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HOMOLYTIC AND HETEROLYTIC ENERGIES OF ALKYL-X BONDS AND IONIZATION

POTENTIALS OF ALKYL RADICALS, ALKANES AND HALOALKANES

by

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TO MY MOTHERLAND --- CHINA, MY WIFE AND PARENTS

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Preface

Professors of physical chemistry and physical organic chemistry are often asked: "How strong is this bond ?"

Three years ago, Drs. Griller, Kaminska and Maccoll stated: "No entirely satisfactory empirical or theoretical approach has yet emerged which successfully accounts for all of the existing data and has some predictive power." (D. Griller, J.M. Kanabus-Kaminska and A. Maccoll, J. Molecular Structure (Theochem), 1988, 163, 125.)

Recently a dependable approach for alkyl-X and alkylsilyl-X bonds, not requiring a computer, has come from this laboratory in Dalhousie University.

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ABSTRACT

New, simple and empirical methods have been proposed for estimating the homolytic and heterolytic dissociation energies of alkyl-X bonds, where X represents a halogen or hydrogen atom and CH_3, SiH_3, GeH_3, NH_2, PH_2, OH, SH, and C- or Si-centered groups. The uncertainties for most values estimated by these methods are within the accuracy of experimental determination ($\pm$ 1 kcal/mol). New and simple algorithms for estimating ionization potentials of alkyl radicals, hydrocarbons, and chloro-, bromo- and iodoalkanes have been established.

A new, step-by-step approach is used to attack these problems. In the first step, Pauling's semi-quantitative electronegativity (EN) scale has been replaced by the covalent potential, $V_X = n_X/r_X$, where n_X is the number of valence electrons in the bonding atom in X, and r_X is the covalent radius of the bonding atom. From this and the many accurate experimental results available in the literature, the rules for calculating homolytic and heterolytic dissociation energies can be devised.

The new procedure correlates quantitatively with the four factors which determine the dissociation energies of alkyl-X and alkylsilyl-X bonds and energetics of species. The four factors are: (1) the new scale of EN or the covalent potential of X, V_X; (2) the degree of methyl substitution on the alkyl radical center or the formal charge center, m; (3) the interactions between the radical center or formal charge center and the distant atoms, "the γ effect"; and (4) the steric compression relief due to bond cleavage. The "constancy" of the bond energies of Si-H, Si-C and Si-Si bonds is explained using these factors.

Abbreviations

ABWY: Anderson-Bayer-Watson-Yoneda

AP: Appearance Potential

BDE: Bond dissociation Energy (or Enthalpy)

C_p^o: Molar Heat Capacity

DFT: Density Functional Theory

$D^o(X-C)$: (Adiabatic) Cleavage Energy of an X-C Bond

DH^o: Bond Dissociation Energy (or Enthalpy)

$\overline{D}(X-C)$: Average Bond Energy of an X-C Bond

EA: Electron Affinity

ED: Electron Density

EN: Electronegativity

ESR: Electron Spin Resonance

E_f: Activation Energy of a Forward Reaction

E_b: Activation Energy of the Backward Reaction

E_{ox}: Oxidation Potential

E_{red}: Reduction Potential

$E_v(C)$: Valence State Energy of a Carbon Atom in a Given Valence State

$\overline{E}_v(C)$: $E_v(C)/4$

FSGO: Floating Spherical Gaussian Orbital

GA: Group Additivity

HA: Hydrogen Atom Affinity

HSAB: Hard and Soft Acids and Bases

IP: Ionization Potential

IR: Infrared

K_p: Equilibrium Constant in Pressure Units

k_f: Rate Constant of a Forward Reaction

k_b: Rate Constant of a Backward Reaction

LFEP: Linear Free Energy Principle

MO: Molecular Orbital

MP2: Second-Order Moller-Plesset Perturbation Theory

MS: Mass Spectrometry

NMR: Nuclear Magnetic Resonance

n_x: Number of Valence Electrons in the Bonding Atom in X

PA: Proton Affinity

pK_a: Acidity Constant

P_{X-C}: Propagator of the Inductive Effect for an X-C Bond

r_x: Covalent Radius of the Bonding Atom in X

SCF: Self-Consistent Field

SR: Stability Ratio

SPST: Single-Pulse Shock Tube

S^o: Entropy of Formation

VLPP: Very Low Pressure Pyrolysis

VLPR: Very Low Pressure Reactor

VLPΦ: Very Low Pressure Photolysis

V(R): Relaxation Energy of the Group R

V_{C-H}: Contribution to Relaxation Energy per C-H Bond

V_x: Covalent Potential, a New Scale of EN, $V_x = n_x/r_x$

X_P: Pauling's Scale of Electronegativity

X_M: Mulliken's Scale of Electronegativity

X_A: Allred and Rochow's Scale of Electronegativity

cal.: Calculated

eq. : Equation

eqs.: Equations

est.: Estimated

exp.: Experimental

obs.: Observed

recal.: Recalculated

ref. : Reference

refs.: References

rev. : Reviewed

theo.: Theoretical

ΔG: Gibbs Energy Change in a Given Reaction

ΔH: Enthalpy Change of a Chemical Reaction

ΔS: Entropy Change in a Chemical Reaction

$\Delta_{at}H^{o}$: Atomization Enthalpy

$\Delta_{f}H^{o}$: Heat of Formation at Standard Conditions

$\sigma(R)$: Taft's Constant for a Group R

Chapter I Fundamentals of Chemical Bond Dissociation Energies

1.1 Introduction

The bond dissociation energy or enthalpy (BDE) is fundamental to chemistry because most chemical reactions include the breaking and making of chemical bonds. There are two types of BDEs of chemical bonds in reaction processes -- homolytic cleavages and heterolytic ones. They are defined as the enthalpy changes in the homolytic fissions

$$X - R \rightleftharpoons X + R \qquad (1)$$

and heterolytic fissions,

$$X - R \rightleftharpoons X^- + R^+ \qquad (2)$$

respectively. In other words, the homolytic BDE is described as

$$DH^o(X-R) = \Delta_f H^o(X) + \Delta_f H^o(R) - \Delta_f H^o(RX) \qquad (3)$$

and the heterolytic BDE is given by

$$DH^o(X^--R^+) = \Delta_f H^o(X^-) + \Delta_f H^o(R^+) - \Delta_f H^o(RX) \qquad (4)$$

where $\Delta_f H^o$ represents the heat of formation of the respective species in the ideal gas state at standard pressure and a reference temperature of 25^oC. These notations emphasize that the BDE is the bond dissociation enthalpy, not the energy, DE. For ideal gases,

$$DH^o(X-R) = DE^o(X-R) + RT \qquad (5)$$

and

$$DH^o(X^--R^+) = DE^o(X^--R^+) + RT \qquad (6)$$

According to eqs. (3) and (4), the two types of BDEs and the heats of formation of radicals and cations and anions are complementary quantities because heats of formation of an extremely large number of organic and organometallic compounds have high precision.

Since mid-century, hundreds of groups have measured the two types of BDEs and heats of formation of radicals, cations and anions. Many values

1

will be discussed later. This wealth of experimental data lays a good foundation for our study. The author wishes to establish a generalized method for estimating the two types of BDEs and the heats of formation of free radicals, cations and anions. It is very difficult to achieve this objective. However there has been considerable progress for X-R bonds, where X = F, Cl, Br, I, H, CH_3, SiH_3, OH, SH, NH_2 and carbon- and silicon-centered groups, and R represents any alkyl group.

Before describing our study, the author wi'l first discuss the three main bases of our work: electronegativity theory, the group additivity rules and the concept of the inductive effect. In addition, we will look back at the contributions from many research groups to the two types of BDEs or heats of formation of free radicals, cations and anions.

1.2 Electronegativity of Atoms

We can make use of many good concepts for describing chemical structure and reactivity. It seems strange that these concepts are widely applied yet commonly debated. Electronegativity, chemical bonding, activation energy and transition states are all very typical examples. Here we will discuss the electronegativity of atoms.

The concept of electronegativity is almost as old as chemistry itself.[1] Elements were classified as electronegative or electropositive in Berzelius' age. In the early stage of our century, the founders of physical organic chemistry tried to find an approximate ordering of the electronegativities of various atoms and radicals.

Nobel laureate L. Pauling was the first person[2-4] to develop an electronegativity (EN) scale.[5] He defined EN as "the power of an atom in a molecule to attract electrons to itself"[6] and bond polarity as the difference in EN values between two bonded atoms. This intuitive concept

rapidly gained popularity among chemists and physicists. Pauling's scale is a semi-quantitative scale. There are some unexpected exceptions when correlating some physical and chemical properties. Since Pauling, many other scales have been proposed. Allen [7,9] reviewed a thousand-odd texts, review papers and journal articles which discussed or commented on EN over the years from 1932 to early 1989. An extensive search of the literature on EN has been submitted for publication in Chemical Reviews.[9] A useful summary of Pauling, Pauling-like, nonempirical as well as absolute EN can be found in a new special publication.[10]

Very recently, Luo and Benson have contributed a new EN scale for correlating heats of formation of alkyl and aklylsilane derivatives, ionization potentials of main-group atoms, group parameters, Lewis acid strengths, and homolytic dissociation energies of X-alkyl bonds, where X represents F, Cl, Br, I, H, CH_3, SiH_3, GeH_3, SnH_3, NH_2, PH_2, AsH_2, OH, SH, SeH and carbon-centered groups. In this thesis, the study of applications of the new EN scale will be extended to correlating the inductive effect of substituents, and homolytic and heterolytic bond dissociation energies. The new EN scale is one of the bases of this work. Below the author will discuss the scale, compare it with about 30 EN scales and explain why this new scale is the best for correlating molecular energies.

