than for those which represent increasing substitution around a charge-bearing site. It is proposed that this is due to the greater and increasing delocalization caused by placing substituents directly around the charge-bearing site. This delocalization of the charge results in lower heats of formation than ions in homologous series having the same number of atoms.

The definition of homologous series leads to the explanation of another phenomenon that is observed, the "first-member effect" as dubbed here. Again with reference to the aromatic hydrocarbons in Figure 9, it is observed that benzene does not form part of the homologous series with toluene, ethyl benzene, etc. By the definition that a homologous series is one formed by increasing methylene substitution to result in chain-lengthening, we see that benzene does not form part of the homologous series. This effect is further illustrated in Figure 10. This figure also illustrates the difference between homologous series and increasing substitution around a charge-bearing site. The need for and the utility of the log-plot method is illustrated by Figure 10 also because such a cross-correlation could not be readily discerned without such a plot.

Figure 10 Illustration of the "First Member Effect", "Homologous Series", and "Increasing Substitution Around a Charge-bearing Site" *



* data from Table 15 and ref. 48

3.6. Effect of Branching or Substituent Position

The series presented in the above examples illustrate only those homologues that were unbranched - that is those series that represent the straight-chain or normal species of their series. In this study, "branched" ions or molecules are defined as those that possess a methyl, ethyl, propyl, etc. "branch" or side-chain from the main chain of the compound. The definition is analogous to the IUPAC system of nomenclature.

The finding of this study as illustrated in Figure 11, is that branching yields constant displacements from the line of the unbranched members. Furthermore, the constant displacement is dependent upon two factors only; if the branching is on the substituent-bearing carbon (the double-bond in the case of the 1-alkenes) or elsewhere on the molecule. It can also be seen from Figure 11 that the correction is additive, ie. that two branches of the same type yield twice the correction as one branch. The mathematical model for the heat of formation of the ion can then be written as:

$$\Delta H_f(\text{Ion}) = A - Bn + C/n - aD - bE \qquad (20)$$

where: A,B,C are again the empirically-determined constants.

n is the total number of atoms

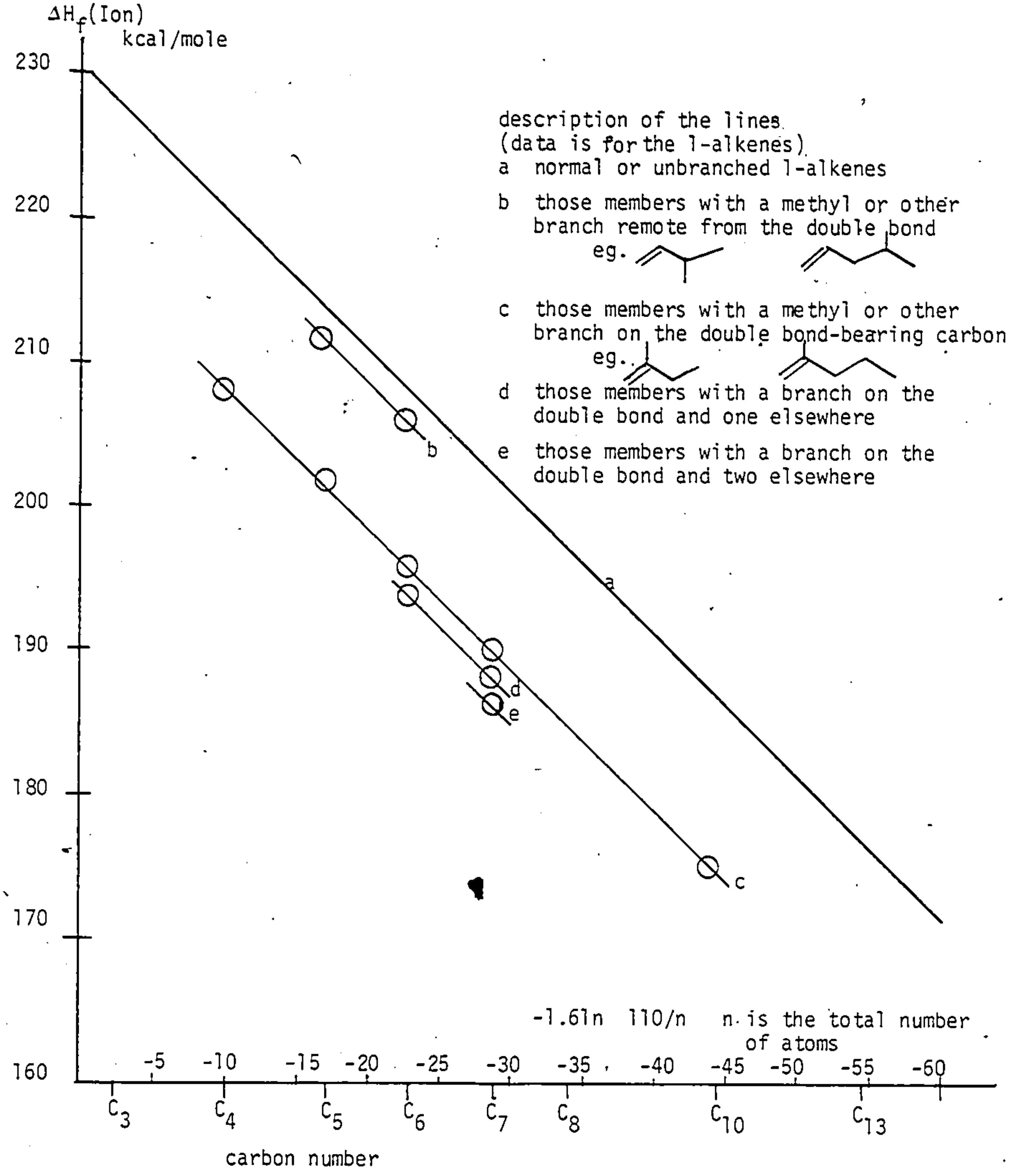
D is the empirically-determined constant for branching on a substituent-bearing carbon

a is the number of branches on a substituent-bearing carbon

E is the correction for branching elsewhere than on the substiuent-bearing carbon

b is the number of branches elsewhere on the molecule

Figure 11 Effect of Branching on the Heat of Formation of the Ion *



* data from Table 6

The effect of substituent position is analogous to that of branching - as can be seen by Figure 12. The effect of substituent position is again a constant displacement from lines representing the heats of formation of ions with a different substituent position.

3.7. The Effect of Geometric Isomerization

The effect of geometric isomerization -specifically that of cis-trans isomerization was also examined. It was found that cis-trans isomerization is again a constant displacement correction. An example of this appears in Figure 13 as applied to the cis and trans 2-alkenes. This yields a generalized model for the heat of formation of an ion:

$$\Delta H_f = A - Bn + C/n - aD - bE - F - cG \qquad (21)$$

Where:

A,B,C are again the empirically-determined constants for a given series

n is the total number of atoms

D is the correction for branching on a substituent-bearing carbon

a is the number of branches on a substituent-bearing carbon

E is the correction for branching elsewhere than above

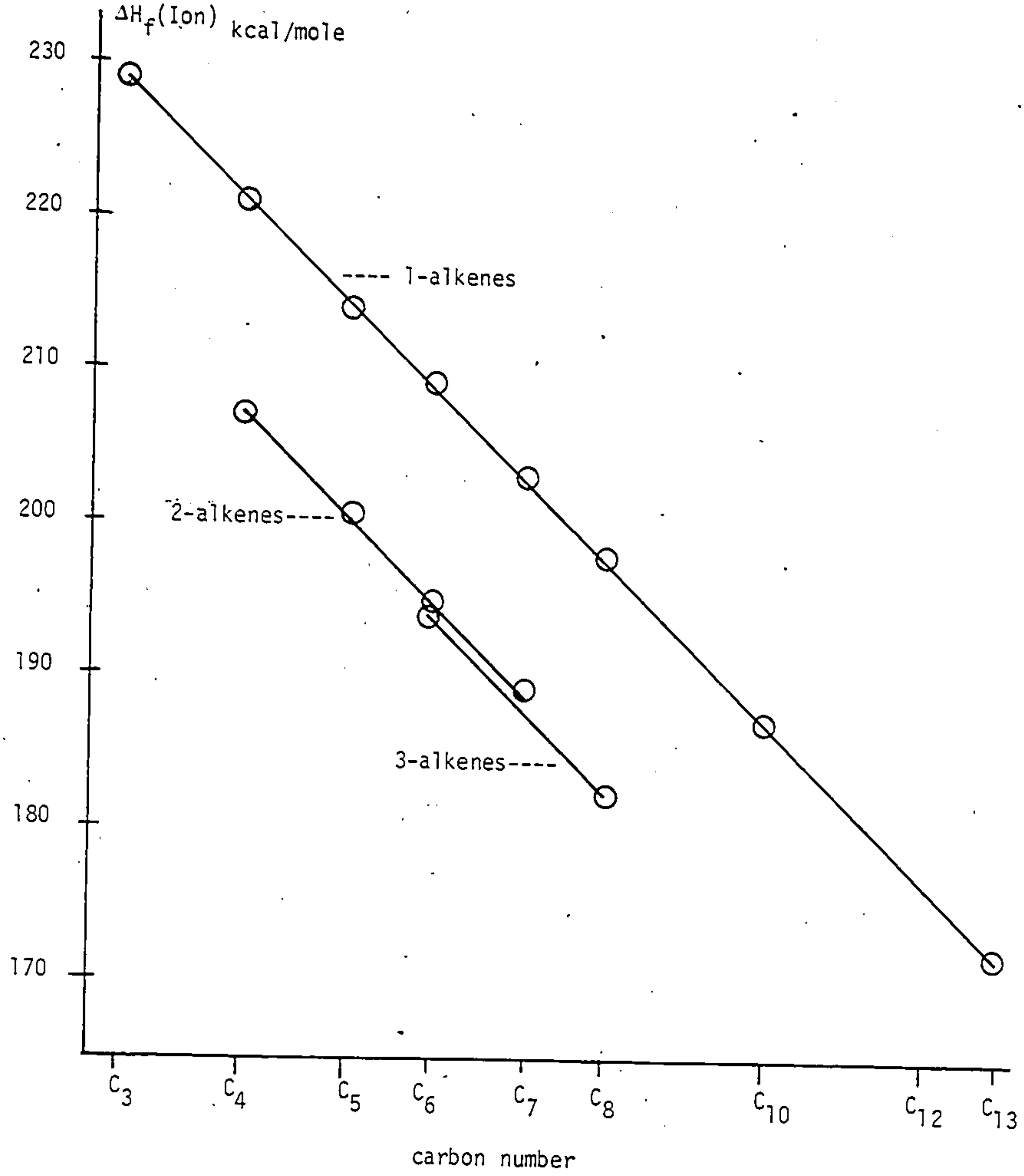
b is the number of branches elsewhere on the molecule

F is the correction for substituent position

G is the correction for geometric isomerism

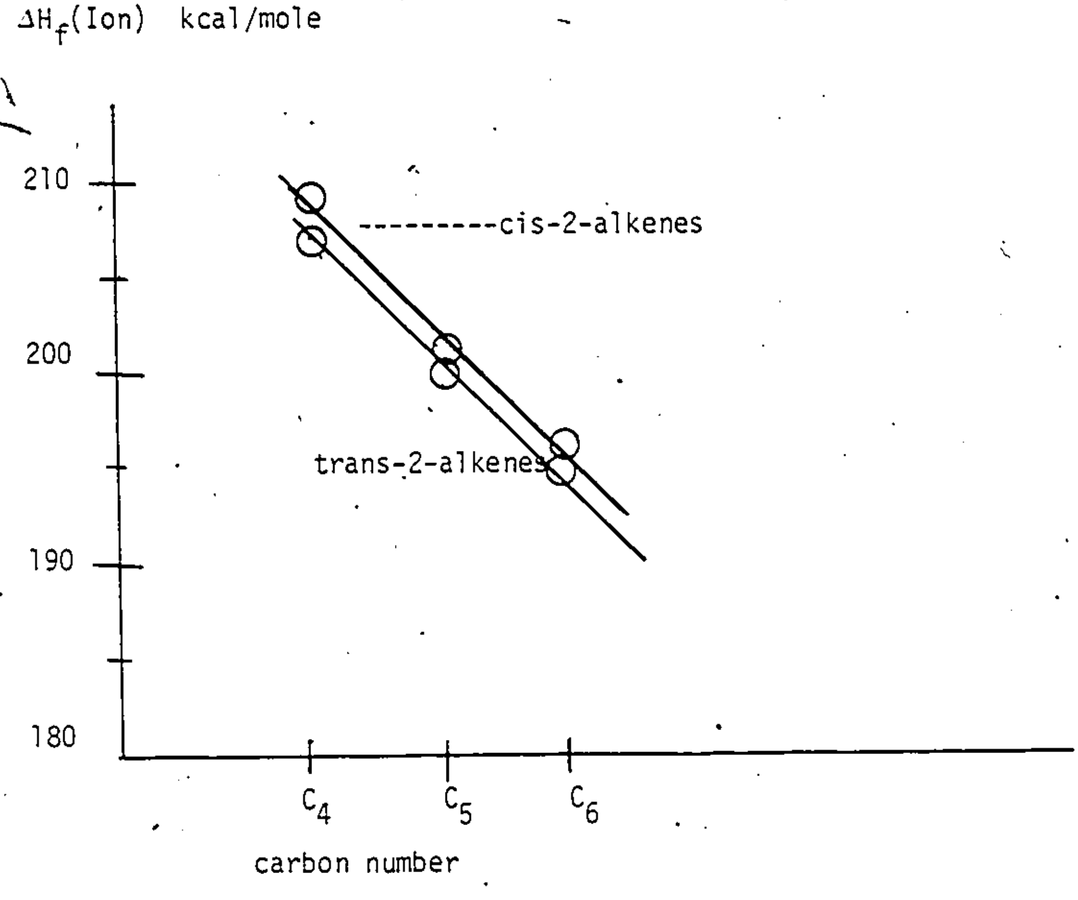
c is the number of geometric isomers present

Figure 12 The Effect of Substituent Position on Ionic Heats of Formation *



* data from Table 6

Figure 13 The Effect of Geometric Isomerism *



* data from Table 6

CHAPTER 4

APPLICATIONS OF THE CORRELATION SCHEME TO SPECIFIC SERIES

CHAPTER 4 APPLICATIONS OF THE CORRELATION SCHEME TO SPECIFIC SERIES

The generalized results as presented above are applied to specific series of ions in this chapter. The data as found in the literature are summarized in tables and graphs (using the log-plot technique in some cases for simplicity). This will enable the construction of a general model for each series and the generation of a specific equation using regression.

4.1 ODD-ELECTRON IONS

4.1.1 Alkanes

The available data for the heats of formation of ionized alkanes are presented in Table 5 and graphically in Figure 14. As can be seen from the latter, unbranched species correlate well along one line and the only remaining correction is for branching. The correction is not specific here since there is no identifiable charge-bearing site.

The equation that applies is:

$$\Delta H_f = A - Bn + C/n - dE \qquad (22)$$

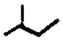
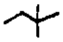
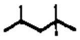
Where: A,B,C are empirically-determined constants

n is the total number of atoms

d is the total number of branches

E is the empirically-determined correction for a branch

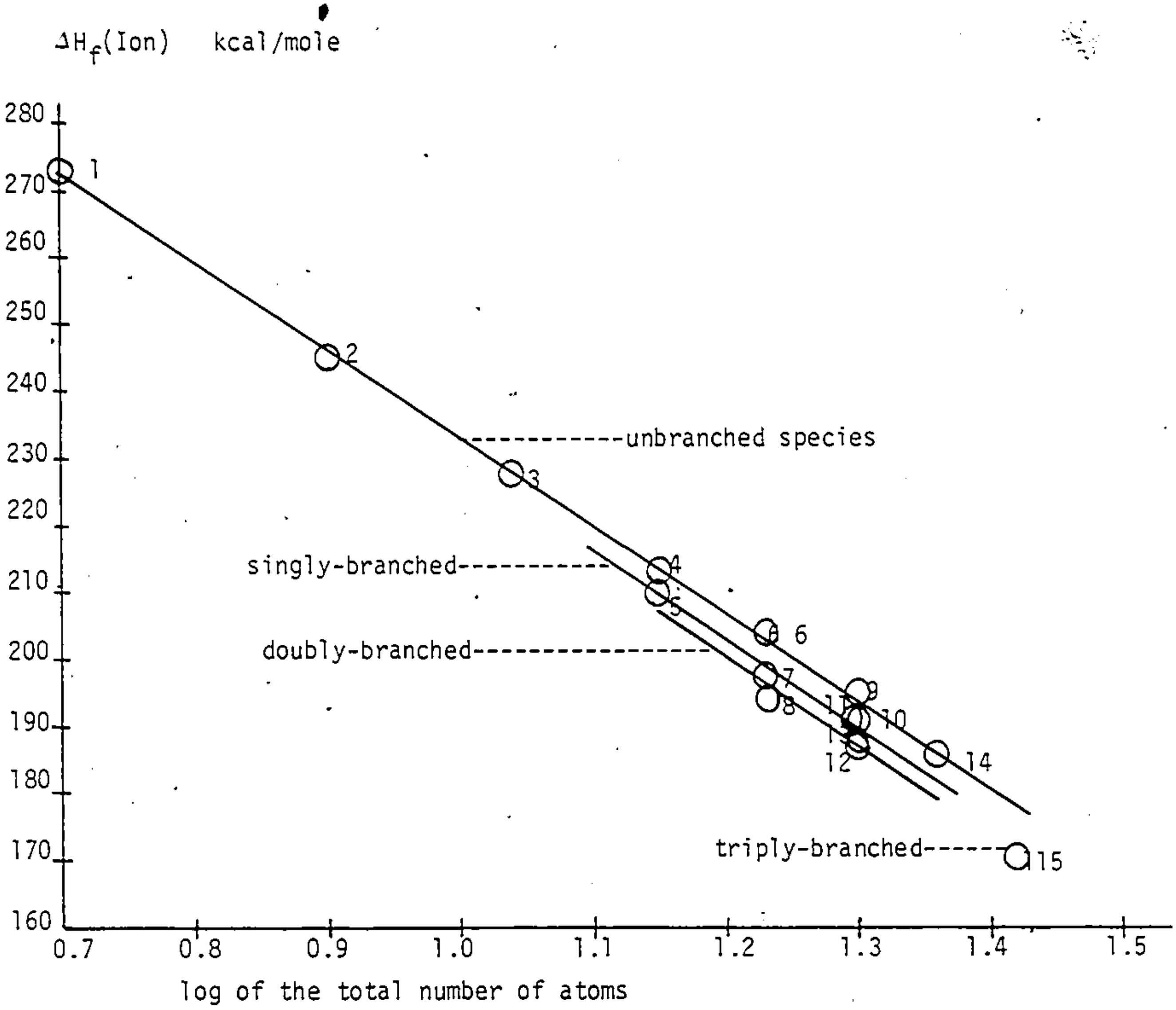
TABLE 5
Experimental and Calculated Data for the Alkanes

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔHf(NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔHf(ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
1	CH_4	Methane		-17.89	24	12.615	PI	27	273	274
2	C_2H_6	Ethane		-20.24	24	11.52	PES	27	245	244
3	C_3H_8	Propane		-28.43	24	10.93	PI	27	228	227
4	C_4H_{10}	n-Butane		-30.36	24	10.55	PI	27	213	214
5		Iso-Butane		-32.41	24	10.57	PI	27	211	211
6	C_5H_{12}	n-Pentane		-35.10	24	10.35	PI	27	204	204
7		Iso-Pentane		-36.85	24	10.20	PES	27	198	200
8		neo-Pentane		-40.27	24	10.21	PES	27	195	197
9	C_6H_{14}	n-Hexane		-39.92	24	10.18	PI	27	195	195
10		2-methyl pentane		-41.77	24	10.12	PI	27	192	192
11		3-methyl pentane		-41.13	24	10.08	PI	27	191	191
12		2,2-dimethyl butane		-44.48	24	10.06	PI	27	187	188
13		2,3-dimethyl butane		-42.61	24	10.02	PI	27	188	188
14	C_7H_{16}	n-Heptane		-44.85	24	9.99	PI	27	186	186
15	C_8H_{18}	2,2,4-trimethyl pentane		-56.80	24	9.86	PI	27	171	169

METHODS:

PES	Is photoelectron spectroscopy
PI	Is photoionization
EM	Is Electron monochromator
S	Is Spectroscopy

Figure 14 Analysis of the Alkanes



* numbers on the graph refer to data in Table 5

A regression was performed as described in Chapter 2 above and the following is the resulting equation:

$$\Delta H_f(\text{Alkane Ion}) = 219.5 - 2.06n + 324/n - 3.2a \qquad (32)$$

Where: n is the total number of atoms in the ion under consideration

a is the number of branches on the ion or molecule

It should be noted that the significant figures are chosen to yield a total accuracy of ΔH_f(Ion) of ± 1 kcal/mole.

The correlation coefficient (R^2) achieved in this regression is 0.998.

4.1.2 Alkenes

The available data on alkenes are presented in Table 6 and graphically in Figure 15. The large number of correlations which this series shows cannot be shown on this graph so only the major lines are presented. The general equation chosen to represent the heats of formation of the alkenes is:

$$\Delta H_f(\text{Ion}) = A - Bn + C/n - E - F - G - H - dJ - eK + fL + gM + hN \qquad (24)$$

Where: A,B,C are empirically-determined constants for this series

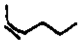
n is the total number of atoms

E is the correction for the 2-alkenes

F is the correction for the 3-alkenes

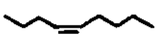
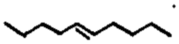
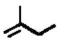
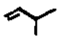
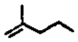
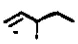
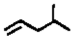
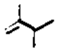
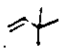
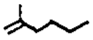
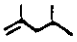
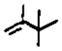
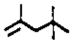
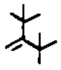
G is the correction for the 4-alkenes

TABLE 6
EXPERIMENTAL AND CALCULATED DATA ON THE OLEFINS

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔHf (NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔHf (ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
		Linear 1-Olefins								
1	C_3H_6	Propene		4.88	24	9.73	PI	27	229	229
2	C_4H_8	1-Butene		-0.20	24	9.625	PES	41	222	221
3	C_5H_{10}	1-Pentene		-5.33	24	9.524	PES	41	214	214
4	C_6H_{12}	1-Hexene		-9.95	24	9.478	PES	41	209	209
5	C_7H_{14}	1-Heptene		-14.81	24	9.442	PES	41	203	203
6	C_8H_{16}	1-Octene		-19.41	24	9.43	PI	27	198	197
7	$C_{10}H_{20}$	1-Decene		-29.7	26	9.48	EM	42	189	186
8	$C_{13}H_{26}$	1-Tridecene		-44.5	26	9.38	EM	42	172	171
		Linear 2-Olefins								
9	C_4H_8	cis-2-Butene		-1.86	24	9.124	PES	41	209	208
10	C_5H_{10}	cis-2-Pentene		-7.00	24	9.036	PES	41	201	202
11	C_6H_{12}	cis-2-Hexene		-11.7	26	8.969	PES	41	195	196
12	C_7H_{14}	cis-2-Heptene		-16.64	26	8.84	PES	43	187	190
13	C_4H_8	trans-2-Butene		-2.99	24	9.122	PES	41	207	207
14	C_5H_{10}	trans-2-Pentene		-7.93	24	9.036	PES	41	200	200
15	C_6H_{12}	trans-2-hexene		-12.7	26	8.966	PES	41	194	194
16	C_7H_{14}	trans-2-Heptene		-17.64	26	8.84	PES	43	186	188
		Linear 3-Olefins								
17	C_6H_{12}	cis-3-Hexene		-11.5	26	8.954	PES	41	195	195
18	C_6H_{12}	trans-3-Hexene		-12.5	26	8.965	PES	41	194	193
19	C_7H_{14}	cis-3-Heptene		-16.5	26	8.77	PES	43	186	189
20	C_7H_{14}	trans-3-Heptene		-17.5	26	8.92	EM	42	188	187

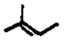
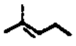
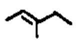
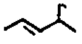
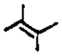
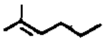
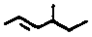
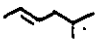
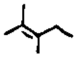
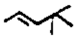
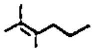
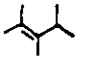
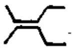
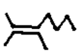
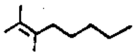
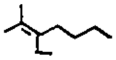
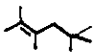
METHODS:
PES is photoelectron spectroscopy
PI is photoionization
EM is Electron monochromator
S is Spectroscopy

TABLE 6 continued
EXPERIMENTAL AND CALCULATED DATA ON THE OLEFINS

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔHf(NEUTRAL) (kcal/mole)	REF.	IONIZATION ENERGY (eV)	METHOD	REF.	ΔHf(ION) (kcal/mole) EXP.	CALC.
		Linear 3-Olefins ctd.								
21	C_8H_{16}	cis-3-Octene		-21.4	26	8.849	PES	41	183	184
		Linear 4- and 5-Olefins								
22	C_8H_{16}	cis-4-Octene		-21.4	26	8.841	PES	41	183	183
23	C_8H_{16}	trans-4-Octene		-22.4	26	8.830	PES	41	181	181
24	$C_{10}H_{20}$	cis-5-Decene		-31.3	26	8.766	PES	41	171	171
25	$C_{10}H_{20}$	trans-5-Decene		-32.3	26	8.760	PES	41	170	170
		Branched 1-Olefins								
26	C_4H_8	iso-Butene		-4.26	24	9.239	PES	41	209	209
27	C_5H_{10}	2-methyl-1-butene		-8.55	24	9.148	PES	41	202	203
28		3-methyl-1-butene		-6.61	24	9.533	PES	41	213	212
29	C_6H_{12}	2-methyl-1-pentene		-13.3	26	9.076	PES	41	196	197
30		3-methyl-1-pentene		-11.7	26	9.44	EM	44	206	206
31		4-methyl-1-pentene		-12.0	26	9.452	PES	41	206	206
32		2,3-dimethyl-1-butene		-14.7	26	9.072	PES	41	194	194
33		3,3-dimethyl-1-butene		-13.7	26	9.450	PES	41	204	204
34		2-ethyl-1-butene		-13.1	26	9.061	PES	41	196	197
35	C_7H_{14}	2-methyl-1-hexene		-18.2	26	9.039	PES	41	190	191
36		2,4-dimethyl-1-pentene		-20.3	26	9.025	PES	41	188	189
37		2,3,3-trimethyl-1-butene		-20.9	26	9.016	PES	41	187	186
38	C_8H_{16}	2,4,4-trimethyl-1-pentene		-26.5	26	8.909	PES	41	179	181
39	$C_{10}H_{20}$	2-t-butyl-3,3-trimethyl-1-butene		-38.5	26	8.795	PES	41	164	165

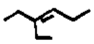
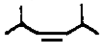
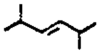
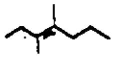
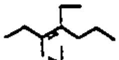
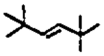
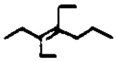
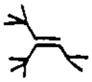
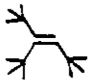
METHODS:
PES is photoelectron spectroscopy
PI is photoionization
EM is Electron monochromator
S is Spectroscopy

TABLE 6 continued
EXPERIMENTAL AND CALCULATED DATA FOR THE OLEFINS

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔH_f (NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔH_f (ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
		Branched 2-Olefins								
40	C_5H_{10}	2-methyl-2-butene		-10.3	26	8.682	PES	41	190	190
41	C_6H_{12}	2-methyl-2-pentene		-15.07	26	8.58	EM	44	183	184
42		cis-3-methyl-2-pentene		-14.07	26	8.58	EM	44	184	184
43		cis-4-methyl-2-pentene		-13.54	26	8.976	PES	41	193	193
44		4-methyl-2-pentene		-14.54	26	8.972	PES	41	192	192
45		2,3-dimethyl-2-butene		-16.64	26	8.271	PES	41	174	173
46	C_7H_{14}	2-methyl-2-hexene		-20.0	26	8.62	EM	42	179	178
47		cis-5-methyl-2-hexene		-18.72	26	8.917	PES	41	187	187
48		4-methyl-2-hexene		-19.49	26	8.912	PES	41	186	186
49		5-methyl-2-hexene		-19.72	26	8.919	PES	41	186	186
50		2,3-dimethyl-2-pentene		-21.4	26	8.213	PES	41	168	167
51		cis-4,4-dimethyl-2-pentene		-17.46	26	8.922	PES	41	188	187
52		4,4-dimethyl-2-pentene		-21.46	26	8.908	PES	41	184	185
53	C_8H_{16}	2,3-dimethyl-2-hexene		-26.35	26	8.186	PES	41	162	162
54		2,3,4-trimethyl-2-pentene		-28.2	26	8.165	PES	41	160	160
55		2-methyl-3-ethyl-2-pentene		-26.12	26	8.170	PES	41	162	162
56	C_9H_{18}	2,3-dimethyl-2-heptene		-31.2	26	8.145	PES	41	157	157
57	$C_{10}H_{20}$	2,3-dimethyl-2-octene		-36.3	26	8.132	PES	41	151	151
58		2-methyl-3-ethyl-2-heptene		-36.1	26	8.101	PES	41	151	151
59		2,3,5,5-tetramethyl-2-hexene		-41.1	26	8.097	PES	41	146	146

METHODS:
PES	is photoelectron spectroscopy
PI	is photoionization
EM	is Electron monochromator
S	is Spectroscopy

TABLE 6 continued
EXPERIMENTAL AND CALCULATED DATA FOR THE OLEFINS

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔHf (NEUTRAL) (kcal/mole)	REF.	IONIZATION ENERGY (eV)	METHOD	REF.	ΔHf (ION) (kcal/mole) EXP.	CALC.
		Branched 3-Olefins								
60	C_8H_{16}	3-ethyl-3-hexene		-24.59	26	8.480	PES	41	171	172
61		cis-3,4-dimethyl-3-hexene		-26.16	26	8.172	PES	41	162	161
62		3,4-dimethyl-3-hexene		-26.16	26	8.156	PES	41	162	161
63		cis-2,5-dimethyl-3-hexene		-25.16	26	8.846	PES	41	179	179
64		2,5-dimethyl-3-hexene		-26.1	26	8.838	PES	41	178	177
65	C_9H_{18}	3,4-dimethyl-3-heptene		-31.1	26	8.077	PES	41	155	155
66		3-methyl-4-ethyl-3-hexene		-30.92	26	8.128	PES	41	157	156
67	$C_{10}H_{20}$	cis-2,2,5,5-tetramethyl-3-hexene		-29.3	26	8.695	PES	41	171	170
68		2,2,5,5-tetramethyl-3-hexene		-39.3	26	8.741	PES	41	162	161
69	$C_{11}H_{22}$	3,4-diethyl-3-heptene		-40.6	26	8.041	PES	41	145	145
70	$C_{12}H_{24}$	2,2,4,6,6-pentamethyl-3-heptene		-50.4	26	8.346	PES	41	142	143
71	$C_{13}H_{26}$	3-t-butyl-2,5,5-trimethyl-3-hexene		-55.8	26	8.307	PES	41	136	136
72	$C_{14}H_{28}$	3-t-butyl-2,2,5,5-tetramethyl-3-hexene		-56.8	26	8.169	PES	41	132	133

METHODS:
- PES is photoelectron spectroscopy
- PI is photoionization.
- EM is Electron monochromator
- S is Spectroscopy

H is the correction for the 5-alkenes

d is the number of branches on double-bond-bearing carbon

J is the correction for branching on a substituent-bearing carbon

e is the number of branches not on a substituent-bearing carbon

K is the correction for branching elsewhere

f is the number of cis corrections

L is the correction term for cis isomers

g is the number of cis methyl to t-butyl isomers

M is the correction for cis methyl-t-butyl

h is the number of cis t-butyl to t-butyl isomers

N is the correction for cis t-butyl-t-butyl

The correlation was performed resulting in the following relationship:

$$\Delta H_f(\mathrm{ION}) = 232.2 - 1.64n + 107/n - 14.5\mathrm{pos2} - 15.3\mathrm{pos3} - 16.2\mathrm{pos4} - 17.0\mathrm{pos5} - 11.9a - 2.4b + 1.5c + 4.0d + 8.7e \tag{25}$$