1.2.1 Pauling's and Pauling-like Scales of EN

According to modern opinion,[1,11,12] the various scales of EN are classified into two types. The first type is the empirical or semi-empirical methods of Pauling and Pauling-like EN for atoms and groups. The second type includes nonempirical and absolute scale. The former is based on some observable or empirical parameters of free atoms and molecules, such as, thermochemical data, ionization energies and electron affinities,

dipole moments, internuclear distances in crystals, atomic and molecular spectral data, dielectric properties, NMR spectra, IR spectra and other properties. The latter is based on nonempirical calculations such as the density functional theory of quantum mechanics, floating spherical Gaussian orbital (FSGO) calculations the electrostatic theory, the bond critical point model, ab initio MO calculation and others. The new scale of EN belongs to the empirical group. These scales of EN will be discussed in turn.

A landmark contribution was Pauling's early work.[2,3,13] In the early 1930's, he found that the actual bond energies of two unlike atoms would be larger than the arithmetic mean of the bond energies of two like atoms. The differences

$$\Delta = DH^o(A\text{-}B) - \frac{1}{2} \{DH^o(A\text{-}A) + DH^o(B\text{-}B)\} \qquad (7)$$

are expressed as a function of the differences in EN of the two elements. In order to formulate the scale of EN, Δ is expanded as a Taylor series in $(X_A - X_B)$ for the bond A-B. The linear term will be 0 and the first significant term will be

$$\Delta = 23.06 \ (X_A - X_B)^2 \qquad (8)$$

where X_A and X_B are the ENs of atoms A and B. It should be noted that EN differences are related to $\Delta^{1/2}$ (rather than Δ) and Δ's are not additive. Because of the availability of thermochemical data, Pauling was able to assign EN values to a large number of atoms. It was soon discovered that some Δ's, such as those for alkali metal hydrides, are not always positive.[15] For these values, the arithmetic mean in eq. (7) was substituted by the geometric mean as

$$\Delta' = DH^o(A\text{-}B) - \{DH^o(A\text{-}A) \ DH^o(B\text{-}B)\}^{1/2} \qquad (9)$$

In most cases, however, Δ and Δ' are similar and do not change most of the

EN values significantly. The geometric mean method has not been generally employed. Arbitrarily setting the value for H at 2.1 yields

$$X_A - X_B = 0.208 \, \Delta^{1/2} \tag{10}$$

Using this path , the EN values for 10 elements were assigned in 1933.[2] In 1939 the EN scale was extended to include 33 elements.[14] In 1960 approximate values for 50 more elements were added.[6]

Pauling's scale of EN has more specific values available than any other scale. Pauling's original work was extended using recent data.[16,17] However, the theoretical basis of Pauling's method of obtaining his scale is weak.[18] Because of the fact that one number is assigned to each atom, changes of hybridization and effects of atomic charges are neglected. In addition, Pauling's scale cannot accurately predict heats of formation of polyatomic or more complicated compounds as it is based on bond energies or heats of formation of diatomic or simple molecules.

An important contribution to EN theory was made by Mulliken [19] in the mid-1930's. He defined EN as the simple average of the first ionization potential, IP, and electron affinity, EA, of the given atoms, i. e.

$$X_M = (\, IP + EA \,) \, / \, 2 \tag{11}$$

Mulliken's scale has theoretical support.[11,18,19] Mulliken's method can calculate the EN of atoms in any state desired, such as the ground state, excited state, valence state and other states of atoms in the molecule. It can also be rendered charge-dependent simply by obtaining IP and EA values for the charged species. Recently, 50 elements have been considered by a revision and extension of Mulliken's EN scale.[20]

Following a suggestion of Pritchard and Skinner,[21] Hinze and coworkers [22,23] interpreted Mulliken's EN as an orbital property, asserting that "EN can only be defined for bonding orbitals". However, Ponce [24] and Reed [25]

have pointed out that differentiation of energies of nonequivalent orbitals is unavoidably arbitrary and ambiguous for atoms in molecules and have recommended the retention of the "global" atomic EN concept. The idea that EN is treated as a "global" atomic property is consistent with the EN as the chemical potential of density functional theory,[12,26] (See Section 1.2.4).

Although Mulliken's method has much greater theoretical support, Pauling's scale remains the most widely used one in references. This is primarily because there is insufficient data available to provide Mulliken EN values for many atoms.

Allred and Rochow's scale [27] is based on the simple assumption that the EN of an atom is given by the force of attraction between the screened nucleus and an electron at the covalent radius. It is described as

$$X_A = 0.36 \, Z_{eff} \, / \, r^2 + 0.74 \qquad (12)$$

where Z_{eff} is an effective nuclear charge obtained from Slater's rules, r is the covalent radius (Å) and the coefficients put the scale into Pauling units. It first introduced the idea of force into EN theory, and is easy to understand and modify. Eq. (12) is simple and both Z_{eff} and r are readily available quantities for many elements. Thus, this scale of EN is one of the most often used, aside from Pauling's one.

Soon, this scale was modified by Huheey.[28] He made two assumptions, that is, the radius is inversely proportional to the effective nuclear charge, Z_{eff}, and the latter varies linearly with partial atomic charge, q. The modified scale is given by

$$X_H = 0.36 \, (Z_{eff} - 3 \, q \,) \, / \, r^2 + 0.74 \qquad (13)$$

Huheey has pointed out that this leads to results which are similar to those obtained in some of the more rigorous methods described below although this method is simplistic.

The Allred-Rochow idea was extended by Mande et al.[29] They used an effective nuclear charge obtained from X-ray spectroscopic data. Since experimental data were used the values for effective nuclear charge were less arbitrary than Slater's ones, thus, the EN scale should be more reliable.

A recent effort by Zhang [30] has led to a modification of this method to account for the oxidation state of the atoms. The EN of an atom in a valence state is defined as the electrostatic f ·o exerted by the effective nuclear charge on the valence electrons. His scale is given by

$$X_Z = 0.241 \; \frac{n^*(I_z/R)^{1/2}}{r^2} + 0.775 \tag{14}$$

where n^* is the effective principal quantum number, I_z, the ultimate ionization potential for an outer electron, R, the Rydberg constant, and r, the covalent radius.

Gordy [31,32] has suggested the EN to be the electrostatic potential at the covalent radius caused by the screened nuclear charge. This is given by

$$X_G = 0.62 \; (Z'/r) + 0.50 \tag{15}$$

where Z' is a screened charge obtained using Gordy's method, i.e. all electrons in closed-shells below the valence shell exert a full screening effect, while the screening constant for one valence shell electron on another is 0.5. Thus, if the atom has n valence electrons Z' = n - 0.5 (n - 1) = 0.5 (n + 1). If we consider the charge on an atom, q in electron units, then eq. (15) reduces to

$$X_G = 0.31 \; (n + 1 \pm q) \; / \; r + 0.5 \tag{16}$$

where constant terms put this scale into Pauling units. Gordy's scale has been applied to a total of 52 elements. It is interesting to note that the correlation with Pauling's scale is not as good [21] if a more reasonable method, e.g. Slater's method, is used for Z' in eq. (15).

Gordy's scale is not used very often by chemists. However, it first introduced the idea of a potential into EN theory. Recent views of EN theory lean more toward the potential point of view.[33,34] This would tend to give Gordy's scale more theoretical support.

Sanderson's scale [35] is based on relative electron densities or the idea of a stability ratio (SR). The SR is the ratio of the average electron density (ED) of the atom to the electron density of an isoelectronic inert atom (ED^o). ED is given by

$$ED = 3 Z / 4\pi r^3 \qquad (17)$$

where Z is the number of electrons in the atom and r is the nonpolar covalent radius. In the case of the isoelectronic inert atoms, r is an interpolated value and, thus, is fictional. The stability ratio is a measure of the compactness of the atom, i.e. how tightly the electrons are held. Sanderson has suggested SR gives a measure of how well the atom is able to hold onto its own electrons.[36] The more compact, the greater the holding power.[37] He argues that if atom A holds its electrons tighter than atom B, then it will also do a better job of attracting bonding electrons in a molecule.

In 1951, Sanderson [38] proposed the concept of electronegativity equalization. When a bond forms between two atoms, he suggested that electrons would flow from the less electronegative to the more electronegative, until the two ENs become equalized. The EN of the compound is intermediate between those of the atoms. Sanderson has used his EN scale, the EN equalization concept and other assumptions to derive expressions for thermochemical quantities for inorganic and organic compounds.[36,39,40] The results obtained appear to correlate well with experimental data.

Sanderson's scale has not been extensively used by others. But his

concept of EN equalization has gained wide acceptance and has been supported by Parr's theory of absolute EN. According to Sanderson's concept, the previous idea of "fixed" EN should be abandoned. The values obtained from EN tables are regarded as characteristic quantities before a given bond is formed. Sanderson's principle could perhaps be a fundamental rule of chemistry.