Where: n is the total number of atoms

pos2 to pos5 are the corrections for the 2- to 5-alkenes

a is the number of branches on the double bond

b is the number of branches elsewhere

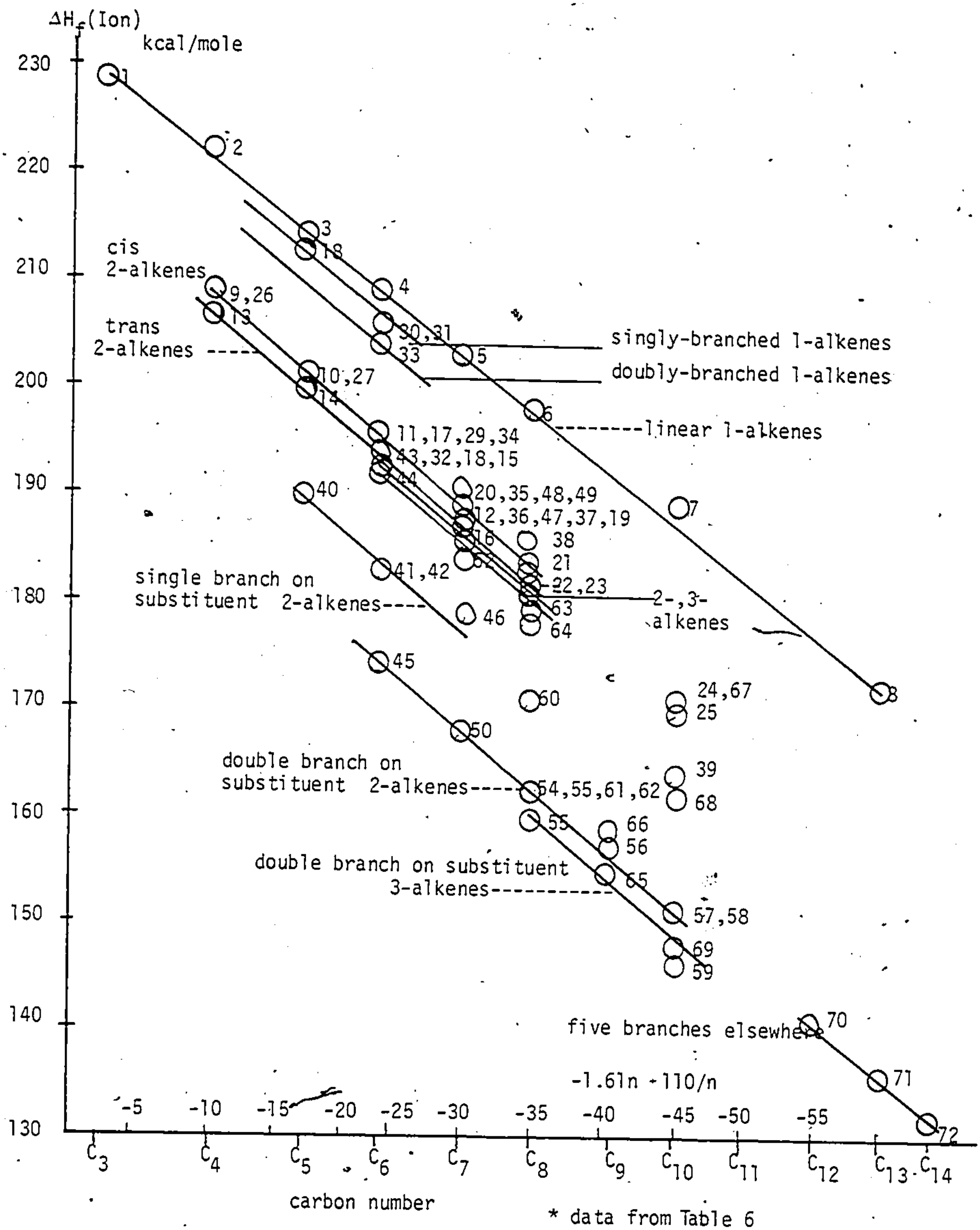
c is the number of cis isomers

d is the number of methyl-t-butyl cis isomers

e is the number of t-butyl-t-butyl cis isomers

The correlation coefficient (R^2) for this regression is 0.998.

Figure 15 Analysis of the Alkenes *



* data from Table 6

4.1.3 Alkynes

The available data for the alkynes are presented in Table 7 and graphically in Figure 16. The correlation of this series is more simple than the previous one in that only a few branched compounds have been measured and the remaining corrections are for substituent position. The model chosen to represent this series and the regression coefficients obtained are:

$$\Delta H_f(\mathrm{ION}) = 277.6 - 1.57n + 116n - 18.0\mathrm{pos}2 - 19.9\mathrm{pos}3 - 21.1\mathrm{pos}4 - 21.7\mathrm{pos}5 - 4.1a \qquad (26)$$

Where: n is the total number of atoms

pos2 to pos5 are the correction terms for substituent position

a is the total number of branches

The correlation coefficient (R^2) for this model is 0.998.

4.1.4 Alkanols

The available data for the alkanols are presented in Table 8 and graphically in Figure 17. The data set is straight-forward in that there are corrections for branching and corrections for substituent position. Two of the corrections derived will be based on one data point, that for branching on the hydroxyl-bearing carbon and that for the 4-alkanols. The model chosen and subsequently derived by regression is:

$$\Delta H_f(\mathrm{ION}) = 176.3 - 1.64n + 214/n - 6.9\mathrm{pos}2 - 8.7\mathrm{pos}3 - 9.0\mathrm{pos}4 - 3.8a - 2.5b \qquad (27)$$

Where: n is the total number of atoms

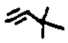
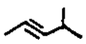
pos2 to pos4 are the corrections for substituent position

a is the number of branches on hydroxyl-bearing carbon

b is the number of branches elsewhere

The correlation coefficent (R^2) achieved is 0.997

TABLE 7
EXPERIMENTAL AND CALCULATED DATA ON THE ALKYNES

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔHf (NEUTRAL) (kcal/mole)	REF.	IONIZATION ENERGY (eV)	METHOD	REF.	ΔHf (ION) (kcal/mole) EXP.	CALC.
		1-Alkynes								
1	C_3H_4	Propyne		44.4	26	10.36	PI EM	27 27	283	283
2	C_4H_6	1-Butyne		39.7	26	10.18	PI EM	27 27	274	274
3	C_5H_8	1-Pentyne		34.72	26	10.05	EM	42	266	266
4		3-methyl-1-butyne		32.6	26	9.97	EM	42	263	262
5	C_6H_{10}	1-Hexyne		29.77	26	9.95	EM	45	259	260
6		3-methyl-1-pentyne		27.7	26	9.79	EM	45	253	255
7		4-methyl-1-pentyne		27.7	26	9.83	EM	45	254	255
8		3,3-dimethyl-1-pentyne		25.7	26	9.80	EM	45	252	252
9	C_8H_{14}	1-Octyne		19.87	26	9.95	PI	46	249	248
10	C_9H_{16}	1-Nonyne		14.92	26	9.93	PI	46	244	243
11	$C_{10}H_{18}$	1-Decyne		9.97	26	9.91	PI	46	239	238
12	$C_{11}H_{20}$	1-Undecyne		5.02	26	9.90	PI	46	233	233
13	$C_{12}H_{22}$	1-Dodecyne		0.07	26	9.90	PI	46	228	228
14	$C_{13}H_{24}$	1-Tridecyne		-4.88	26	9.90	PI	46	223	223
15	$C_{14}H_{26}$	1-Tetradecyne		-9.83	26	9.89	PI	46	218	218
		2-Alkynes								
16	C_4H_6	2-Butyne		34.9	26	9.56	EM	27	255	255
17	C_5H_8	2-Pentyne		30.2	26	9.45	EM	27	248	248
18						9.439	PES	47		
19	C_6H_{12}	2-Hexyne		25.3	26	9.37	EM	45	241	242
20						9.366	PES	47		
21		4-methyl-2-pentyne		23.1	26	9.31	EM	45	238	238
22						9.346	PES	47		

METHODS:
PES is photoelectron spectroscopy
PI is photoionization
EM is Electron monochromator
S is Spectroscopy

TABLE 7 continued
EXPERIMENTAL AND CALCULATED DATA ON THE ALKYNES

DATA NO.	FORMULA	PARENT MOLECULE ? NAME	PARENT STRUCTURE	ΔHf (NEUTRAL) (kcal/mole)	REF.	IONIZATION ENERGY (eV)	METHOD	REF.	ΔHf (ION) (kcal/mole) EXP.	CALC.
		2-Alkynes continued								
23	C_7H_{12}	2-Heptyne		20.4	26	9.326	PES	47	235	236
24	C_8H_{14}	2-Octyne		15.36	26	9.31	PI	46	230	230
25						9.302	PES	47		
26	C_9H_{16}	2-Nonyne		10.41	26	9.32	PI	46	230	230
27						9.289	PES	47		
28	$C_{10}H_{18}$	2-Decyne		5.46	26	9.30	PI	46	220	220
29	$C_{11}H_{20}$	2-Undecyne		0.51	26	9.28	PI	46	215	215
30	$C_{12}H_{22}$	2-Dodecyne		-4.44	26	9.29	PI	46	210	210
31	$C_{13}H_{24}$	2-Tridecyne		-9.39	26	9.28	PI	46	205	205
32	$C_{14}H_{26}$	2-Tetradecyne		-14.34	26	9.26	PI	46	199	200
		3-Alkynes								
33	C_6H_{10}	3-Hexyne		25.5	26	9.34	EM	45	240	240
34						9.323	PES	47		
35	C_7H_{12}	3-Heptyne		20.6	26	9.260	PI	46	234	234
36	C_8H_{14}	3-Octyne		15.66	26	9.222	PI	46	228	228
37	C_9H_{16}	3-Nonyne		10.71	26	9.202	PI	46	223	223
38	$C_{10}H_{18}$	3-Decyne		5.76	26	9.19	PI	46	218	218
39	$C_{11}H_{20}$	3-Undecyne		0.81	26	9.17	PI	46	212	213
40	$C_{12}H_{22}$	3-Dodecyne		-4.14	26	9.17	PI	46	207	208
41	$C_{13}H_{24}$	3-Tridecyne		-9.09	26	9.14	PI	46	202	203
42	$C_{14}H_{26}$	3-Tetradecyne		-14.04	26	9.17	PI	46	197	198

METHODS: PES Is photoelectron spectroscopy
PI Is photoionization
EM Is Electron monochromator
S Is Spectroscopy

TABLE 7 continued
EXPERIMENTAL AND CALCULATED DATA ON THE ALKYNES

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔH$_f$(NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔH$_f$(ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
		4-Alkynes								
43	C_8H_{14}	4-Octyne		15.66	26	9.20	PI	46	228	227
44						9.196	PES	47		
45	C_9H_{16}	4-Nonyne		10.71	26	9.17	PI	46	222	222
46	$C_{10}H_{18}$	4-Decyne		5.76	26	9.17	PI	46	217	217
47	$C_{11}H_{20}$	4-Undecyne		0.81	26	9.13	PI	46	211	212
48	$C_{12}H_{22}$	4-Dodecyne		-4.14	26	9.14	PI	46	207	207
49	$C_{13}H_{24}$	4-Tridecyne		-9.09	26	9.07	PI	46	200	202
50	$C_{14}H_{26}$	4-Tetradecyne		-14.04	26	9.11	PI	46	196	197
		5-Alkynes								
51	$C_{10}H_{18}$	5-Decyne		5.76	26	9.14	PI	46	216	216
52						9.125	PES	47		
53	$C_{11}H_{20}$	5-Undecyne		0.81	26	9.11	PI	46	211	211
54	$C_{12}H_{22}$	5-Dodecyne		-4.14	26	9.09	PI	46	206	206
55	$C_{13}H_{24}$	5-Tridecyne		-9.09	26	9.09	PI	46	201	201
56	$C_{14}H_{26}$	5-Tetradecyne		-14.04	26	9.10	PI	46	196	196

METHODS:
PES is photoelectron spectroscopy
PI is photoionization
EM is Electron monochromator
S is Spectroscopy