St. John and Bloch's quantum-defect scale [41] is based on the Pauli force model.[42] They define an orbital EN, X_1, for valence orbitals as

$$X_1 = 1 / r_1 \tag{18}$$

where r_1 is the radius for the valence orbital with angular momentum quantum number, 1. The radius is obtained by fitting the Pauli model to experimental data. Atomic EN can be written as

$$X_{JB} = 0.43 \sum_{1=0}^{2} X_1 + 0.24 \tag{19}$$

where X_0, X_1 and X_2 represent s, p and d orbital ENs, respectively. The constants put this scale into Pauling units. The scale is related to the electrostatic potential idea and introduces the idea of hybridization in an explicit manner. The scale has been improved a bit.[314]

In the early 1960's, Iczkowski and Margrave [43] first noted that the energy, E_A, of an atom A can be expressed as a function of the charge, q, on the atom. They suggested that the EN of atom A should be given by

$$X_{IM} = - (dE_A/dq)_{q=0} \tag{20}$$

In order to reduce exactly to Mulliken's EN definition, EN becomes

$$X_{IM} = a + 2bq \tag{21}$$

where a and b may be termed the "inherent EN" and the charge coefficient, respectively. Both are functions of hybridization and charge. A suitable definition of the EN of the neutral atom is

$$X_{IM}(q=0) = a = (IP + EA)/2 \tag{22a}$$

and

$$b = (IP - EA)/2 \qquad (22b)$$

which is precisely the definition suggested by Mulliken [19] and employed by Hinze and Jaffe. [22,23] Using Sanderson's EN equalization, the partial charge in an AB molecule can be determined

$$X_{A,eq} = a_A + 2b_A q_A = X_{B,eq} = a_B - 2b_B q_B \qquad (23)$$

where X_{eq} is the equalized EN after the given A-B bond is formed and

$$q_A = \frac{a_B - a_A}{b_A + b_B} \qquad (24)$$

Eqs. (20) and (21) represent the current thinking in EN theory. They do not provide a new formula for calculating specific values, but provide a new approach to understanding EN.

Very recently, Allen [8] has proposed a redefinition of EN, which he called valence-shell energy. His scale is termed "spectroscopic electronegativity". It is the average one-electron energy of valence shell electrons in ground-state free atoms and is given by

$$X_A = \frac{mE_p + nE_s}{m + n} \qquad (25)$$

where m and n are the number of p and s electrons in the valence shell of atoms, respectively. The corresponding one-electron energies, E_p and E_s, are the multiplet-averaged total energy differences between a ground-state neutral and a singly ionized atom. The values for this scale are obtained to high accuracy from NBS high-resolution atomic spectroscopy tables. The new scale closely matches Pauling's and Allred and Rochow's scales and seems to be an average between them. Allen argued that valence-shell energies form the third (vertical) or energy dimension of the periodic table. The three-dimensional periodic table is fresh and provocative.

There are other scales [9,10,18,21,44,45,46] which have not been widely accepted by chemists. Yes, EN is concerned with atoms in molecules rather than with atoms in isolation. Thus, EN cannot be measured, unlike the electron affinity and ionization potential of a free atom, which are capable both of precise definition and of precise measurement. A lot of lively debates are expected. The scales have different units or dimensions. The units can be summarized as follows:

Pauling	$(Energy)^{1/2}$
Mulliken	Energy/charge
Allred-Rochow	Force
Gordy	Energy/charge
Allen	Energy/charge
Sanderson	Dimensionless

However, all new scales of EN or new methods of calculating values of EN are tested by seeing if they agree with the original Pauling scale and the new scales are put into Pauling units. The reason appears to be two-fold: Pauling's scale was published first and for nearly 60 years it had more specific values available than any other scale. But, Pauling's scale is considered one of several available useful empirical correlations rather than as a preferred means of understanding the fundamental concept.[11]

1.2.2 Group Electronegativity

The concept of EN originally arose out of an attempt to understand the mechanism of a number of simple reactions in organic chemistry. Since the establishment of an EN scale for atoms, many efforts have been made to extend from atomic EN to group EN. Here polyatomic groups are regarded as pseudo-atoms. The intrinsic problem associated with non-observability of atomic EN carries over into group EN. Nevertheless, a concept of group EN

is highly desirable in understanding the effects of substituents on the reactivity and physical properties of organic molecules.

The estimation of group EN has been approached in a variety of ways [47-54] and provides further difficulties. Organic chemists have developed sets of substituent constants from kinetic data, as discussed later in Section 1.5. Other values have been obtained from physical measurements and direct calculations based on atomic EN. Now let us discuss them.

Data on IR bond stretching frequencies, NMR chemical shifts and proton-proton coupling constants have been used to estimate group EN.[43,55-9] For example, a simple expression has been suggested by Wilmshurst [56] involving the stretching frequencies, ν_{HX}, of hydrides which depend in turn on the force constants, k_{HX}. It is given by

$$X_X = 1.1\ 10^{-4}\ (1 + M_H/M_X)^{-1/2} \nu_{HX} - 0.24 \tag{26}$$

where M is the reduced mass. Ionization potentials and electron affinities,[23] solubility products of predominantly covalent compounds,[60] basicities and oxidative coupling potentials [61,62] have been correlated with group EN by means of Pauling, Mulliken, and Gordy's methods. These methods and others have been reviewed by Wells.[47] The values of group EN from spectroscopic and thermochemical data and other experimental quantities are termed "empirical values" or "experimental values". The empirical values of group EN are regarded as reference values in comparing with the values estimated by various authors. The empirical EN values, in fact, are discordant and may be unreliable.

In the mid-1960's, Huheey [63,64] presented a much simpler procedure for estimating group EN. He took eq. (21) as his starting point. But his EN refers to an atomic orbital. He assumed complete equalization of the EN of

all of the atoms to one average value. Huheey calculated the EN values for 99 different groups using his scheme. He showed these values to be reasonably consistent with experimental values. His procedure has been extended to groups with multiple bonds.[64]

The method developed by Huheey appears to have two drawbacks: (1) it is not able to account for differences in isomers and (2) it apparently overestimates the effect of the atoms or groups attached to the bonding atom.

A very simple scheme has been presented to account for the isomer problem.[66] It is based on the assumption that inductive effects are not operative when there are three or more bonds separating atoms and that the propagator of the inductive effect is one third for the first two bonds. In addition, it assumes that the parameter value, b, for the group is the same for all isomers. The authors have correlated their EN with regiochemistry in asymmetric sulfide chlorinations for fifty known instances.

Recently, a further simplification of Huheey's method has been presented.[66,67] The following simple relations for group or molecule EN are derived

$$X_{eq} = (N_G + q_G) / \Sigma(\nu/X_A) \qquad (27)$$

$$q_G = N_G(X_{eq}/X_G - 1) \qquad (28)$$

$$q_A = X_{eq}/ X_A - 1 \qquad (29)$$

where X_{eq} is the equalized EN for the group or molecule, X_A is the initial, pre-bonded EN of a particular atom A; ν is the number of A atoms in the species, $N_G(= \Sigma(\nu))$ is the total number of atoms in the species. q_G is the net charge on the group, q_A is the partial charge on any particular atom A. For the neutral group, $q_G = 0$, then

$$X_G = N_G / \Sigma(\nu/X_A) \qquad (30)$$

The method represents an advance over previous methods by the basic criterion of simplicity.

According to Sanderson,[36,40] there are two methods for estimating group EN. The first is to use the geometric mean of all of the atomic EN values in the group as the final value. The second is derived from the first via the following conversion to Pauling units

$$X_P = (0.33 \ X_S + 0.66)^2 \tag{30}$$

where X_S and X_P are Sanderson's and Pauling's scale of EN, respectively.

Mullay[68-70] has provided a simplified calculational procedure both for atomic or orbital EN and also for group EN based on a theoretical analysis by Klopman.[71] The following relation for estimating the EN of atom A has been obtained

$$X_{Mu} = (1.67 \ G_i Z_{eff}^2 \ /n_e^2 + 0.41) \tag{32}$$

where G_i is a linear function of % p hybridization in the orbital i (i.e., $G_i = 1 - kp_i$ where k is a constant), n_e and Z_{eff} are Slater's effective principal quantum number and modified screened nuclear charge, respectively. The constants put the scale into Pauling units. The group EN is modified to account for its cnarge. It is given by

$$X_G = (\ M + 1.5 \ q_G)/ \sum_{i=1}^{M} (1/ \ X_{Mu}) \tag{33}$$

where q_G is the charge on the group, and M is the total number of atoms.

Inamoto and his co-workers[72-74] have proposed a different method to obtain Z' in Gordy's EN, i.e. eq. (15). Their scale is defined as

$$X_I = (Z_{eff} + 1)/ \ n_{eff} \tag{34}$$

where Z_{eff} and n_{eff} are the effective nuclear charge in the valence shell and the effective principal quantum number, respectively. For the second period group substituents, the Z_{eff} values are calculated using the charge obtained from the bond dipole moment. There are good linear relations

between X_I and Gordy's scale. The values from this scheme have been compared extensively to NMR data. Results indicate the method to be quite useful in correlating data.

The fractional difference in the bonded atom EN per bond length is used to calculate the group EN.[75] It is described as

$$X_{JD} = \Sigma \left(\frac{X_A - X_B}{X_A + X_B} \right)_i P / r_{iAB} \qquad (35)$$

where X_A and X_B are atomic ENs of bonded atoms A and B, respectively, r is the bond length of the A-B bond, P is the propagator of the inductive effect which is assigned to be a constant, that is 1/2.7 (0.37).

An important difference [20] between atoms and groups is the ability of the latter to dissipate charge over several atoms, increasingly so with increase in the number of atoms in the group formula. Polyatomic groups may be viewed as reservoirs of enhanced charge capacity, potentially able to donate or withdraw considerable amounts of charge with only small variations in EN. Therefore, a group cannot really be treated as a "pseudo-atom" in EN discussions, and it follows that some of the "experimental" or empirical methods of determination of group EN mentioned above may be unreliable.

1.2.3 Nonempirical Electronegativity

The first nonempirical EN scale was from ab initio calculations using the floating spherical Gaussian orbital (FSGO) wavefunctions.[76] The simplest definition of the EN difference between atoms A and B is a direct proportionality:

$$X_B - X_A = K (f_{AB} - 0.5) \qquad (36)$$

where f_{AB}, the orbital multiplier from the ab initio calculations, is equal to $R_A/(R_A + R_B)$ in which R_A and R_B are the distances from the atoms to the

floating orbital center. K is the ratio constant. Li and F (in LiH and HF)
were assigned the EN values 1.00 and 4.00, respectively, the EN values of
other atoms can be obtained from their molecular hydrides.

Recently Boyd and Markus [77] have performed nonempirical calculations
using the concept of the electrostatic force between the effective nuclear
charge and an electron at a distance equal to the relative radius of the
atom. Their EN is expressed as

$$X_{BM} = \frac{kZ_A}{r^2} \left[1 - \int_0^{r_A} D(r)dr \right] \tag{37}$$

where Z_a and r_A are the atomic number and relative radius of a and $D(r)$ is
the radial density function. Setting $X_F = 4$ gives $k = 69.4793$. r_A was
chosen in terms of the electron density contour corresponding to 10^{-4}
atomic units for each atom. The authors obtained good correlation with
other classical scales for the first 54 elements using Hartree-Fock (free
atom) wavefunctions. The proposed model is also consistent with the major
conclusion of the theory of absolute EN of Parr and his co-workers.

Boyd and Edgecombe have a second method to evaluate atomic and group
EN.[78] Using the topological properties of the electron density
distributions of molecules, the EN of an atom relative to hydrogen was
calculated from properties associated with the bond critical point of the
corresponding diatomic hydride. The EN values for 21 main-group elements
from Li to Br have been calculated from the bond critical point model. A
straightforward extension of the method is used to obtain the ENs of 30
groups from the electron density distributions of polyatomic molecules. The
EN from the bond critical point method correlates well with a variety of
methods, the exceptions being ones based on Sanderson's EN equalization.

Taft and his co-workers [79,80] reported a scale of atomic and group EN
values from ab initio molecular orbital (MO) calculations on molecules HX

at the 6-31G* basis level with geometry optimization on molecules HX. The atomic electron densities (or fractional ionic charge) on the hydrogen atom in compounds HX were regarded as the scale of EN parameters. They compared the scale with various scales and with NMR coupling constants.

1.2.4 Absolute Electronegativity

A new landmark contribution was made by Parr, Pearson and their co-workers.[81,82,330,399] They have attempted to raise the concept to a rigorous, quantum mechanical level with a sophisticated mathematical treatment called density functional theory (DFT). The theory is a branch of quantum mechanics which focuses on the one-electron density function of a molecule, rather than its wave function.[395,408]

Parr and co-workers showed that any chemical system, such as an atom, radical, ion, or molecule, is characterized by a quantity, μ, called the electronic chemical potential. In the density functional theory of Hohenberg and Kohn,[10,12,83,84] the electronic chemical potential is introduced as the Lagrange multiplier which insures that the number of particles will be conserved in the minimization of the energy. It is equal to the functional derivative with respect to the density of the energy. That is[12,85,86]

$$\mu = \left(\frac{\delta E(Z,N)}{\delta N}\right)_Z \tag{38}$$

where $E(Z,N)$ is the total energy of the chemical system, Z is the number of the nuclear charge, which is held constant, and N is the number of electrons in this system. The electronic chemical potential is a global property of a ground state, constant from point to point in the atom, ion, radical or molecule. The EN of the chemical system is redefined as the negative of the electronic chemical potential, i.e.

$$X_{ab} = -\mu \qquad (39)$$

Using the three-point finite-difference approximation, the slope of $E(Z, N)$ vs. N is $-(IP + EA)/2$. Therefore we have

$$X_{ab} = -\mu \approx (IP + EA)/2 = X_M \qquad (40)$$

Where IP and EA are now the ground state values. Because of the close analogy to the Mulliken EN, X_M, it was proposed that $(IP + EA)/2$ be called the absolute EN. The adjective "absolute" was selected because of the near equality to the fundamental property, $-\mu$. The EN and the electronic chemical potential are the same concept in Parr's theory.

But μ has just this property. If two systems, C and D, are brought into a state of interaction, the electron density will flow from one system into the other until a single value, μ_{CD}, exists. The chemical potential or the EN is now constant everywhere in the combined system and measures the escaping tendency of the electrons in the combined system. In general, it will be different from the original values, μ_C and μ_D. Hence ENs are equalized in the combining of two different systems. That means that Sanderson's principle of the EN equalization has been proven by Parr's theory.[12,87] This is a second reason to identify the electronic chemical potential with EN. The behavior of the electronic chemical potential parallels that of chemical potential in classical macroscopic thermodynamics.

Recently the absolute hardness, a new chemical concept, has been derived from density functional theory.[1,12,88-90] The exact and approximate definition of the absolute hardness are

$$\eta = -\frac{1}{2}\left(\frac{\delta X_{ab}}{\delta N}\right)_Z \qquad (41)$$

and

$$\eta \approx (IP - EA)/2 \qquad (42)$$

In a number of cases, the value of η is greater than that of X_{ab}. The absolute hardness, η is also a global or average value. The absolute softness, S, is simply the reciprocal of η, that is

$$S = \frac{1}{2\eta} \left(\frac{\delta N}{\delta \mu} \right)_Z \qquad (43)$$

If two chemical systems, C and D, are brought into contact, electrons will flow from the one of lower X_{ab} to that of higher X_{ab} until the ENs become equalized. An approximate value for ΔN, the number of electrons transferred, is given by

$$\Delta N = \frac{(X_C - X_D)}{2(\eta_C + \eta_D)} \qquad (44)$$

A large value of ΔN gives rise to strong bonds. Thus, bond energies will be dependent on the absolute hardness and EN. Pearson has integrated Parr's theory into his well-known theory of hard and soft acids and bases (HSAB).[1]

The absolute EN theory gives the direction of electron flow and an estimate of the initial amount of electron density transferred. This, in turn, is related to energy barriers for reaction and, in some cases, to the strength of the coordinate bond formed. In other words, the absolute EN applies to molecules, ions, and radicals, as well as to atoms. It is a measure of the chemical reactivity of an atom, radical, ion, or molecule. But, like the Pauling and Pauling-like scales, it is not a reliable measure of final bond polarity.

The extension of the concept of EN to molecules seems to be a natural and useful step. Donor-acceptor interactions are at the very heart of chemical bonding. The absolute EN is a measure of the intrinsic donor-acceptor character of a species.

There is no inconsistency in the EN of a free atom being different from that of an atom in a valence state. Both the absolute EN scale and

Pauling-like scales can be commensurable.[1] Each scale is correct in its own area of use. It is not a meaningful question to ask which scale is more correct since the applications are so different.

EN theory is stil. making progress although it is nearly 60 years old.[1,3,4,9,11,21,44-47] Why has it had such a long existence? Mullay offered a good answer.[11] The idea of EN is a direct consequence of fundamental concepts of modern chemistry, specifically the following three:

(1) molecules are made up of atoms held together by chemical bonds.

(2) chemical bonds involve a sharing of electrons between the atoms.

(3) the electrons are not always shared equally.

The atomic and group EN is regarded as the cause of this unequal electron sharing. Pauling's original definition of EN, "The power of an atom in a molecule to attract electrons to itself"[6,14], needs to be revised to accommodate our modern views of the EN concept. A new scale-independent definition of atomic or group EN has been addressed:[20]

"Electronegativity = the ability of an atom or group to attract or

hold electrons to itself when combining with other atoms or groups"

Note the word combining (which is not synonymous with combined) is a dynamic term, and is compatible with Sanderson's EN equalization principle.

The author wished to establish a new theory or method for estimating bond dissociation energies. Thus the author needed to use the idea of EN and had to find, evaluate, compare and choose the most satisfactory EN scale for this topic from many EN scales. A more satisfactory scale for the correlation of heats of formation and bond dissociation energies of organic and organo-metallic compounds was selected three years ago. It will be addressed below.

1.2.5 A New Scale of Electronegativity, V_x

In the mid-1960's, a simple scale of atomic EN was proposed by Yuan.[93] The atomic scale is defined as

$$X_Y = n_x / r_x \tag{45}$$

where n_x is the number of valence electrons in atom X, and r_x is its covalent radius. Yuan's equation for calculating the group EN [94] is more complicated. The group EN is the ratio of the number of effective valence electrons, n_x^*, on the central atom X in the group to the effective radius, r_x^*, of this atom X. His r_x^* was determined by Sanderson's method,[95] and n_x^* is given by

$$n_x^* = n_x + 2 \Sigma m \frac{X_A}{X_A + X_B} + P \Sigma \alpha \frac{X_B - X_A}{X_A + X_B} \tag{46}$$

where r_x is the number of valence electrons on the free atom X minus the number of electrons taking part in the bonding to B, X_A and X_B are the EN of the atoms A and B respectively, m and α represent the number of bonded electrons and unbonded electrons of atom B, respectively, and P is the propagator of the inductive effect along the chemical bond and is to be assigned $P = 1/2.7$ (0.37). Yuan's scale has never been employed, even by Yuan himself.