Figure 16 Analysis of the Alkynes

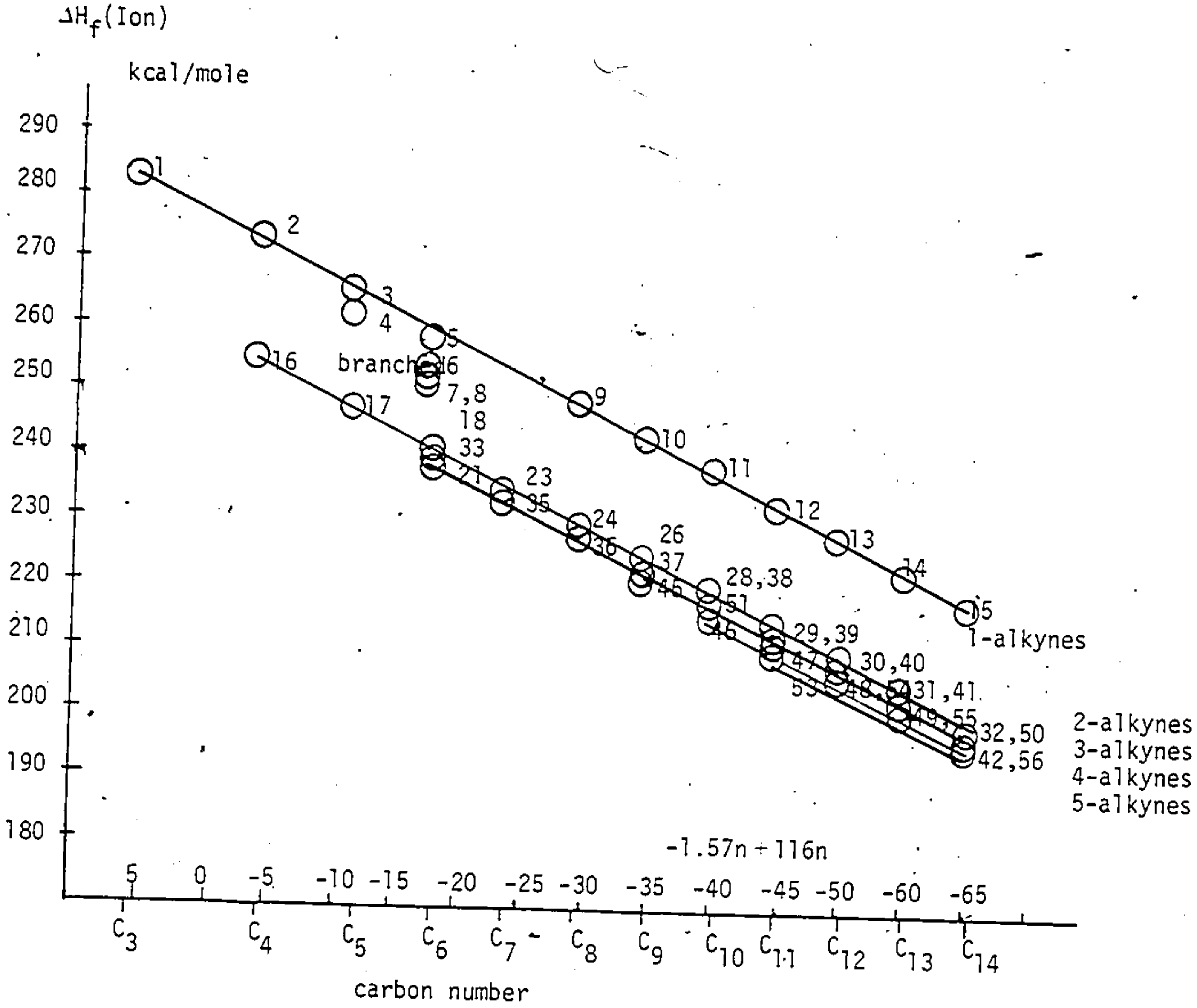


Figure 17 Analysis of the Alkanols

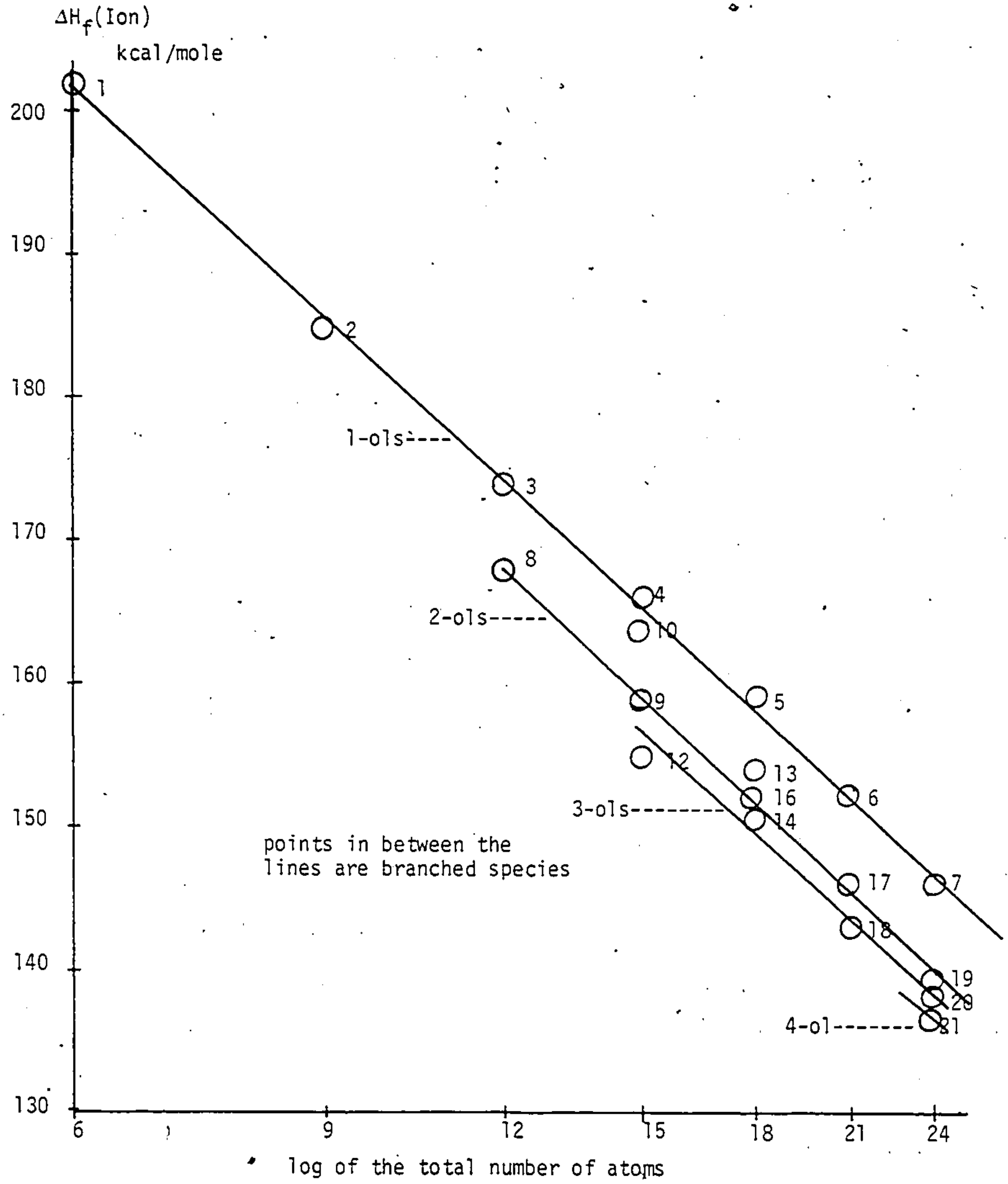
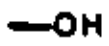
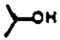
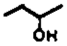
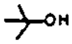
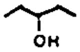
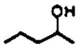
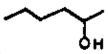
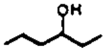
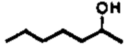
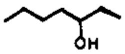
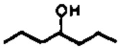


TABLE 8
EXPERIMENTAL AND CALCULATED DATA ON THE ALKANOLS

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔH$_f$(NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔH$_f$(ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
1	CH_4O	Methanol		-48.07	24	10.84	PES PI	27 27	202	202
2	C_2H_6O	Ethanol		-56.24	24	10.47	PES PI	27 27	185	185
3	C_3H_8O	Propanol		-61.24	26	10.22	PES PI	27 27	174	174
4	$C_4H_{10}O$	Butanol		-66.4	26	10.07	PES PI	27 27	166	166
5	$C_5H_{12}O$	Pentanol		-71.3	26	10.00	PES	43	159	159
6	$C_6H_{14}O$	Hexanol		-76.26	26	9.89	PES	43	152	152
7	$C_7H_{16}O$	Heptanol		-81.21	26	9.84	PES	43	146	146
8	C_3H_8O	Isopropanol		-65.15	26	9.88	PES PI	27 27	169	168
9	$C_4H_{10}O$	sec-Butanol		-69.88	26	9.88	EM	42	158	159
10		Iso-Butanol		-68.5	26	10.09	PES	27	165	164
11						10.12	EM	42		
12		tert-Butanol		-74.72	24	9.97	PES	27	155	155
13	$C_5H_{12}O$	2-methyl-butanol		-73.4	24	9.86	EM	42	154	156
14		tert-Pentanol		-75.21	26	9.78	EM	42	151	150
15						9.73	PES	43		
16		sec-Pentanol		-75.18	26	9.78	PES	43	150	152
17	$C_6H_{14}O$	Hexan-2-ol		-79.89	26	9.80	PES	43	146	145
18		Hexan-3-ol		-79.89	26	9.63	PES	43	145	143
19	$C_7H_{16}O$	Heptan-2-ol		-84.84	26	9.70	PES	43	139	139
20		Heptan-3-ol		-84.84	26	9.68	PES	43	138	138
21		Heptan-4-ol		-84.84	26	9.61	PES	43	137	137

METHODS:	PES	is photoelectron spectroscopy
	PI	is photoionization
	EM	is Electron monochromator
	S	is Spectroscopy

4.1.5 Ethers

The available data for the ethers are presented in Table 9 and graphically in Figure 18. Only two corrections are needed; one for branching on a substituent-bearing carbon and a correction for substituent position. The latter can be treated as a correction for asymetry which is equivalent to substituent position, but results in a simpler model. The model chosen and the values subsequently obtained by regression are:

$$H_f(ION) = 148.3 \quad -1.18n \quad +443/n \quad -4.3a \quad +2.4b \qquad (28)$$

Where: n is the total number of atoms

a is the number of branches on a substituent-bearing carbon

b is the number of carbon atoms that would have to be rearranged for the molecule to be in its most symmetrical state

The correlation coefficient (R^2) for this model is 0.996;

4.1.6 Aldehydes

The available data for the aldehydes are presented in Table 10 and graphically in Figure 19. Since the aldehydes have a fixed substituent position only corrections for branching are required. The model chosen and the values subsequently derived by regression are:

$$H_f(ION) = 187.3 \quad -1.63n \quad +140/n \quad -5.0a \quad -3.0b \qquad (29)$$

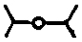
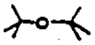
Where: n is the total number of atoms

a is the number of branches on the carbonyl-bearing carbon

b is the number of branches elsewhere in the molecule

The correlation coefficient (R^2) for this model is 0.996

TABLE 9
EXPERIMENTAL AND CALCULATED DATA ON THE ETHERS

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔH_f(NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔH_f(ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
1	C_2H_6O	Dimethyl Ether		-43.2	26	9.95	S	27	186	187
2	C_3H_8O	Methyl Ethyl Ether		-51.7	26	9.72	PES EM	27 42	172	172
3	$C_4H_{10}O$	Diethyl Ether		-60.2	26	9.52	PES	27	159	159
4		Isopropyl Methyl Ether		-60.0	26	9.42	PI EM	27 42	157	158
5	$C_5H_{12}O$	Ethyl Propyl Ether		-65.2	26	9.45	EM	49	153	152
6		Butyl Methyl Ether		-61.7	26	9.54	EM	42	158	157
7	$C_6H_{14}O$	Di-n-propyl Ether		-70.1	26	9.30	PES	27	144	144
8		Di-isopropyl Ether		-76.8	26	9.20	PI PI	27 27	135	136
9		Butyl Ethyl Ether		-70.2	26	9.36	EM	42	146	146
10		Ethyl sec-butyl Ether		-74.5	26	9.32	EM	42	140	142
11	$C_8H_{18}O$	Di-secbutyl Ether		-85.7	26	9.11	EM	42	124	124
12		Di-tert-butyl Ether		-87.2	26	8.81	EM	50	116	116

METHODS:		
	PES	is photoelectron spectroscopy
	PI	is photoionization
	EM	is Ejectron monochromator
	S	is Spectroscopy

Figure 18 Analysis of the Ethers

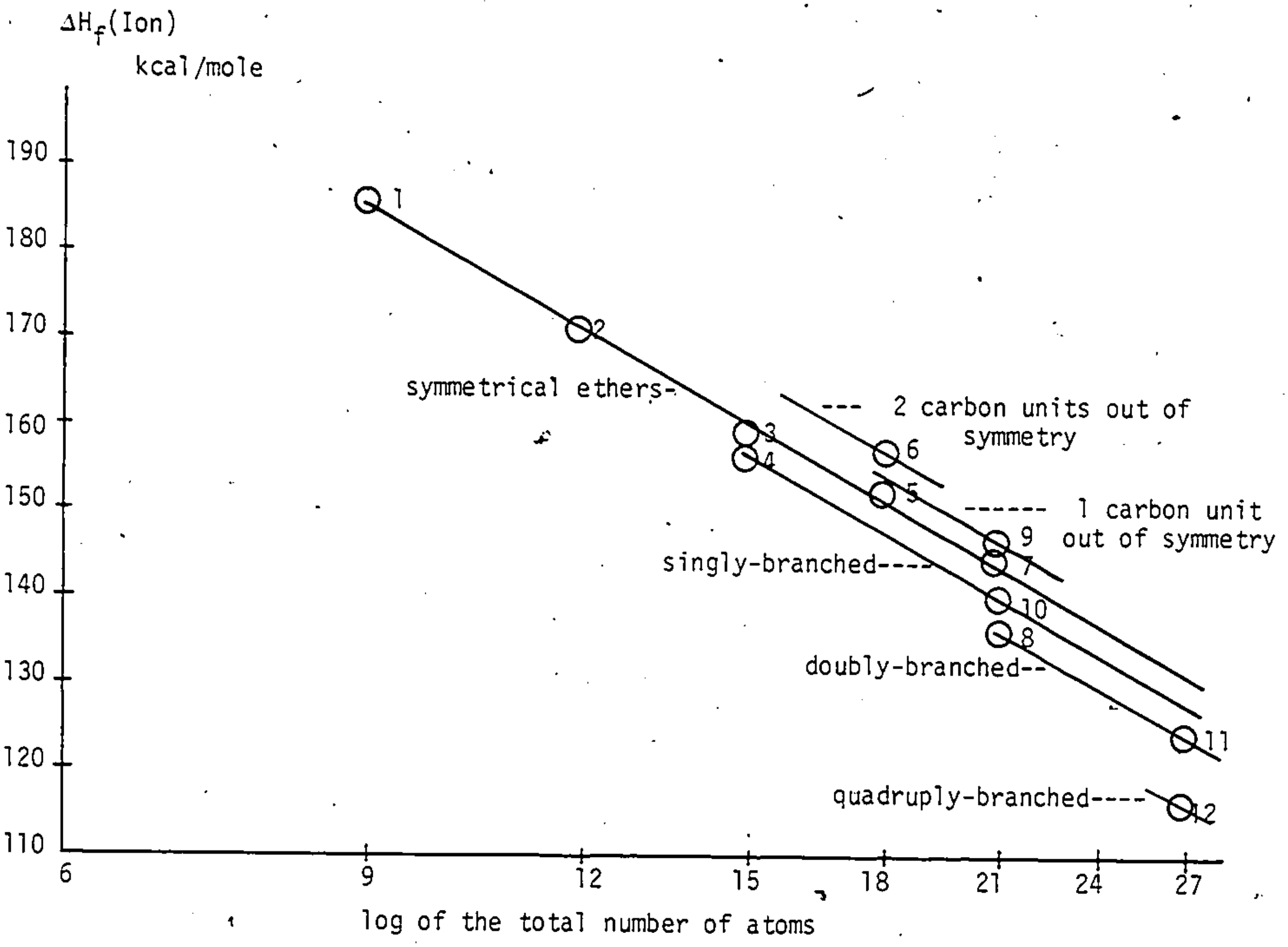
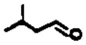
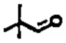
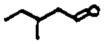
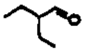
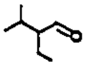
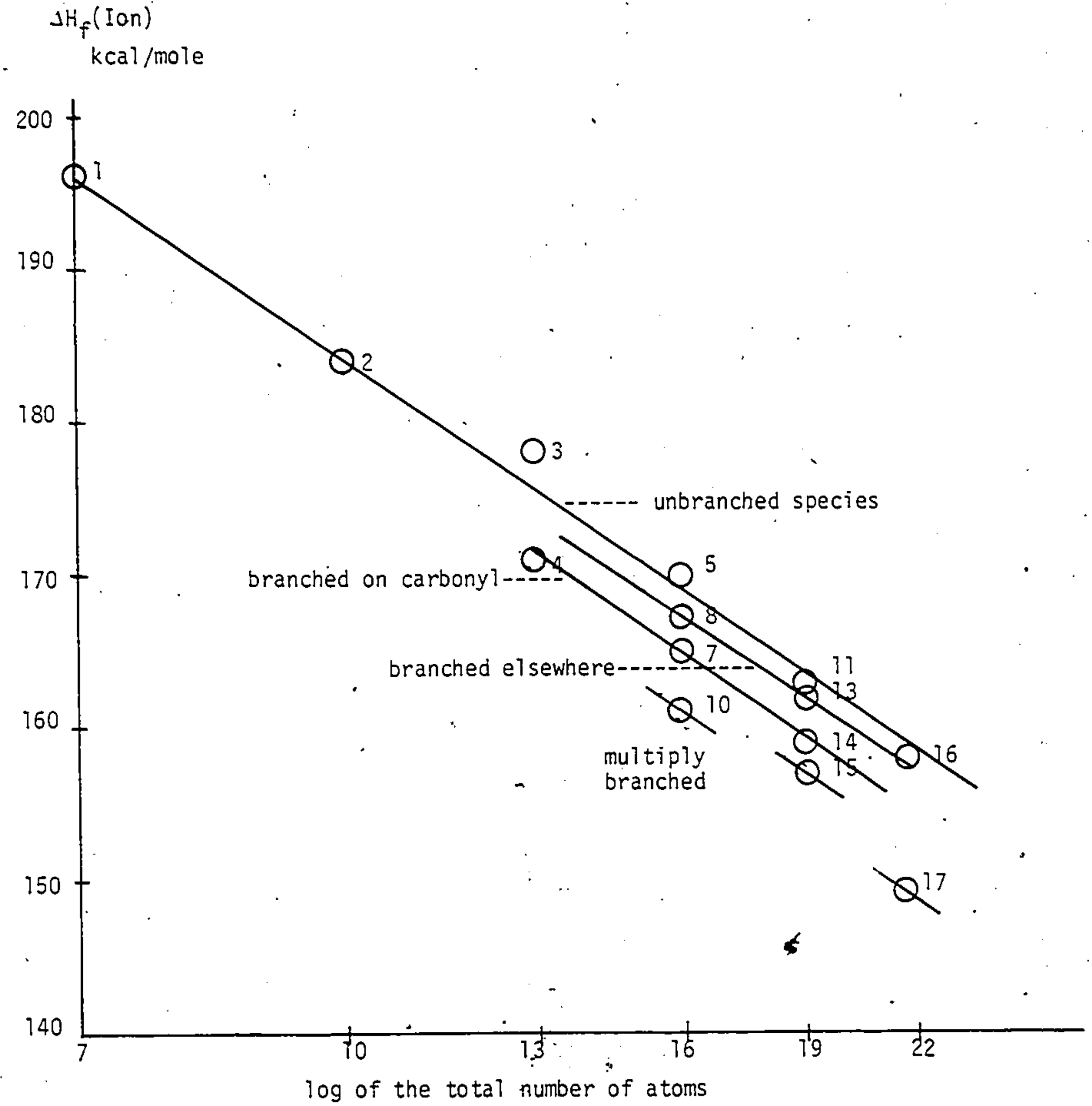


TABLE 10
EXPERIMENTAL AND CALCULATED DATA ON THE ALDEHYDES

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔH_f (NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔH_f (ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
1	C_2H_4O	Acetaldehyde		-39.68	24	10.23	S	27	196	196
2	C_3H_6O	Propionaldehyde		-45.45	24	9.95	PES	51 52	184	185
3	C_4H_8O	Butanal		-48.94	24	9.83	PES	52 53	178	177
4		Isobutanal		-52.25	24	9.70	PES	52	171	172
5	$C_5H_{10}O$	Pentanal		-54.58	24	9.74	PES	52	170	170
6						9.72	EM	42		
7		2-methyl Butanal		-56.5	26	9.59	PES	52	165	165
8		3-methyl Butanal		-56.7	26	9.69	PES	52	167	167
9						9.72	EM	42		
10		2,2-dimethyl Propanal		-58.3	26	9.50	PES	52	161	160
11	$C_6H_{12}O$	Hexanal		-59.53	26	9.72	PES	52	163	164
12						9.62	PES	43		
13		3-methyl Pentanal		-61.6	26	9.68	EM	42	162	161
14		2-ethyl Butanal		-61.5	26	9.54	EM	42	159	159
15		3,3-dimethyl Butanal		-64.29	26	9.61	PES	52	157	158
16	$C_7H_{14}O$	Heptanal		-64.7	26	9.65	PES	52	158	158
17		2-ethyl,3-methyl Butanal		-68.5	26	9.44	EM	42	149	150

METHODS:		
	PES	is photoelectron spectroscopy
	PI	is photoionization
	EM	is Electron monochromator
	S	is Spectroscopy

Figure 19 Analysis of the Aldehydes



4.1.7 Ketones

The available data for the ketones are presented in Table 11 and graphically in Figure 20. As evidenced in the Figure only three corrections are necessary; branching on a substituent-bearing carbon, branching elsewhere, and a correction for substituent position. The model chosen and the values subsequently obtained by regression are:

$$\Delta H_f(\mathrm{ION}) = 165.9 - 1.73n + 238/n - 3.8a - 2.2b - 1.5c \qquad (30)$$

Where: n is the total number of atoms

a is the number of branches on a carbonyl-bearing carbon

b is the number of branches elswhere

c is the number of carbon atoms that would be rearranged to produce the most symmetrical ketone

The correlation coefficient (R^2) for this model is 0.989.