Three years ago, the author made an effort to correlate the heats of formation by means of atomic and group EN. None of the widely used scales, such as Pauling's, Mulliken's and Allred-Rochow's, provided satisfactory correlations. The scales which have been less widely used, such as Gordy's, Sanderson's and Well's, were also not better. The nonempirical and absolute scales, such as FSGO, Boyd's and Taft's, also led to difficulties (See Section 1.3). Pauling's scale was initially developed from excellent experimental data on heats of formation or bond energies of diatomic and simple molecules. Why does it not work well for correlating heats of

formation of polyatomic molecules ? The theoretical scales although very sophisticated do not help to correlate molecular energetics quntitatively.

An unexpected and interesting event happened. The author modified Yuan's scale, as will be shown later. The modified or new scale gave the least scatter and the highest correlation coefficient.[96] And of all scales, the modified Yuan's scale was also the simplest, just the ratio of n_x to r_x. It has only two parameters that every introductory student knows.

The new scale of EN was defined by Luo and Benson [97]

$$V_x = n_x / r_x \tag{47}$$

where n_x can be regarded as the number of valence electrons in the bonding atom in X, where X represents atoms or groups. In this way, our definition of EN is strongly different from Yuan's original idea, although r_x is the same as that in Yuan's scale. Note that the concept of group EN becomes unnecessary for our topic. This is strongly different from Yuan's idea and the traditional ones. We do not say the EN of a carbon atom. We should say the EN of a carbon atom with an sp^3, sp^2 or sp hybridized valence state. The EN value of a carbon atom with sp^3 hybridized valence state is equal to 4e /0.771. Here 4 represents four valence electrons of the carbon atom. The 0.771 (Å) is the covalent radius of the carbon atom with an sp^3 valence state. In the author's opinion, the ratio 4e/0.771 represents the EN value of the bonded carbon atom with an sp^3 hybridization in all carbon-centered or alkyl groups, such as t-butyl, CH_2COCH_3, CH_2CCH, CH_2CHCH_2, cyclo-C_6H_{11} and $CH_2C_6H_5$. The dimension of V_x is charge divided by distance, equivalent to electronic potential. If we multiply V_x by charge the units of this product become energy. For simplicity we omit the charge in eq. (47), which then gives it the dimension of inverse length, or $Å^{-1}$. By the same reasoning, we may say that an oxygen atom in OH, OCH_3 and other alkoxy groups have the same value of EN, which is 6/0.74.

The differences between methyl, ethyl and other alkyl groups in energy and reactivity will be attributed to electronic and steric effects. The electronic effects and charge capacity effects of the groups, in fact, have the same connotation. The concept of a group, or pseudo-atom, EN will be abandoned. It will be shown that the method of atomic EN plus the electronic and steric effects are sufficient for our topic. In this way, the concept of the fixed group EN or substituent constant, which is very widely used, will not again be employed in this thesis. The dynamic, not static, electronic and steric effects will be very significant.

In the idea modified by the author, the EN values which are determined from eq. (45) seem to be "fixed". But this is the initial or pre-bonded EN, like the absolute EN. If the initial EN values between two pre-bonded atoms are not equal to each other, the e^- ,ctrons flow when both combine. This pattern is similar to that of the electronic effects in the classical theory which are transferred within polyatomic groups, ions and molecules. "Transfer" is a dynamic expression. This implies that classical and intuitive language may express approximately that of the absolute EN theory and Sanderson's EN equalization. The modified concept contains some new ideas. Thus the author called this concept a new scale of EN although the equation for calculating EN values is same as eq. (45).

There could be two challenges to this new concept.

First, what is the source of data for the covalent radii? Have these data been pieced together? Have most chemists accepted these data? In order to check the data the author selected from references, as in Table 1.

TABLE 1: The Values of the Covalent Radii and V_x for Some Atoms

X	r_x/ Å					$V_x{}^a$
	LB[a]	Huhey[b]	Gordy[c]	OB[d]	Sanderson[e]	
F	0.706	0.71	0.72	0.70	0 681	9.915
O(OH)	0.74	0.73	0.74	0.74	0.702	8.11
Cl	0.994	0.99	0.99	0.99	0.994	7.04
N(NH$_2$)	0.75	0.75	0.74	0.75	0.734	6.67
Br	1.141	1.14	1.14	1.14	1.142	6.13
S(SH)	1.04	1.02	1.04	1.03	1.049	5.77
I	1.333	1.33	1.33	1.33	1.333	5.25
C(CH$_3$)	0.771	0.77	0.772	0.77	0.772	5.19
Si(SiH$_3$)	1.173	1.18	1.17	1.17	1.169	3.41
H	0.3707	0.37	0.32	0.37	0.32	2.70

[a] From ref. 97. [b] Ref. 44. [c] Ref. 32. [d] Ref. 388. [e] Ref. 98.

The covalent radii in the second column in Table 1 were taken from the bond lengths measured from homonuclear diatomic molecular spectra[99] for the monovalent elements of groups I and VII. The other values are from Pauling's paper[100] and a common handbook.[101] For halogen and hydrogen atoms, the values selected are very dependable. The values for O, N, S, Si and C are also dependable. The values selected are in agreement with a typical and popular textbook by Huhey[44] and many publications, such as those by Gordy and Cook,[32] and by Brese and O'Keeffe.[388] These chemists also developed scales of EN. Our values for F, O and H are different from Sanderson's ones. For F, O and H, Sanderson chose to use different values, that were not derived from the diatomic molecules.

A second possible challenge to our new concept would be to question the relevance of absolute EN theory, when present values of absolute EN do not correlate well with thermochemical data. The author believes the concept, method and results of the absolute EN theory are correct and exact. As with most quantum chemical calculations, the absolute EN theory cannot offer satisfactory calculated values within experimental uncertainty or chemical accuracy ($\pm$ 1 kcal/mol) at the present. The new idea and new scale of EN are still within the classical framework although most of calculations based on it are within chemical accuracy and are useful for thermochemistry and kinetics of free radicals, ions and molecules in the gas phase.

Equation (45) is also good for different valence states, charges and ligand numbers on the central atom. For example, Pd-containing compounds have two kinds of ligand numbers: Pd(IV) and Pd(II). Their values of EN are 4/1.278 (or 3.13) and 2/1.278 (or 1.57), respectively.

The new scale of EN may be related to Pauling's scale, X_P, by a linear equation for main group atoms omitting H.[96] The relationship is illustrated in Fig. 1.

$$X_P = 0.343 \ V_x + 0.674 \qquad\qquad (48)$$

Luo and Benson[96] compared the values of V_x, X_P and a revised scale derived directly from V_x using eq. (48). The three items have been listed in Table 2. The revised values are in the parentheses. The average difference between Pauling's values and the revised ones is only 0.08 Pauling units.
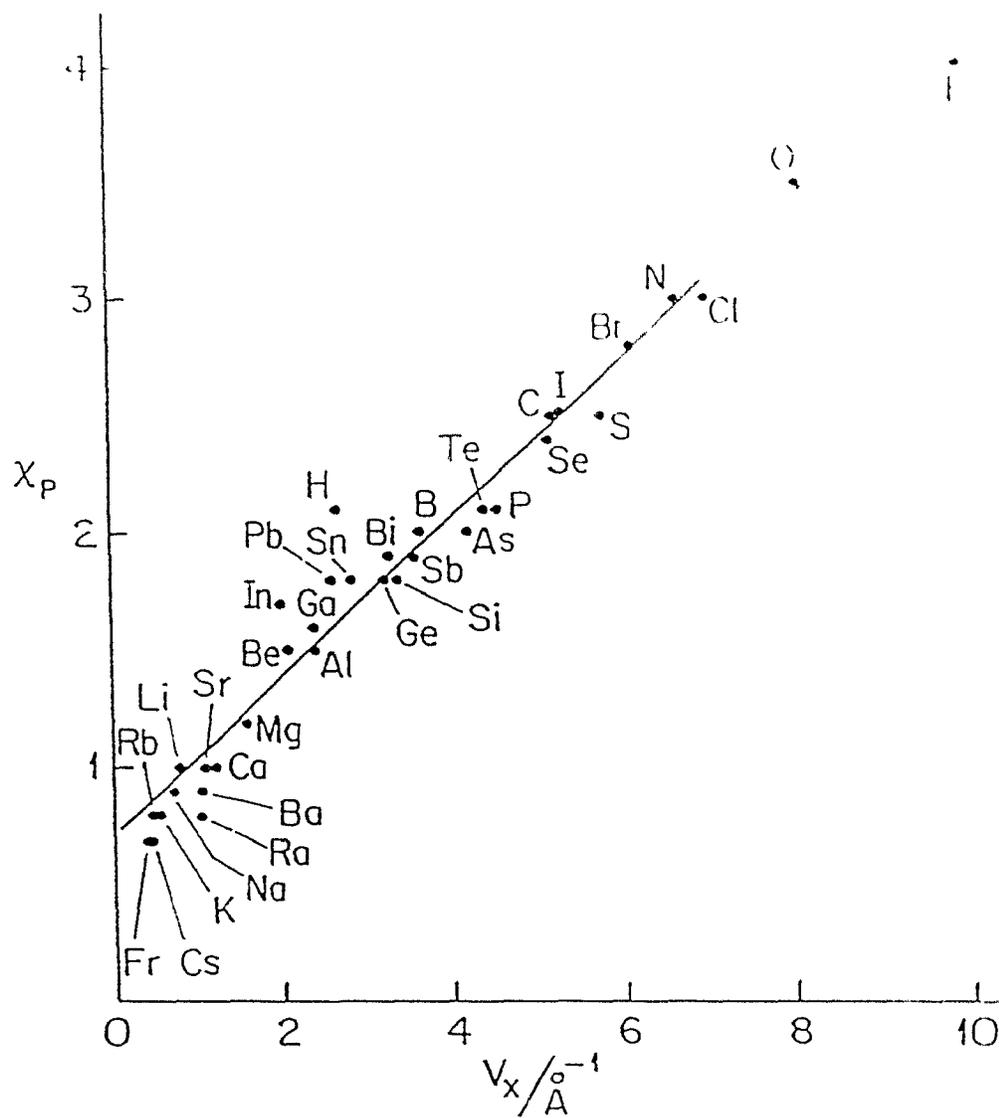
Fig. 1:
Relation between the Covalent Potentials and Pauling's Scale