4.1.8 Carboxylic Acids

The available data for the carboxylic acids are presented in Table 12 and Figure 21. All data points lie along the straight line except for one branched member. The model chosen and coefficients obtained are:

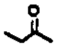
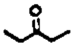
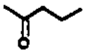
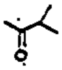
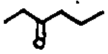
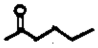
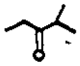
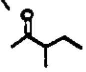
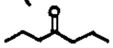
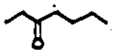
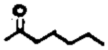
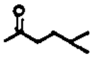
$$\Delta H_f(\mathrm{ION}) = 124.4 - 1.40n + 237/n - a \qquad (31)$$

Where: n is the total number of atoms in the molecule

a is the branching correction which in the case of this model was not available due to error suppression in the SPSS computer package used

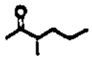
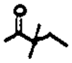
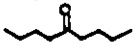
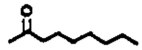
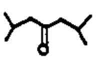
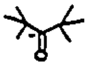
The correlation coefficient obtained for this model is 0.963.

TABLE 11
EXPERIMENTAL AND CALCULATED DATA ON THE KETONES

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔHf(NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔHf(ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
1	C_3H_6O	Acetone		-51.9	24	9.705	S	54	172	172
2	C_4H_8O	Methyl Ethyl Ketone		-57.02	24	9.52	PES	52	163	162
3	$C_5H_{10}O$	Diethyl Ketone		-61.7	26	9.30	PES	52	153	153
4		Methyl n-Propyl Ketone		-61.7	26	9.38	EM PES	42 52	155	155
5		Methyl Iso-Propyl Ketone		-63.6	26	9.29	PES	52	151	151
6	$C_6H_{12}O$	Ethyl n-Propyl Ketone		-66.6	26	9.12	PES	43	146	146
7						9.30	EM	42		
8		Methyl n-Butyl Ketone		-66.6	26	9.33	PES	52	147	147
9						9.24	EM	42		
10		Ethyl Iso-Propyl Ketone		-68.6	26	9.09	PES	52	141	142
11		Methyl Iso-Butyl Ketone		-68.6	26	9.29	PES	52	146	145
12		Methyl sec-Butyl Ketone		-68.5	26	9.20	PES	52	144	143
13						9.22	EM	42		
14		Methyl tert-Butyl Ketone		-70.2	26	9.11	PES	52	140	140
15	$C_7H_{14}O$	Di-n-propyl Ketone		-71.6	26	9.10	PES	52	137	138
16						9.02	PES	43		
17		Ethyl n-Butyl Ketone		-71.6	26	9.04	PES	52	139	139
18						9.26	EM	42		
19		Methyl n-Pentyl Ketone		-71.5	26	9.29	PES	52	142	142
20						9.18	PES	42		
21		Methyl Iso-Propyl Ketone		-73.6	26	9.28	PES	52	140	140

METHODS:
PES Is photoelectron spectroscopy
PI Is photoionization
EM Is Electron monochromator
S Is Spectroscopy

TABLE 11 continued
EXPERIMENTAL AND CALCULATED DATA ON THE KETONES

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔH$_f$(NEUTRAL) (kcal/mole)	REF.	IONIZATION ENERGY (eV)	METHOD	REF.	ΔH$_f$(ION) (kcal/mole) EXP.	CALC.
22	$C_7H_{14}O$	Methyl sec-Pentyl Ketone		-73.5	26	9.22	EM	42	139	138
23		Methyl neo-Pentyl Ketone		-76.3	26	9.22	PES	52	136	137
24		Methyl tert-Pentyl Ketone		-75.2	26	9.01	PES	52	133	134
25		Di-isopropyl Ketone		-75.5	26	8.96	PES	27	131	131
26						8.94	PES	52		
27	$C_8H_{16}O$	tert-Butyl·iso-Propyl Ketone		-82.1	26	8.79	PES	52	121	121
28	$C_9H_{18}O$	Di-n-butyl Ketone		-81.5	26	9.07	EM	42	128	127
29		Methyl n-Heptyl Ketone		-81.4	26	9.16	EM	42	130	129
30		Di-iso-butyl Ketone		-85.6	26	8.98	PES	52	121	122
31		Di-tert-butyl Ketone		-88.9	26	8.67	PES	52	111	111

METHODS:

PES	is photoelectron spectroscopy
PI	is photoionization
EM	is Electron monochromator
S	is Spectroscopy

Figure 20 Analysis of the Ketones

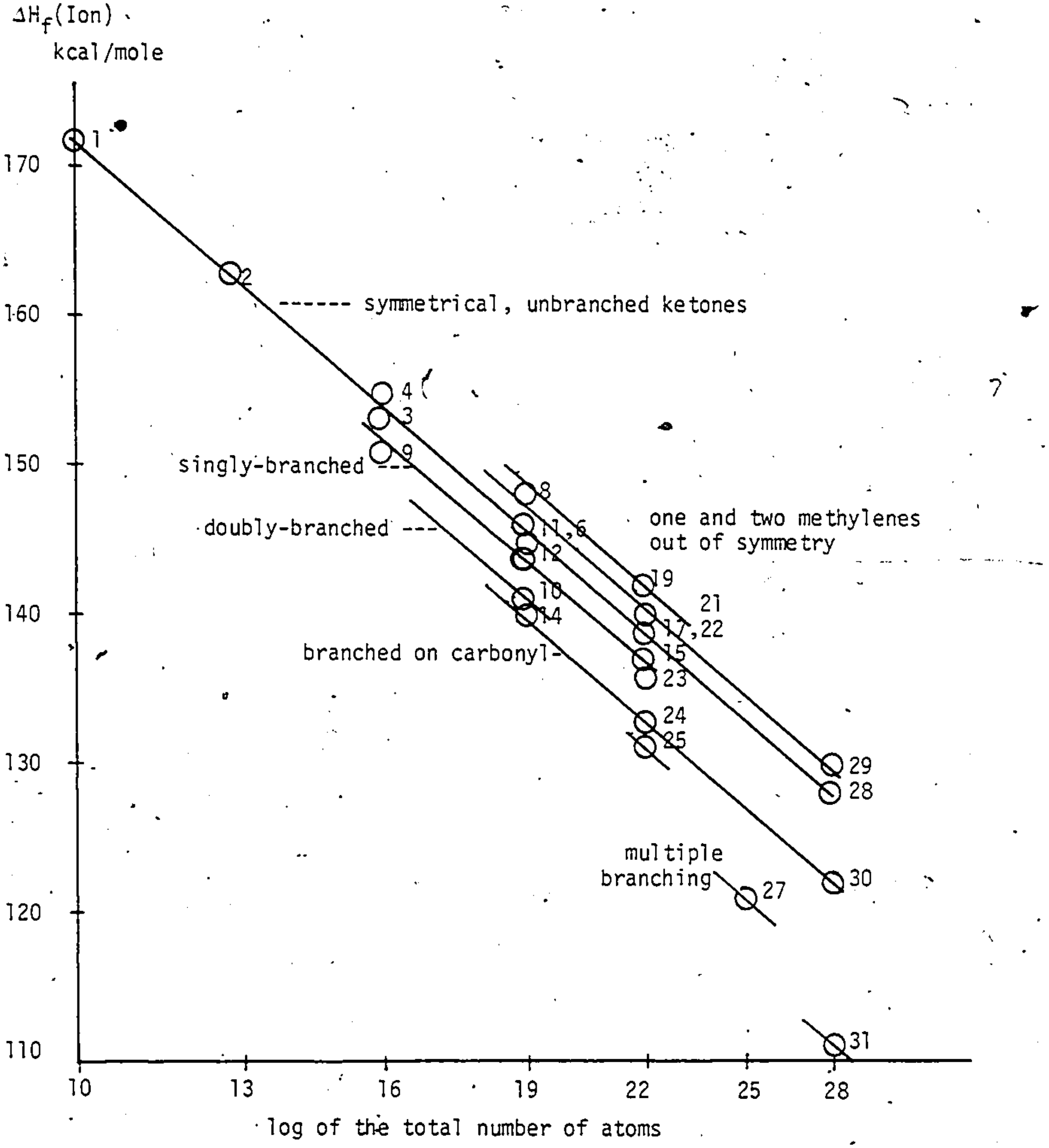
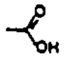
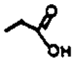
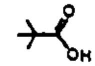
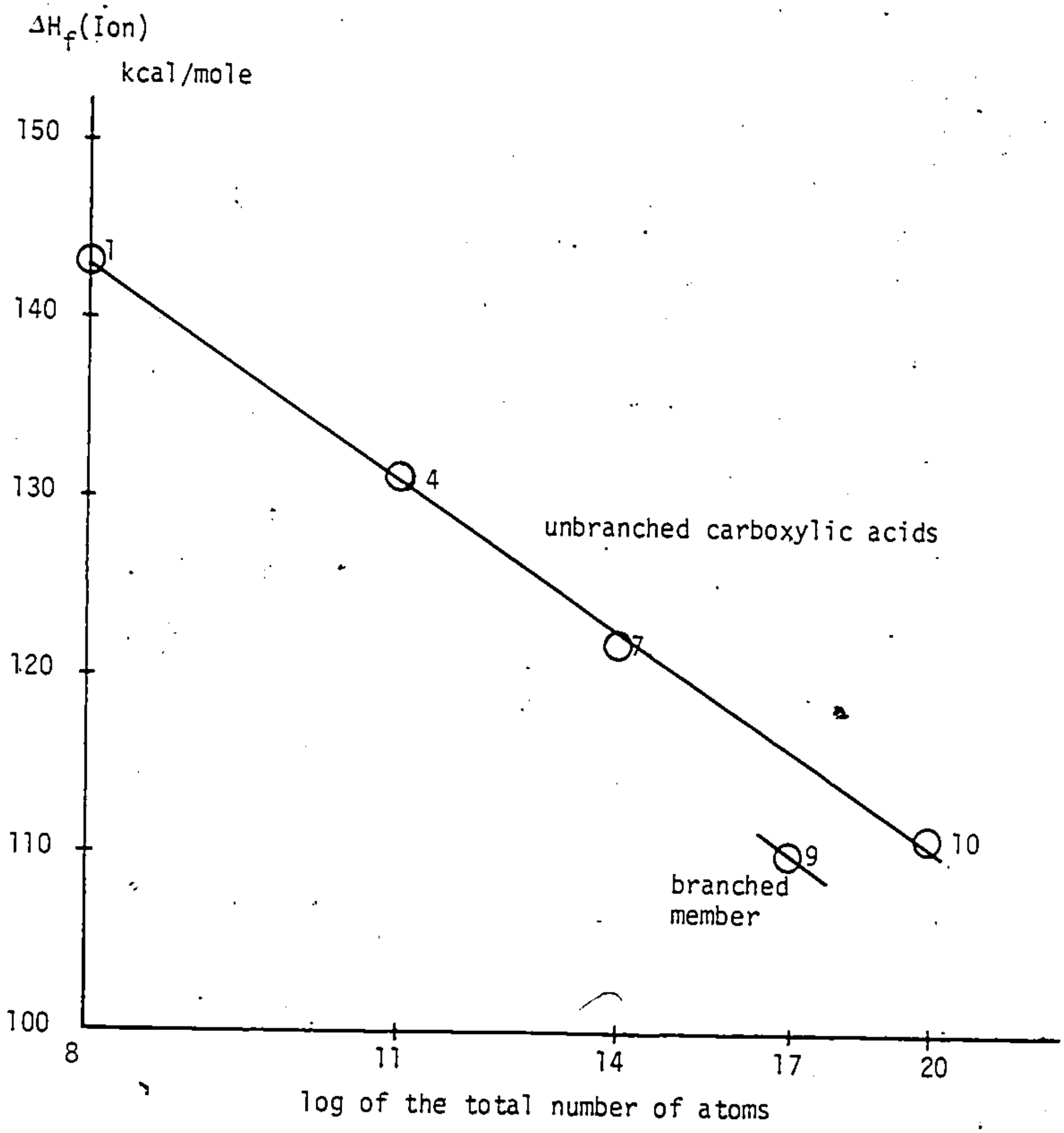


TABLE 12
EXPERIMENTAL AND CALCULATED DATA ON THE CARBOXYLIC ACIDS

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔH$_f$(NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔH$_f$(ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
1	$C_2H_4O_2$	Acetic acid		-103.26	24	10.70	PES	55	143	143
2						10.63	PES	56		
3						10.66	EM	42		
4	$C_3H_6O_2$	Propanoic acid		-108.4	24	10.51	PES	56	131	131
5						10.24	PI	27		
6						10.41	EM	42		
7	$C_4H_8O_2$	Butyric acid		-112.8	26	10.16	PI	27	122	122
8						10.24	PI	27		
9	$C_5H_{10}O_2$	Pivalic acid		-122.4	26	10.08	EM	42	110	112
10	$C_6H_{12}O_2$	Hexanoic acid		-122.7	24	10.12	EM	42	111	110

METHODS: PES is photoelectron spectroscopy
PI is photoionization
EM is Electron monochromator
S is Spectroscopy

Figure 21 Analysis of the Carboxylic Acids



4.1.9 Chloroalkanes

The available data for the chloroalkanes are presented in Table 13 and in Figure 22. The model proposed and coefficients obtained in the regression are:

$$\Delta H_f(\text{ION}) = 238.8 \quad -2.24n \quad +52/n \quad -3.4a \quad -6.1b \quad -4.0c \qquad (32)$$

Where: n is the total number of atoms

a is the number of branches not on a chlorine-bearing carbon

b is the number of branches on a chlorine-bearing carbon

c is the correction applicable to a secondary chloroalkane

The correlation coefficient (R^2) obtained is 0.998.

4.1.10 Bromoalkanes

The available data for the bromoalkanes are presented in Table 14 and in Figure 23. The model chosen and the coefficients obtained are:

$$\Delta H_f = 220.5 \quad -1.40n \quad +102/n \quad -4.5a \quad -3.2b \quad -5.4c \qquad (33)$$

Where: n is the total number of atoms

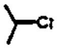
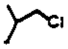
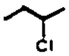
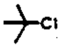
a is the number of branches on the bromine-bearing carbon

b is the number of branches elsewhere

c is the correction applicable to a secondary bromoalkane

The correlation coefficient obtained is 0.997

TABLE 13
EXPERIMENTAL AND CALCULATED DATA ON THE CHLOROALKANES

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔHf (NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔHf (ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
1	CH_3Cl	Chloromethane		-20.55	26	11.22	S	27	238	238
2	C_2H_5Cl	Chloroethane		-26.1	26	10.97	PES PI	57 27	227	227
3	C_3H_7Cl	Chloropropane		-31.0	26	10.82	PI	27	219	219
4						10.88	PES	58		
5		Isopropylchloride		-33.6	26	10.78	PI	27	215	215
6	C_4H_9Cl	n-Butylchloride		-35.1	26	10.67	PI	27	211	211
7		Iso-Butylchloride		-38.1	26	10.66	PI	27	208	208
8		sec-Butylchloride		-38.6	26	10.65	PI	27	207	207
9		tert-Butylchloride		-43.7	26	10.61	PI	27	201	201

METHODS:	PES	is photoelectron spectroscopy
	PI	is photoionization
	EM	is Electron monochromator
	S	is Spectroscopy

Figure 22 Analysis of the Chloroalkanes

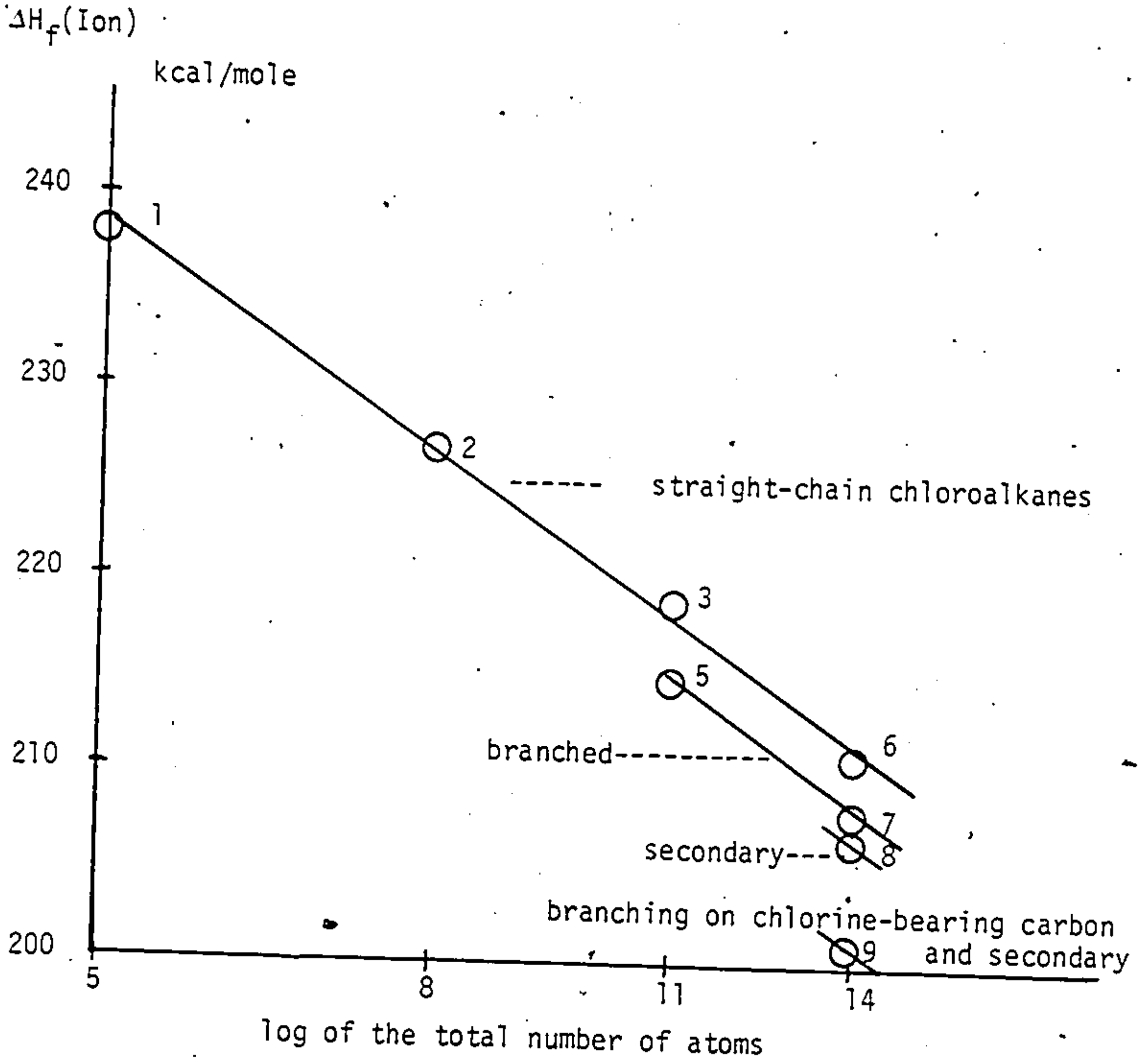
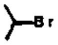
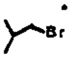
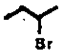
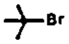
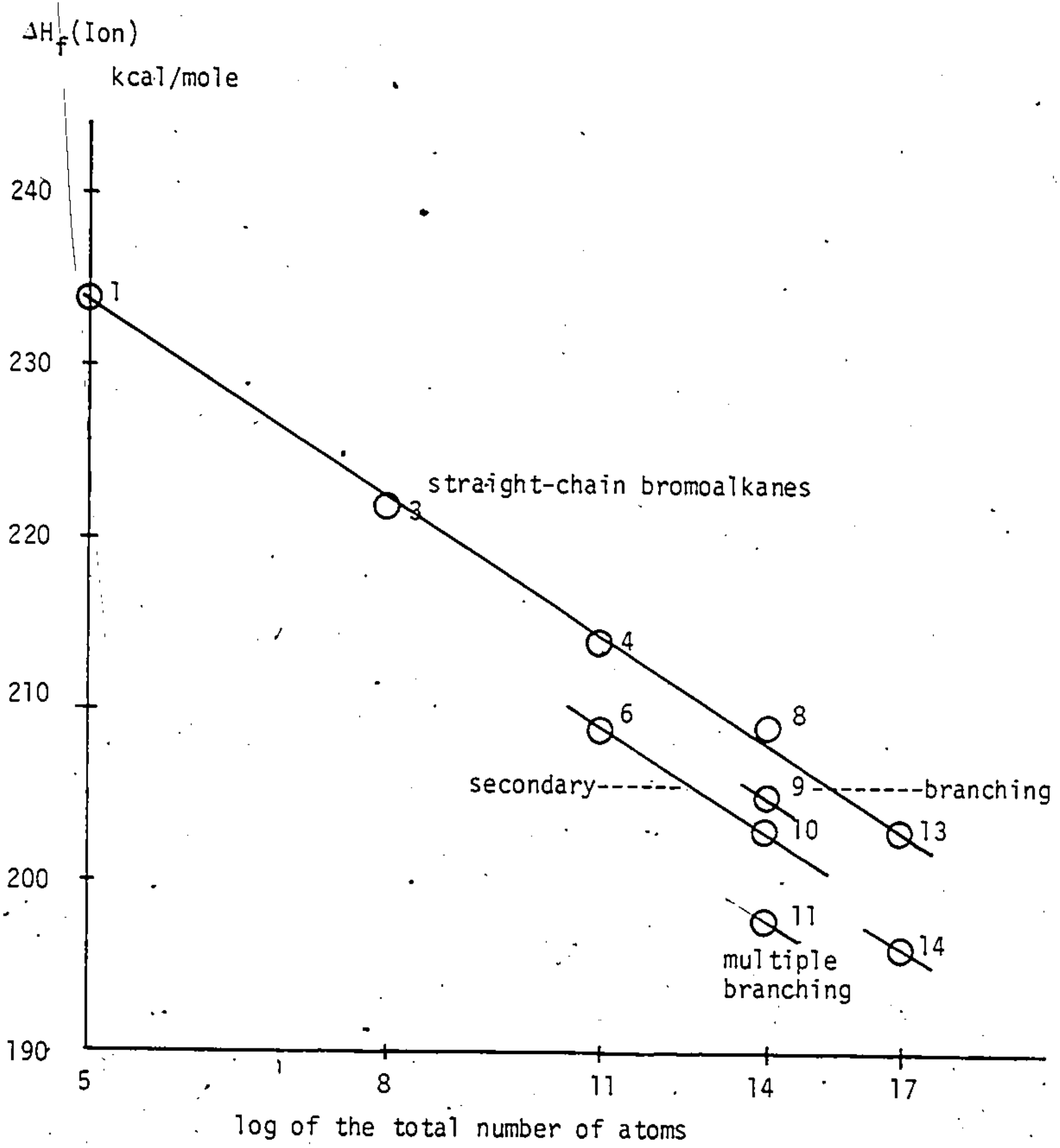


TABLE 14
EXPERIMENTAL AND CALCULATED DATA ON THE BROMOALKANES

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔH_f(NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔH_f(ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
1	CH_3Br	Methylbromide		-9.1	24	10.54	S	27	234	234
2						10.53	PI	27		
						10.53	EM	42		
3	C_2H_5Br	Ethylbromide		-15.2	24	10.29	S	27	222	222
							PI	27		
							PES	27		
4	C_3H_7Br	Propylbromide		-20.5	24	10.13	PES	27	214	214
							PI	27		
5						10.18	PES	59		
6		Isopropylbromide		-23.5	24	10.08	PES	27	209	209
7						10.12	PI	27		
8	C_4H_9Br	n-Butylbromide		-25.4	26	10.18	PES	27	209	208
							PI	27		
9		Iso-Butylbromide		-27.5	26	10.09	PES	27	205	205
							PI	27		
10		sec-Butylbromide		-28.5	26	9.98	PI	27	202	203
11		tert-Butylbromide		-30.6	26	9.89	PI	27	198	198
12						9.95	PES	27		
13	$C_5H_{11}Br$	n-Pentylbromide		-30.3	26	10.10	PI	27	203	203
14		tert-Pentylbromide		-35.1	26	10.04	PES	27	196	196

METHODS:		
	PES	Is photoelectron spectroscopy
	PI	Is photoionization
	EM	Is Electron monochromator
	S	Is Spectroscopy

Figure 23 Analysis of the Bromoalkanes



4.1.11 Iodoalkanes

The available data for the iodoalkanes are presented in Table 15 and in Figure 24. The series is similar to the chloroalkanes and bromoalkanes in that there are sufficient data to calculate corrections for both forms of branching and corrections for secondary iodoalkanes. The model chosen and the coefficients obtained upon regression are:

$$\Delta H_f(\text{ION}) = 219.4 \quad -1.66n \quad +60/n \quad -5.3a \quad -2.6b \quad -5.0c \qquad (34)$$

Where: n is the total number of atoms

a is the number of branches on iodide-bearing carbon

b is the number of branches elsewhere

c is the correction applicable to secondary iodoalkanes

The correlation coefficient (R^2) for this model is 0.999.

4.2. APPLICATION TO EVEN ELECTRON IONS

4.2.1 Primary Carbonium Ions

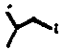
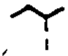
The available data for the primary carbonium ions are presented in Table 16 and graphically in Figure 25. The data are available for the unbranched members and thus no corrections are obtained. The model chosen and the coefficients obtained upon regression are:

$$\Delta H_f = 202.6 \quad -1.23n \quad +175/n \qquad (35)$$

Where: n is the total number of atoms

The correlation coefficient for this model is 0.999.

TABLE 15
EXPERIMENTAL AND CALCULATED DATA ON THE IODOALKANES

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔH_f(NEUTRAL) (kcal/mole)	REF.	IONIZATION ENERGY (eV)	METHOD	REF.	ΔH_f(ION) (kcal/mole) EXP.	CALC.
1	CH_3I	Methyliodide		3.4	24	9.53	PES	27	223	223
2	C_2H_5I	Ethyliodide		-2.0	24	9.35	S,PI PES	27 60	214	214
3	C_3H_7I	Propyliodide		-7.1	24	9.26	PES PI	27 27	206	207
4		Isopropyliodide		-9.8	24	9.18	PES PI	27 27	202	201
5	C_4H_9I	n-Butyliodide		-12.1	26	9.22	PES PI	27 27	201	200
6		Isobutyliodide		-14.0	26	9.18	PES PI	27 27	198	198
7		sec-Butyliodide		-14.4	26	9.09	PI	27	195	196
8		tert-Butyliodide		-17.2	26	9.02	PI PES	27 27	191	189
9	$C_5H_{11}I$	n-Pentyliodide		-17.1	26	9.18	PI PES	27 27	195	195
10		Iso-Pentyliodide		-19.1	26	9.17	PES	27	192	192
11		neo-Pentyliodide		-22.2	26	8.93	PES	27	184	185
12	$C_6H_{13}I$	n-Hexyliodide		-22.0	26	9.17	PES	26	189	189

METHODS:		
	PES	is photoelectron spectroscopy
	PI	is photoionization
	EM	is Electron monochromator
	S	is Spectroscopy