TABLE 2: Pauling's Scale and V_x of Main Group Elements

	H						
X_P	2.1						
	(1.60)						
V_x	2.70						

	Li	Be	B	C	N	O	F
X_P	1.0	1.5	2.0	2.5	3.0	3.5	4.0
	(0.93)	(1.39)	(1.93)	(2.45)	(2.96)	(3.45)	(4.07)
V_x	0.75	2.08	3.66	5.19	6.67	8.11	9.915

	Na	Mg	Al	Si	P	S	Cl
X_P	0.9	1.2	1.5	1.8	2.1	2.5	3.0
	(0.90)	(1.20)	(1.50)	(1.84)	(2.23)	(2.65)	(3.09)
V_x	0.65	1.54	2.40	3.41	4.55	5.77	7.04

	K	Ca	Ga	Ge	As	Se	Br
X_P	0.8	1.0	1.6	1.8	2.0	2.4	2.8
	(0.85)	(1.07)	(1.49)	(1.79)	(2.11)	(2.43)	(2.77)
V_x	0.51	1.15	2.38	3.27	4.20	5.13	6.13

	Rb	Sr	In	Sn	Sb	Te	I
X_P	0.8	1.0	1.7	1.8	1.9	2.1	2.5
	(0.84)	(1.03)	(1.36)	(1.64)	(1.91)	(2.17)	(2.47)
V_x	0.48	1.05	2.00	2.83	3.62	4.38	5.25

	Cs	Ba	Tl	Pb	Bi	Po	At
X_P	0.7	0.9	1.8	1.8	1.9	2.0	2.4
	(0.82)	(1.02)		(1.56)	(1.80)	(2.05)	(2.27)
V_x	0.43	1.01		2.60	3.29	4.03	4.67

	Fr	Ra
X_P	0.7	0.8
	(0.82)	(1.02)
V_x	0.42	1.00

As shown in Table 2, the largest deviation between the revised and original values occurs for H. This may be termed as the hydrogen anomaly. The reason for the anomaly has to do with the EN assigned to H in the various scales. In our V_x scale, we have used as the covalent radius for the H atom the value obtained from the bond length in H_2, namely 0.7414 Å. This is consistent with the values for the other univalent and polyvalent elements.

The new scale, V_x, was called "the unshielded core potential of X at

the covalent radius of X".[96] In our later work, it has been be termed the "covalent potential" for short. The covalent potential is proportional to the "real" core potential of X at the covalent radius of X. The proportionality factor varies systematically with the group in the periodic table so that V_X is a measure of the strength of the covalent bond in both diatomic and polyatomic molecules. This is only a guess. Is it reasonable? This question will be discussed in Chapter II.

1.3 Heats of Formation of Organic and Organometallic Compounds

1.3.1 Data on Heats of Formation and Units

It is difficult to find another reference source for the thermochemical data of physical chemistry that has achieved the level of success of three books, the JANAF Thermochemical Table,[106] Thermochemical Data of Organic Compounds,[102] and Thermodynamic Properties of Individual Substances.[316] The reasons for the long-standing popularity of the books are apparent: the important topic affects many scientific and engineering areas; a highly professional and critical approach is used for the selection of the data; and the format is concise, and easy-to-use. The first book contains about 1800 substances; the second, approximately 3000 organic compounds of the elements C, H, O, N, S, and the halogens. The third, nearly 1600 inorganic and organic compounds at temperatures from 100K to over 6000K. In addition, data on the thermochemistry of silicon and organometallic compounds have recently been provided by Walsh,[103] Pilcher and Skinner, and Varonkov et al.[107-8,296-8,392-4]. These books and Walsh's paper are sufficient for our work.

Ref. 102 is the main source of thermochemical data we use. There most of the experimental measurements are of standard enthalpies of combustion by static and rotating bombs and by flame calorimetry. Approximately 1000

enthalpies of reactions other than combustion are also included. Ref. 102 also contains a few data derived from second and third law analyses of chemical equilibria. The uncertainties of most of the required experimental heats of formation are within chemical accuracy ($\pm$ 1 kcal/mol).

The energy unit currently recommended internationally is the Joule. However, the great majority of the original experimental data in thermochemistry are given in calories (1 cal = 4.1840 J). Therefore, heats of formation, enthalpies of reaction and bond dissociation energies in our work are given in kcal/mol. Ionization potentials and electron affinities of species are usually reported in ev (1 ev = 23.06036 kcal/mol = 96.4845 kJ/mol). Furthermore, because of the duplication in units, the data can always be displayed as they appeared in the original paper, a practice which helps in elimination of transcription errors.

All the thermochemical data given in our work refer to 298.15 K and a standard-state pressure of 100000 Pa (1 bar). The change of the pressure from 1 atm (101325 Pa) to 1 bar results in small alterations in standard values of some thermodynamic quantities for all substances. For condensed phases the magnitude of these alterations is almost always negligible in comparison with the uncertainty of the data. For gaseous species, it is well below 0.1 kcal/mol for $\Delta_f H^o$ and 0.1 cal/mol.K for C_p^o and S^o.

1.3.2 Estimation of Heats of Formation

The number of organic compounds of interest to chemists is in the millions but the number of compounds for which standard enthalpies of formation or heats of formation are accurately known is very limited and likely to remain so. Thus we need theory and empirical rules.

Many thermodynamic functions, fortunately, are additive, which means that these functions could be obtained by the summation of atom, bond and

group contributions with some corrections. Examples are heats of combustion,[109-10] heats of formation,[111] heats of atomization [112] and zero-point energies.[113,303-4]

There are many methods based on atom, bond or group additivity for estimating heats of formation of organic and organometallic compounds.[102-3,114-8] Benson [111,116] pointed out that the zero-order, first-order or second-order approximation in additivity schemes is the additivity of atom, bond or group properties, respectively. The most generally applicable schemes are Benson's, Laidler's, Allen's and ABWY (Anderson-Bayer-Watson-Yoneda) ones. The methods have been evaluated. Cox and Pilcher [114] have shown that these three procedures are mathematically equivalent. Reid, Prausnitz and Poling [117] have shown that Benson's and the ABWY methods yield the smallest errors with only a few larger deviations. However, Benson's group additivity (GA) method was preferred.[124,406] Very recently, Benson's GA scheme has been developed and modified.[102,119] As pointed out by Domalski and Hearing, Benson's method has the most desirable characteristics and appears to be generally acceptable to scientists within the disciplines of physical chemistry and chemical engineering. The attractive features of the Benson approach consist of simple additivity, clarity of notation, second order character (inclusion of nearest-neighbor interactions), ease of application, and satisfactory agreement between the estimated thermodynamic property and its experimentally determined value. The development of the method oriented toward the estimation of thermochemistry in the liquid and solid phases and in polymers has also been reported.[120-3] Benson's method has been adopted into CHETAH, the ASTM Chemical Thermodynamic and Energy Release Evaluation Program [124] and NIST Thermodynamic Databases.[406]

1.3.3 Benson's Group Additivity Rules

Benson's method was stated in 1958.[111] The method has been extended and up-dated by Benson and co-workers.[116, 120-3, 125-31, 401-2]

A group is defined as a centered atom together with its ligands. This scheme includes all nearest neighbor interactions. In other words, Benson's GA scheme can describe very well the second order interactions between atoms. All higher order interactions between atoms are considered as corrections. To describe all alkanes, four group parameters are sufficient. There is not any correction for n-alkanes. Steric corrections (1,4-gauche and/or 1,5-H repulsion) must be considered for branched alkanes. For alkenes, alkynes, aromatic and cyclic hydrocarbons and their derivatives, group parameters and corrections have been given.

The determination of values of the group parameters, however, has so far been limited to empirical inferences from data on heats of formation. To find alternative methods to predict or estimate the values of group parameters could be of great value in extending group additivity. Recently Luo and Benson [131] made a beginning. The group parameters can be written as

$$\Delta_f H^o[C-(C)_m(H)_{3-m}] = 0.9 + (m - 1)(10.08 - 1.5m) -$$

$$- \frac{m}{0.67 + 0.21m} V_x \qquad (1)$$

where V_x is the covalent potential of the substituent X and m is the degree of methyl substitution. Here X represents many nonmetallic and metallic groups, such as C-, O-, N-, S-, Si-, Ge-, Pb-, P-, As-, Se-, Zn-, Cd-, Hg-, B-, Al-, Ga-, Ti-, Cr- and Pd-centered groups. Equation (1) is dependable. Here is an example. Walsh and his co-workers [132] have calculated heats of formation using second-order Moller-Plesset perturbation theory (MP2) and 6-31G(d) basis sets at the self-consistent field (SCF) geometries. The agreement between the values predicted by Luo and Benson and the ab initio

ones is very good, within 0.3 kcal/mol.