Figure 24 Analysis of the Iodoalkanes

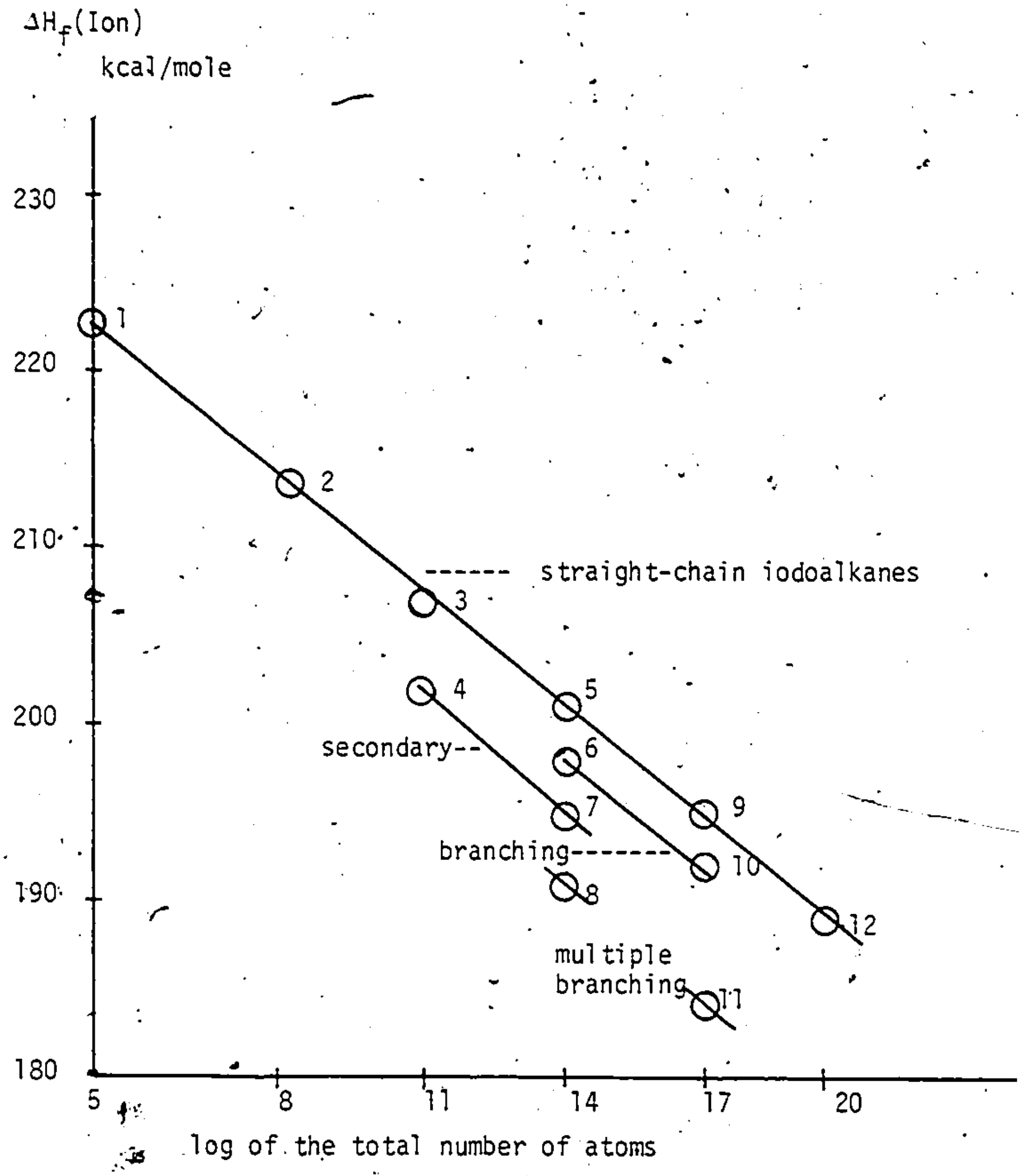


TABLE 16

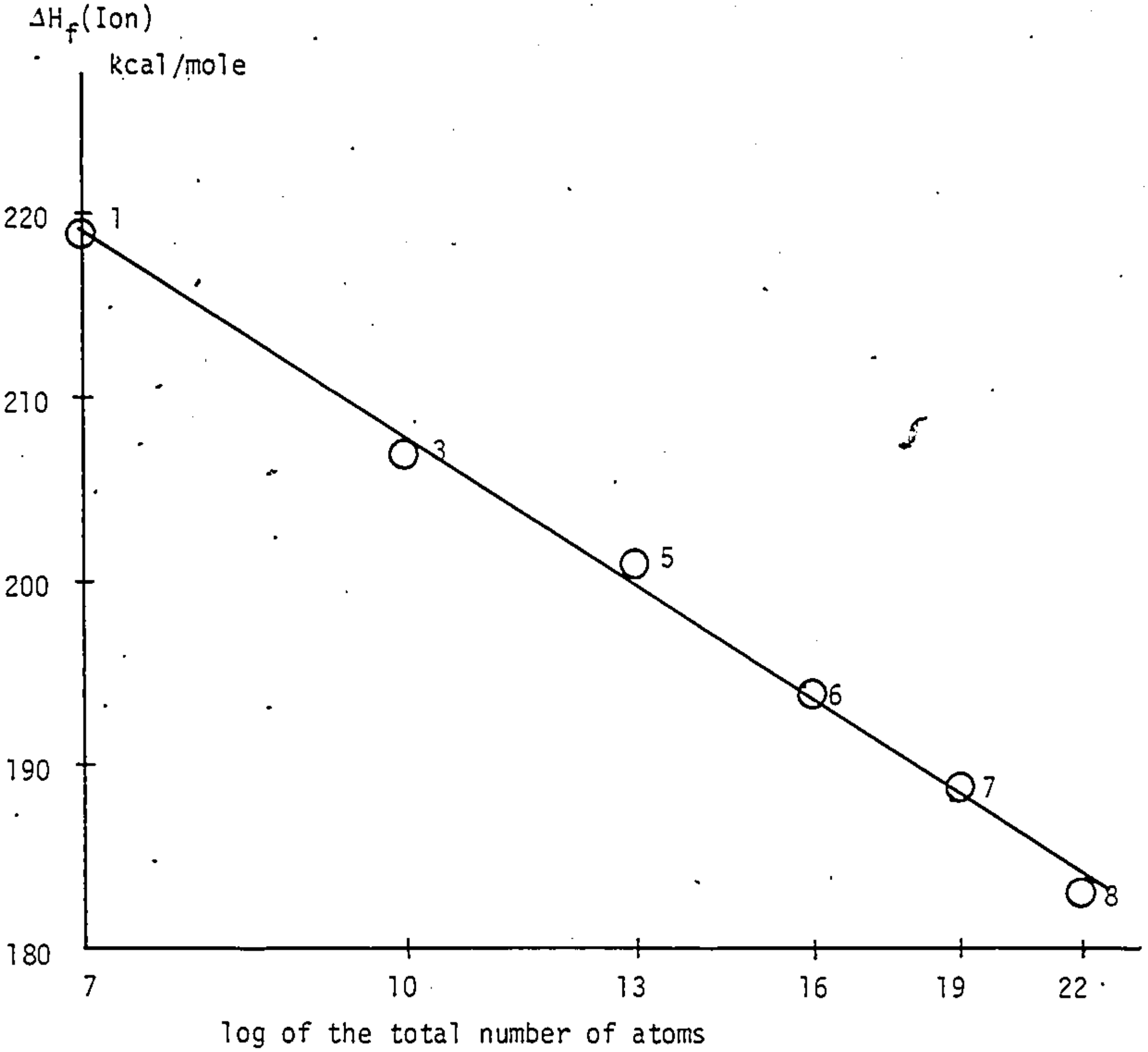
EXPERIMENTAL AND CALCULATED DATA ON THE PRIMARY CARBONIUM IONS

DATA NO.	FORMULA	PROCESS	ΔH_f (NEUTRAL) (kcal/mole)		IONIZATION ENERGY (AE) (eV)			ΔH_f (ION) (kcal/mole)	
				REF.		METHOD	REF.	EXP.	CALC.
1	C_2H_5	Ionized from the radical	25.7	27	8.4	PI	27	219	219
2					8.38	EM	27		
3	C_3H_7	Ionized from the radical	20.7	27	8.1	PI	27	208	208
4					8.10	EM	27		
5	C_4H_9	Ionized from the radical	15.7	27	8.01	EM	27	200	200
6	C_5H_{11}	Ionized from the radical	11	61	7.94	EM	61	194	194
7	C_6H_{13}	Ionized from the radical	6.0	61	7.92	EST	61	189	188
8	C_7H_{15}	Ionized from the radical	1.0	61	7.90	EST	61	183	184

METHODS:

PES	is photoelectron spectroscopy
PI	is photoionization
EM	is Electron monochromator
S	is Spectroscopy
EST	is an estimation
HT	is Hydride Transfer

Figure 25 Analysis of the Primary Carbonium Ions



4.2.2 Secondary Carbonium Ions

The available data for the secondary carbonium ions are presented in Table 17 and graphically in Figure 26. This series is similar to that of the primary carbonium ions in that data are available for the unbranched members only. The model chosen and the coefficients obtained upon regression are:

$$\Delta H_f(\mathrm{ION}) = 191.4 \quad -1.34n \quad +131/n \qquad (36)$$

Where: n is the total number of atoms

The correlation coefficient (R^2) obtained for this model is 0.997.

4.2.3 Tertiary Carbonium Ions

The available data for the tertiary carbonium ions are presented in Table 18 and graphically in Figure 27. This series includes one branched member which provides an estimate of the correction term for branching. The model chosen and the coefficients obtained upon regression are:

$$\Delta H_f(\mathrm{ION}) = 183.2 \quad -1.66n \quad +66/n \quad -2.3a \qquad (37)$$

Where: n is the total number of atoms

a is the number of branches

The correlation coefficient obtained for this regression is 0.998.

An interesting point to note is that two recent papers put forth the proposal that $\Delta H_f(C_4H_9^+)$ = 162 or 163 kcal/mole.[62,63] This is noted in Table 18 and Figure 27. These values could only be valid if the scheme proposed in this thesis is not applicable to this series or if the heats of formation of the higher homologues were lowered by the same amount (4,5 kcal).

TABLE 17
EXPERIMENTAL AND CALCULATED DATA ON THE SECONDARY CARBONIUM IONS

DATA NO.	FORMULA	PROCESS	ΔHf(NEUTRAL) (kcal/mole)		IONIZATION ENERGY (AE) (eV)			ΔHf(ION) (kcal/mole)	
				REF.		METHOD	REF.	EXP.	CALC.
1 2	C_3H_7	Ionized from the radical	17.6	27	7.5 7.55	PI EM	27 27	191	191
3	C_4H_9	Ionized from the radical	12.6	27	7.41	EM	27	184	184
4	C_5H_{11}	Ionized from the radical	7.4	36	7.41	EM	36	178	178
5	C_6H_{13}	Ionized from the radical	3.0	61	7.38	EM	61	173	173
6	C_7H_{15}	Ionized from the radical	-2.0	61	7.35	EST	61	168	168

METHODS:		
	PES	is photoelectron spectroscopy
	PI	is photoionization
	EM	is Electron monochromator
	S	is Spectroscopy
	EST	is an estimation
	HT	is Hydride Transfer

Figure 26 Analysis of the Secondary Carbonium Ions

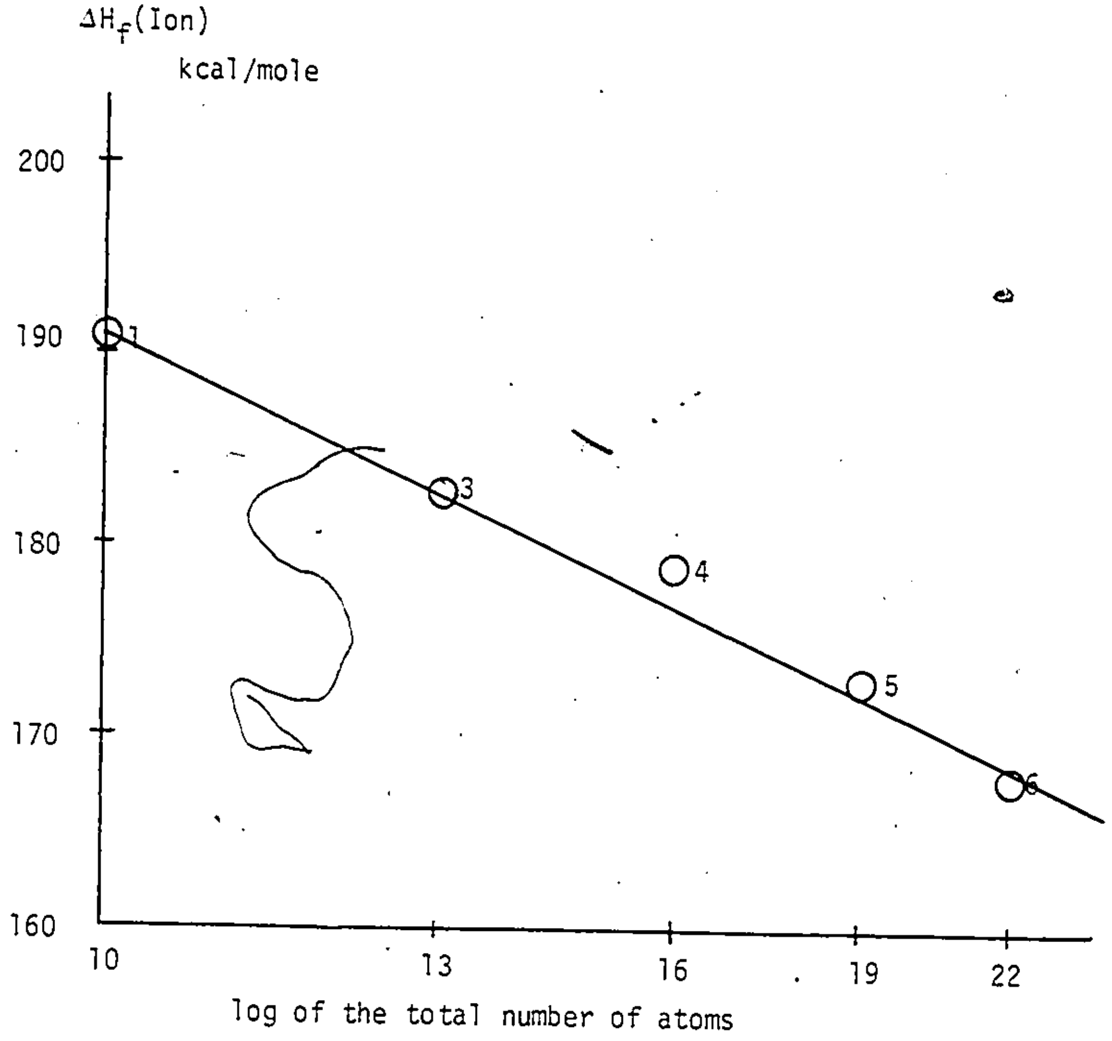


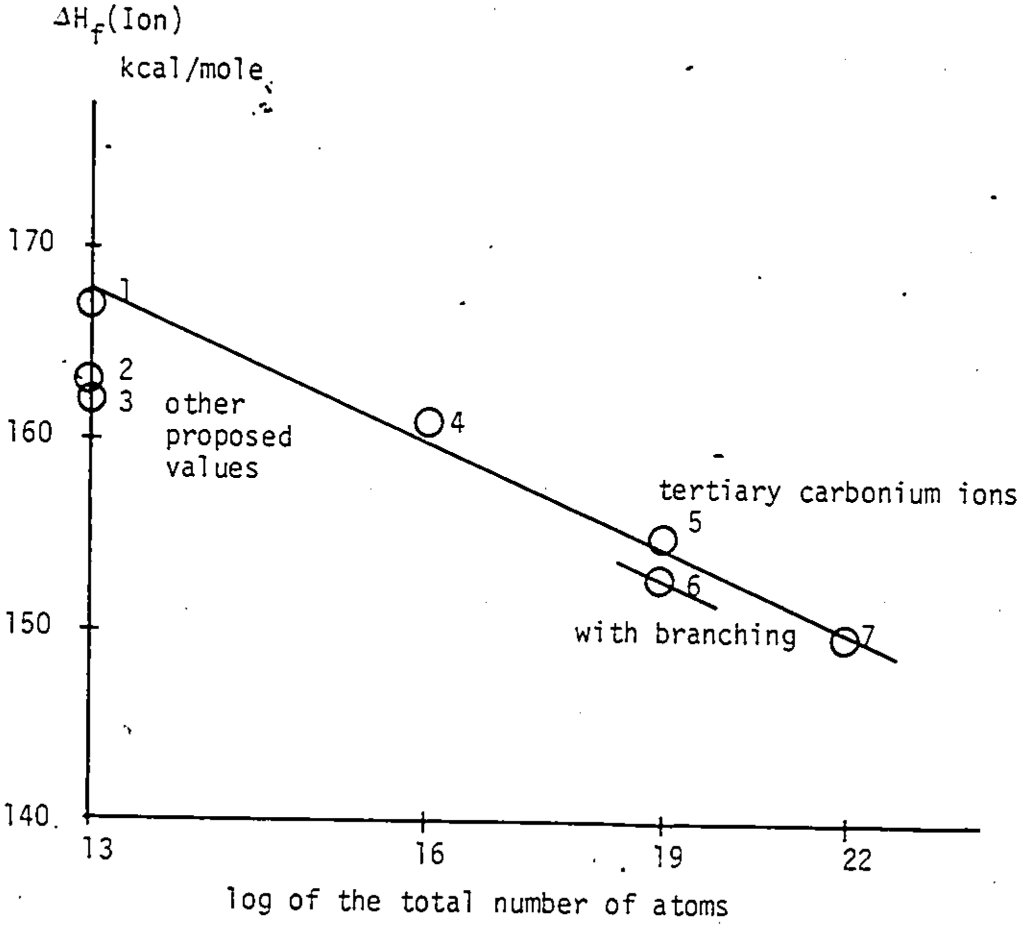
TABLE 18
EXPERIMENTAL AND CALCULATED DATA ON THE TERTIARY CARBONIUM IONS

DATA NO.	FORMULA	PROCESS	ΔHf (NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)	(AE)		ΔHf (ION) (kcal/mole)	
				REF.		METHOD	REF.	EXP.	CALC.
1	C_4H_9	ionized from the radical	6.8	27	6.93	EM	27	167	167
2			8.4	62	6.70	PI	62	163	comment
3		from tert-Butane through loss of H	-32.07	63	10.68	PI	63	162	only
			52.10	63					
4	C_5H_{11}	ionized from the radical	3.1	36	6.85	EM	36	161	161
						EM	61		
5		equilibrium measurement of t-butyl and isopentyl			(6.85)*	HT	64		
6	C_6H_{13}	ionized from the radical	-1.9	61	6.80	EM	61	155	156
7		equilibrium measurement of t-butyl and isohexyl			(6.80)*	HT	64		
8	C_6H_{13}	2,2-dimethyl butane--equil. meas. of t-butyl and 2,2 species			(6.63)*	HT	64	153	153
9	C_7H_{15}	ionized from the radical	-6.6	61	6.79	EM	61	150	149

*Values in brackets are calculated from the heat of formation to produce an artificial ionization potential for calculation

METHODS:		
	PES	is photoelectron spectroscopy
	PI	is photoionization
	EM	is Electron monochromator
	S	is Spectroscopy
	EST	is an estimation
	HT	is Hydride Transfer

Figure 27 Analysis of the Tertiary Carbonium Ions



4.3 APPLICATION TO CYCLIC AND AROMATIC SERIES

4.3.1 Alkyl Benzenes

The available data for the alkyl benzenes are presented in Table 19 and in Figure 28. The corrections required are for branching at the carbon atom adjacent to the benzene and for branching elsewhere. The model chosen and coefficients determined by regression are:

$$\Delta H_f(\text{ION}) = 233.7 \quad -1.73n \quad +114/n \quad -1.9a \quad -1.1b \tag{38}$$

Where: n is the total number of atoms

a is the number of branches not adjacent to the benzene

b is the number of branches adjacent to the benzene

The correlation coefficient obtained for this model is 0.999.

4.3.2 Cyclic Ketones

Available data for the cyclic ketones are presented in Table 20 and in Figure 29. This series has been included to demonstrate the versatility of the scheme proposed in this thesis. The data in Table 20 include three values that are vertical ionization energies, which are the only data available. Figure 29 shows that when the heats of formation of the cyclic ketones are plotted against the total number of atoms, no correlation is achieved. If, however, the heats of formation minus the ring strain of the neutral alkyl ring is plotted a correlation is achieved. This indicates that the ring strain in the ion is similar to the ring strain of the neutral alkyl ring. Accordingly a regression was performed using this scheme yielding the following model:

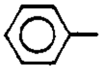
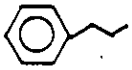
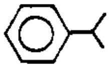
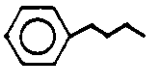
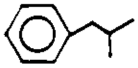
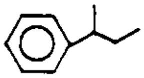
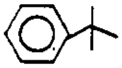
$$\Delta H_f(\text{ION}) = 198.6 \quad -2.47n \quad +8/n \quad +a \tag{39}$$

Where: n is the total number of atoms

a is the ring strain applicable to the neutral alkyl ring

The correlation coefficient applicable to this model is 0.901

TABLE 19
EXPERIMENTAL AND CALCULATED DATA ON THE ALKYLBENZENES

DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔHf(NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔHf(ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
1	C_7H_8	Toluene		11.99	24	8.82	S,PI	27	215	215
							PES	27		
2							PI	65		
							PI	66		
3	C_8H_{10}	Ethyl Benzene		7.15	24	8.76	PI	65	209	208
4	C_9H_{12}	n-Propyl Benzene		1.89	24	8.72	PI	27	203	203
5						8.71	PI	65		
6		iso-Propyl Benzene		0.96	24	8.69	PI	27	202	202
7						8.72	PI	65		
8	$C_{10}H_{14}$	n-Butyl Benzene		-3.28	24	8.69	PI	27	197	197
9						8.68	PI	65		
10		iso-Butyl Benzene		-5.14	24	8.69	PI	27	195	195
11						8.68	PI	65		
12		sec-Butyl Benzene		-4.15	24	8.68	PI	27	196	196
							PI	65		
13		tert-Butyl Benzene		-5.4	24	8.68	PI	27	195	195
14						8.69	PI	65		

METHODS:		
	PES	is photoelectron spectroscopy
	PI	is photoionization
	EM	is Electron monochromator
	S	is Spectroscopy

Figure 28 Analysis of the Alkylbenzenes

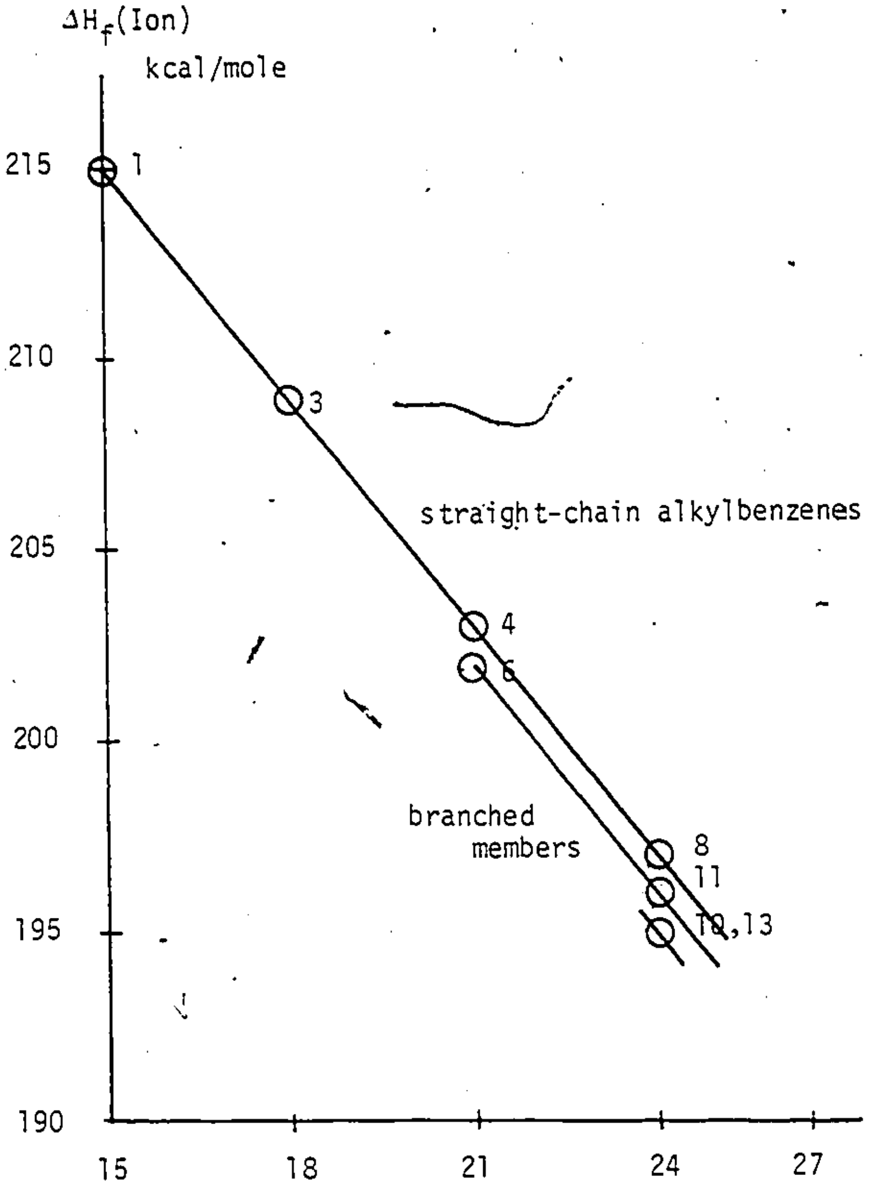


TABLE 20
EXPERIMENTAL AND CALCULATED DATA ON THE CYCLIC KETONES

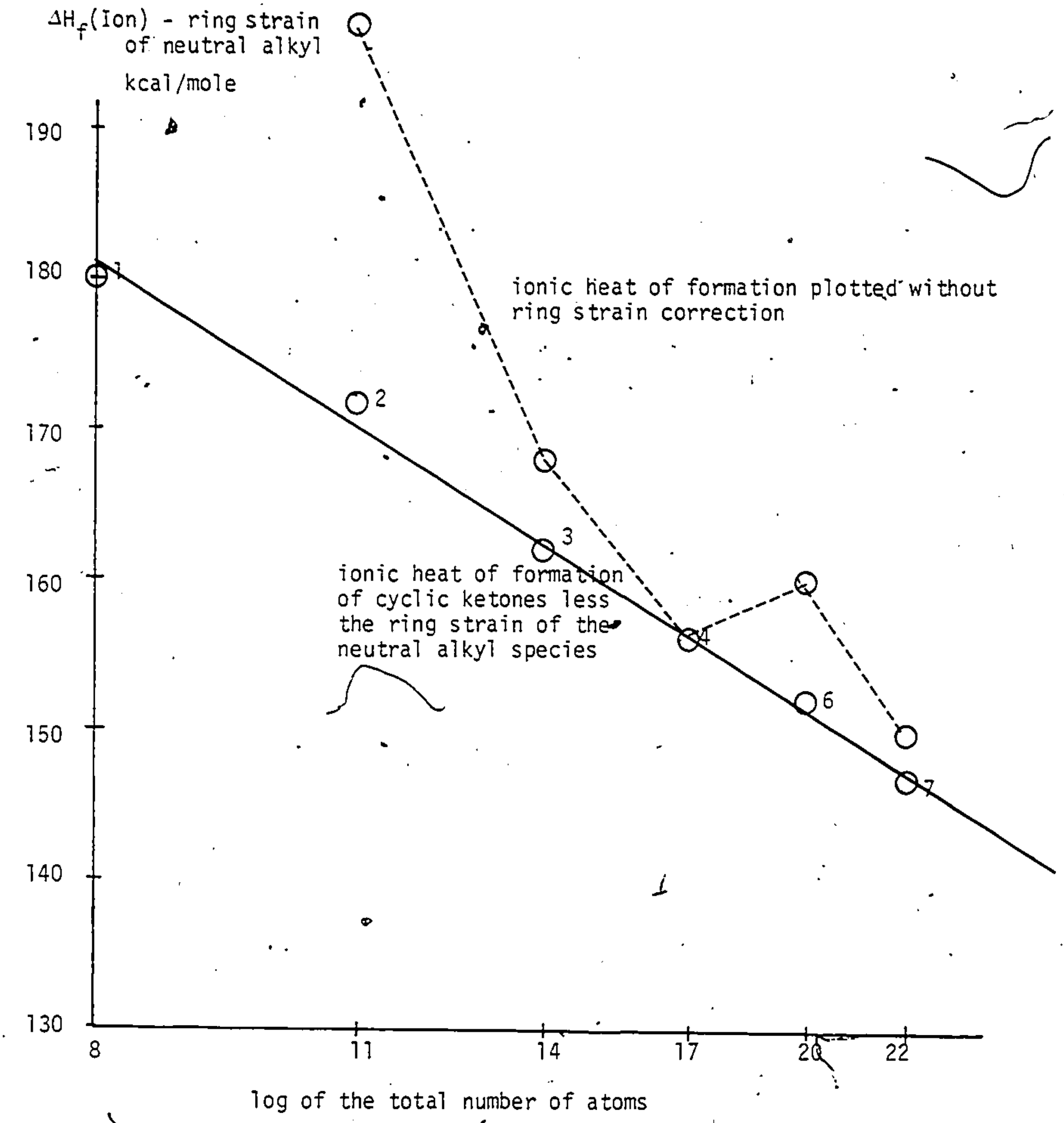
DATA NO.	FORMULA	PARENT MOLECULE NAME	PARENT STRUCTURE	ΔH_f (NEUTRAL) (kcal/mole)		IONIZATION ENERGY (eV)			ΔH_f (ION) (kcal/mole)	
					REF.		METHOD	REF.	EXP.	CALC.
1	C_3H_4O	Cyclopropanone		-13.9 (27.6)*	26 26	9.63v	PES	67	208	208
2	C_4H_6O	Cyclobutanone		-20.25 (26.2)	26 26	9.47	PES	68	198	197
3	C_5H_8O	Cyclopentanone		-46.03 (6.3)	27 26	9.26	PI PES	27 27	168	168
4	$C_6H_{10}O$	Cyclohexanone		-55.0 (0)	27 26	9.15	PI PES	27 27	156	156
5	$C_7H_{12}O$	Cycloheptanone		-54.1 (6.4)	26 26	9.49	PES	27	160	160
6						9.14v	PES	69		
7	$C_8H_{14}O$	Cyclooctanone		-61.1 (9.9)	26 26	9.00v	PES	69	147	148

* Values in brackets are the ring strains of the neutral alkyl rings

v refers to vertical ionization energies

METHODS:		
	PES	is photoelectron spectroscopy
	PI	is photoionization
	EM	is Electron Monochromator
	S	is Spectroscopy

Figure 29 Analysis of the Cyclic Ketones



CHAPTER 5

DISCUSSION

CHAPTER 5 DISCUSSION

The scheme for the correlation of the heats of formation has been applied to a large variety of homologous series. Table 21 is a summary of the regression formulae presented in this thesis. The correlation coefficients obtained in these regressions range from 0.910 to 0.999 and average 0.997. The predicted values in most cases are identical to that of the experimental values. In view of the wide applicability of the model and of the accuracy achieved, it is concluded that a model of the type; $\Delta H_f(\text{ION}) = A - Bn + C/n$ (15) (where n is the total number of atoms), is an appropriate model for the prediction of ionic heats of formation. The application of this model to the heats of formation of various homologous series has also shown that the following variations in molecule or ion structure can be corrected for by a constant factor from the formula (15) above:

1. substituent position,
2. branching,
3. cis-trans isomerism, and
4. ring strain.

The reciprocal formula, (15), has been demonstrated to function by merit of the fact that it is a combination of a linear term, (-Bn), corresponding to the heat of formation of the neutral and a reciprocal term, (+C/n), corresponding to the ionization energy of the molecule.

It has also been demonstrated that a simple plot of ionic heats of formation against the log of the total number of atoms provides reasonably accurate correlations up to about carbon number 8.

TABLE 21
SUMMARY OF REGRESSION FORMULAE

(all values in kcal/mole, n is the total number of atoms)

HOMOLOGOUS SERIES	FORMULA	CORRECTION FOR SUBSTITUENT POSITION	CORRECTION FOR BRANCHING	OTHER CORRECTIONS
Alkanes	219.5 -2.06n +324/n		any branch -3.2	
Alkenes	232.2 -1.64n +107/n	2-alkenes -14.5 3-alkenes -15.3 4-alkenes -16.2 5-alkenes -17.0	on double bond -11.9 elsewhere -2.4	cis +1.5 cis t-butyl +4.0 cis t-bu/t-bu +8.7
Alkynes	277.6 -1.57n +116/n	2-alkynes -18.0 3-alkynes -19.9 4-alkynes -21.1 5-alkynes -21.7	any branch -4.1	
Alkanols	176.3 -1.64n +214/n	2-alkanols -6.9 3-alkanols -8.7 4-alkanols -9.0	on hydroxyl -3.8 elsewhere -2.5	
Ethers	148.3 -1.18n +443/n	for each C atom out of symmetry +2.4	on oxygen-bearing -2.4	
Aldehydes	187.3 -1.63n +140/n		on carbonyl -5.0 elsewhere -3.0	
Ketones	165.9 -1.73n +238/n	for each C atom out of symmetry +1.5	on carbonyl -3.8 elsewhere -2.2	
Carboxylic Acids	124.4 -1.40n +237/n			
Chloroalkanes	238.8 -2.24n +52/n	2-chloro -4.0	on chlorine-bearing -6.1 elsewhere -3.4	
Bromoalkanes	220.5 -1.40n +102/n	2-bromo -5.4	on bromine-bearing -4.5 elsewhere -3.1	
Iodoalkanes	219.4 -1.66n +60/n	2-iodo -5.0	on iodine-bearing -5.3 elsewhere -2.6	
Primary Carbonium	202.6 -1.23n +175/n			
Secondary Carbonium	191.4 -1.34n +131/n			
Tertiary Carbonium	183.2 -1.66n +66/n		branching -2.3	
Alkylbenzenes	233.7 -1.73n +114/n		on benzene-bearing -1.1 elsewhere -1.9	
Cyclic Ketones	198.6 -2.47n +8/n			plus ring strain applicable to neutral alkyl compound

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This work would not have been possible without the patience of the author's wife, who for three years endured a solitary life while the work was in progress.

CLAIMS TO ORIGINAL RESEARCH

Predictive models for the ionic heats of formation for the following series have been derived:

1. Alkanes.
2. Alkenes
3. Alkynes
4. Alkanols
5. Ethers
6. Aldehydes
7. Ketones
8. Carboxylic Acids
9. Chloroalkanes
10. Bromoalkanes
11. Iodoalkanes
12. Primary Carbonium Ions
13. Secondary Carbonium Ions
14. Tertiary Carbonium Ions
15. Alkyl Benzenes
16. Cyclic Ketones

It has been shown that a relationship of type, $A - Bn + C/n$, can faithfully reproduce the heats of formations of homologous series of ions.

It has also been shown that a simple relationship of the type, $A - B \log n$, reproduces heats of formation of homologous series of ions up to about carbon number 8.

A predictive scheme for ionization energies, $IE = A + B/n$, has also been described.

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