1.3.4 Steric Corrections

Benson's scheme can be improved by incorporating higher order interactions for species. These corrections could include:

(1) 0.8 kcal/mol for the alkane gauche correction;

(2) 0.5 kcal/mol for the alkene gauche correction;

(3) 1.0 kcal/mol for the cis-correction;

(4) 0.6 kcal/mol for the ortho-correction;

(5) 1.5 kcal/mol for 1,5 H repulsion;

(6) a ring-compound correction;

(7) a correction for non-next-nearest neighbors between halogens.

The corrections are small quantities for most compounds. The correction quantities are also approximate. For example, 0.5 to 1.0 kcal/mol per gauche correction[114,116-7,125,377] has been quoted. This implies that understanding of the steric, space or strain effect in species is not complete.

We need only to consider the 1,4 gauche and 1,5 H repulsion corrections because only alkyl derivatives will be addressed in this work.

1.3.5 Applications of Molecular Mechanics and Quantum Theory

Two methods that have received considerable attention during the past two decades are the empirical force-field method (also called molecular mechanics)[133-4,403-4] and the semiempirical molecular orbital method, including MINDO, MNDO and AM1 and AM2.[135-7] In principle, heats of formation of species can be calculated by ab initio methods, but in practice the results are usually less accurate than those of empirical and semi-empirical methods.[133,315]

Molecular mechanics methods in particular have proven capable of

computing standard enthalpies of formation agreeing with experimental

values to within ± 1 kcal/mol and standard absolute entropies generally

agreeing within less than ± 1 cal/mol.K. In molecular mechanics, an

approximation has been made

$$\Delta_f H^o = 4RT + BE + SE \qquad (2)$$

where 4RT accounts for the translation, rotation, and PV term required to

convert the energy of a nonlinear molecule to enthalpy; BE is the summing

bond (or group) energy terms and SE is the steric energy of the molecule

calculated from the force field. The gauche interaction is included in the

SE terms.

It is noted that the strain-free group increment from Schleyer et al.

[138], Benson's group parameters [116,125] and those estimated by Luo and

Benson [131] are in reasonable agreement, as shown in Table 3.

TABLE 3:   Comparison between Three Increments

Groups	Schleyer et al.[138]	Benson[116-25]	Luo-Benson[131]
$[C-(C)(H)_3]$	-10.05	-10.08	-10.08
$[C-(C)_2(H)_2]$	-5.13	-5.0	-5.0
$[C-(C)_3(H)]$	-2.16	-1.9	-1.5
$[C-(C)_4]$	-0.3	0.5	0.1

Two force-field programs are the MOLBD3 program of Boyd and co-workers

[139] and the programs of MM2 [140] and MM3 [405] of Allinger's group. Agreement

of the programs is seen to be quite good. [134,403-4]

1.3.6 Relation between $\Delta_f H^o(RX)$ and V_x

Very recently, Luo and Benson [96] compared and evaluated the

correlation of heats of formation of alkyl derivatives with 17 scales of

electronegativity. Tables 4 and 5 give the input data. It was found that

the covalent potential, V_x, gives the least scatter and the highᵌᵗᵌᵌ correlation coefficients. Now more than 30 scales of electronegativity are available, as shown in Table 6. The result is the same as before. The scales have been expressed and discussed in the previous text. Table 7 gives the correlation coefficients on the rank orders. Here

$$\Delta\Delta_f H^o(RX/CH_3X) = \Delta_f H^o(RX) - \Delta_f H^o(CH_3X) \tag{3}$$

TABLE 4: Heats of Formation of a Number of Alkyl Derivatives, kcal/mol[a]

X	CH_3	C_2H_5	C_3H_7	C_4H_9
F	-55.9^b			
OH	-48.2 ± 0.1	-56.3 ± 0.1	-65.1 ± 0.1	-74.7 ± 0.2
Cl	-19.6 ± 0.1	-26.8 ± 0.3	-34.6 ± 0.3	-43.6 ± 0.5
NH_2	-5.5 ± 0.1	-11.3 ± 0.2	-20.0 ± 0.2	-28.9 ± 0.2
Br	-8.5 ± 0.3	-14.8 ± 0.4	-23.8 ± 0.6	-31.6 ± 0.4
SH	-5.5 ± 0.2	-11.1 ± 0.2	-18.2 ± 0.2	-26.2 ± 0.2
I	3.5 ± 0.3	-1.8 ± 0.4	-9.6 ± 0.9	-17.2 ± 0.8
CH_3	-20.0 ± 0.1	-25.0 ± 0.1	-32.1 ± 0.2	-40.2 ± 0.2
H	-17.8 ± 0.1	-20.0 ± 0.1	-25.0 ± 0.1	-32.1 ± 0.2

[a] From ref.102.   [b] Ref. 141.

TABLE 5: $\Delta\Delta_f H^o(RX/CH_3X)$ for Various Atoms and Groups, kcal/mol

					X				
	F	OH	Cl	NH_2	Br	SH	I	CH_3	H
$\Delta\Delta_f H^o(C_2H_5X/CH_3X)$	-8.1	-7.2	-5.8	-6.3	-5.6	-5.3	-5.0		-2.2
$\Delta\Delta_f H^o(i-C_3H_7X/CH_3X)$	-16.9	-15.0	-14.5	-15.3	-12.7	-13.1	-12.1		-7.2
$\Delta\Delta_f H^o(t-C_4H_9X/CH_3X)$	-26.5	-24.0	-23.4	-23.1	-20.7	-20.7	-20.2		-14.3

TABLE 6: EN Values for Atoms or Groups X According to Various Scales

					X				
Scales	F	OH	Cl	NH$_2$	Br	SH	I	CH$_3$	H
Pauling[6]	4.0	3.5	3.0	3.0	2.8	2.5	2.5	2.5	2.1
Mulliken[19]	3.91	3.17	3.00	2.33	2.76	2.41	2.56	2.63	2.28
Revised Mulliken[20]	3.91	3.41	3.10	2.90	2.95	2.69	2.74	2.48	2.25
Gordy[32]	3.94	3.47	3.00	3.01	2.68	2.58	2.36	2.52	2.17
Allred-Rochow[27]	4.10	3.50	2.83	3.07	2.74	2.44	2.21	2.50	2.20
Li[142]	4.0	3.5	2.93	3.0	2.79	2.68	2.41	3.5	--
Sanderson[36]	3.92	3.46	3.28	2.93	2.96	2.66	2.50	2.47	2.31
Gao[143]	4.44	3.61	3.07	2.72	2.83	2.58	2.68	2.43	--
Wells[47]	3.95	3.7	3.03	3.35	2.80	2.8	2.47	2.7	2.28
FSGO[76]	4.00	3.52	2.84	3.16	2.52	2.52	--	2.35	--
Inamoto[72-4]	3.05	3.02	2.37	2.71	2.32	--	2.15	2.21	2.00
John-Blotch[41]	4.01	3.51	2.35	3.01	--	2.12	--	2.50	--
Mande[29]	4.34	3.71	2.97	3.26	2.89	2.63	2.56	2.73	--
Boyd-Markus[77]	4.00	3.53	3.14	3.23	2.78	2.65	2.48	2.53	1.94
Boyd-Edgecombe[78]	4.00	3.62	3.05	3.08	2.75	2.64	--	2.60	--
Zhang[30]	4.19	3.64	2.84	3.06	2.53	2.48	2.14	2.54	2.27
MRTT[79]	0.517	0.434	0.245	0.332	--	0.109	--	0.165	0.0
$^{13}J_{CC}$[80]	14.84	9.7	9.21	5.2		4.2		1.07	0
Mullay[68-70]	4.00	3.97	3.07	3.15	2.81	2.42	2.47	2.32	2.08
Allen[8]	4.193	3.610	2.869	3.066	2.685	2.589	2.359	2.544	2.300
Parr-Pearson[12]	10.41	7.50	8.31	6.07	7.60	6.40	6.67	4.96	7.17
	7.01	5.67	4.70	5.33	4.24	4.10	3.70	4.87	6.42
Robles-Bartolotti	9.85	6.45	7.50	5.78	6.74	5.18	6.04	6.39	5.27
318	10.76	7.67	8.53	6.67	7.92	6.39	7.22	6.52	5.74

Nagle[368]	4.23	3.62	2.82	3.12	2.56	2.49	2.27	2.55	2.27
Baumer et al.[369]	3.952	3.479	3.076	2.986	2.832	2.631	2.611	2.518	2.202
Datta-Singh[374]	4.0	3.46	3.0	3.10		2.65		2.68	2.1
Datta[375]	4.73	4.17		3.58				2.80	
Luo-Benson[97]	9.915	8.11	7.04	6.67	6.13	5.77	5.25	5.19	2.70

TABLE 7: Correlation Coefficients for the Seven Best Electronegativity Scales for the Description of $\Delta\Delta_f H^o$(RX/CH$_3$X)

Rank Order	$\Delta\Delta_f H^o$		
	C_2H_5X/CH_3X	$i\text{-}C_3H_7X/CH_3X$	$t\text{-}C_4H_9/CH_3X$
1	Luo-Benson (0.9806)	Luo-Benson (0.9674)	Luo-Benson (0.9910)
2	Revised Mulliken (0.9523)	Revised Mulliken (0.9346)	Boyd-Markus (0.9569)
3	Boyd-Markus (0.9208)	Boyd-Markus (0.9110)	Revised Mulliken (0.9515)
4	Pauling (^.9136)	Pauling (0.9033)	Pauling (0.9459)
5	Sanderson (0.9032)	X_P^2 (0.8707)	X_P^2 (0.9189)
6	X_P^2 (0.8890)	Sanderson (0.8554)	Gordy (0.9018)
7	Mullay (0.8497)	Gordy (0.8392)	Mullay (0.8843)

The combustion reaction of hydrocarbons can be written as

$$\frac{C_nH_{2n+2}}{n} + \frac{3n+1}{2n} O_2 \longrightarrow \frac{3n+1}{n} H_2O + CO_2 \tag{4}$$
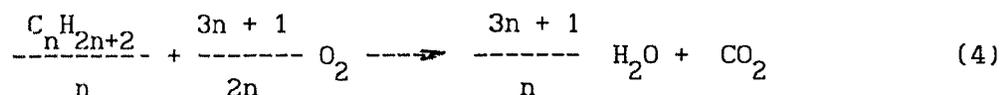
Then the uncertainty in the heats of formation for the average carbon atom in carbon compounds may be estimated to be, at least,

$$(3 + 1/n) \Delta(H_2O) + \Delta(CO_2) \approx 0.1 \text{ kcal/mol}$$

This implies that some uncertainties listed in Tables 4 and 5, which are from ref. 102, are too small. Luo and Benson [97] have shown that in general heats of formation of carbon compounds are not known to better than $\pm$ 0.1 n kcal/mol, where n is the number of carbon atoms.

As pointed out in Table 7, the revised Mulliken scale, published three years ago, is also a good one for correlating heats of formation. Boyd and Markus' scale of 1981 is also good. Other scales, including Pauling's scale and absolute electronegativity, hardness and softness, are less satisfactory for correlating heats of formation of alkyl substituents.

Luo and Benson [144] found a linear relation linking $\Delta_fH^o(CH_3X)$, $\Delta_fH^o(HX)$ and V_x. It is given by

$$\Delta\Delta_fH^o(CH_3X/HX) = a V_x + b \tag{5}$$

where

$$\Delta\Delta_fH^o(CH_3X/HX) = \Delta_fH^o(CH_3X) - \Delta_fH^o(HX) \tag{6}$$

and both a and b are constants. According to these relations, we may estimate heats of formation of complicated molecules from those of simple molecules. Examples are Si-, Ge-, Ga-, P-, As-, Sn-, Pb-containing compounds.

1.3.7 Alkylsilane Derivatives

Based on the Walsh's preferred values [103] for heats of formation of silicon-containing compounds, Luo and Benson [145-7] obtained a generalized

equation:

$$\Delta\Delta_f H^o(Si(CH_3)_m H_{3-m} X/CH_3 X) = \begin{cases} (41.1 - 15.5m) - (5.23 + 0.20m)V_X \\ \quad X = H, \ CH_3, \ SiH_3 \\ (19.0 - 15.5m) - (4.80 + 0.20m)V_X \\ \quad X = halogen, \ OH, \ SH, \ NH_2 \end{cases} \quad (7)$$

$$\Delta\Delta_f H^o(Si(CH_3)_m H_{3-m} X/CH_3 X) = \Delta_f H^o(Si(CH_3)_m H_{3-m} X) - \Delta_f H^o(CH_3 X) \quad (8)$$

Here, m is the degree of methyl substitution and has the values 1, 2 or 3. The need for two separate relations appears to be due to p-d pi backbonding between the Si atom and the donor atom X. The backbonding energy can be estimated from the difference of two cases in eq. (7), that is

$$E_{pd} = 22.1 \cdot 0.43 \ V_X \quad (9)$$

It is noteworthy that the estimated back-bonding energies are nearly independent of V_X or the types of bonding or of the donor atom X, halogen or oxygen. Neglecting this small effect, we can take an average value, $\langle E_{pd} \rangle$ = 19.3 ± 1.0 kcal/mol. Eq. (9) would appear to contradict the popular assumption[148] that p-d pi back-bonding is stronger for the more electronegative atoms. The greater strength of silicon bonds to more electronegative elements would appear from our correlations to be attributable to sigma bonding.

1.4 Bond Dissociation Energies and Heats of Formation of Free Radicals

1.4.1 Values from the Second and Third Laws

BDEs may, in principle, be determined directly if an experiment is designed to measure the enthalpy change of eq. (1) in Section 1.1. Based on eq (3) in Section 1.1, the BDEs may also be obtained if the three heats of formation in the equation are known from independent experiments. The problem is often one of determining the heats of formation of atoms and/or radicals, X and/or R, because heats of formation of an extremely large

number of organic and organometallic compounds have high precision, as has been discussed in Section 1.3. Thus, determining BDEs is equivalent to finding any previously unknown heats of formation of free radicals. For atoms, we can accept the spectroscopically determined values.[99,149-50] This case is not discussed in this thesis.

It is impossible to make a direct (calorimetric or first law) determination of the absolute heats of formation for most radicals. Experimental techniques are available to determine relative values, which can be anchored with accessible absolute values such as heats of formation of atoms.

Among the experimental methods, kinetic studies of three types of reaction are included:

(1) bond dissociation and recombination

$$AB \rightleftharpoons A^\bullet + B^\bullet \qquad (1)$$

(2) abstraction reactions of free radicals

$$A^\bullet + BC \rightleftharpoons AC + B^\bullet \qquad (2)$$

(3) dissociation of free radicals

$$AB^\bullet \rightleftharpoons A^\bullet + B \qquad (3)$$

If kinetic data for the forward and reverse reactions are available over a relatively wide temperature range ($\Delta T > T_m \pm 50$ K), equilibrium constants can be found as follows:

$$K_p(T) = k_f / k_r \qquad (4)$$

and using the Van't Hoff equation, the reaction enthalpy

$$\Delta H(T_m) = -R \frac{d\ln K_p}{d(1/T)} \qquad (5)$$

can be easily derived. Notice that for equilibria the rate constants of reactions (1) and (3) should be expressed in units of atmosphere^{-1} per second or K_p in atmospheres. This procedure is usually known as the "second

law" method. Although it is apparently self-contained, it has actually proved inaccurate on account of the unfavorable propagation of temperature measurement errors into the activation energies and reaction enthalpies. The uncertainty may be as much as $\pm$ 2 or 3 kcal/mol because of its sensitivity to the accuracy of the activation energies of the forward and reverse reactions.

Alternatively, a single temperature value of K_p, from eq. (4) and the values of the forward and reverse rate constants at a given temperature T, can be combined with entropy data for all species to calculate a "third law" value of ΔH:

$$\Delta H(T) = - RT \ln K_p + T\Delta S \qquad (6)$$

This value relies on the accuracy of the calculated entropies. It is worth noting that typical combined uncertainties of 1 cal/mol.K in the estimated ΔS and a factor of 2 in the measured K_p value would lead to a maximum error of $\pm$ 1.2 kcal/mol at 500K, which is rather typical. Thus, values of the BDEs and heats of formation of free radicals from third law determinations have a significantly higher precision than do those from the second law. The third law procedure permits determination of the reaction enthalpy from more limited measurements of equilibrium constants at a single temperature or in a narrow temperature range. An example is offered below.

Using a Van't Hoff plot showing the three equilibrium constants measured by VLPR, Benson and co-workers [152] obtained the following results in the system $Cl + CH_4 \longrightarrow CH_3 + HCl$

$$\Delta H = 1.6 \pm 0.7 \text{ kcal/mol} = \{\Delta_f H^o(CH_3) + \Delta_f H^o(HCl)\} -$$
$$- \{\Delta_f H^o(Cl) + \Delta_f H^o(CH_4)\}$$
$$\Delta S = 5.6 \pm 2.4 \text{ kcal/mol K} = \{S_f^o(CH_3) + S_f^o(HCl)\} -$$
$$- \{S_f^o(Cl) + S_f^o(CH_4)\}$$

Combining with the known thermochemistry of methane, chlorine atoms and

hydrogen chloride allows one to calculate the thermochemistry of the methyl radical:

$$\Delta_f H^o(CH_3) = 34.8 \pm 0.7 \text{ kcal/mol}$$

$$S^o(CH_3) = 45.0 \pm 2.4 \text{ cal/mol.K}$$

Taking the third law procedure and using the known values of S^o for all species allows an improved estimate of ΔH. Now $\Delta S = 6.9 \pm 0.3$ cal/mol.K at 298K. Then

$$\Delta H = 1.95 \pm 0.15 = \{\Delta_f H^o(CH_3) - 22.06 \pm 0.05\} -$$
$$- \{28.99 - 17.88 \pm 0.08\} \text{ kcal/mol.}$$

and

$$\Delta_f H^o(CH_3) = 35.1 \pm 0.1 \text{ kcal/mol}$$

It should be emphasized that by invoking detailed balance it is implicitly assumed that the reactants of one step are identical with the products of its reverse reaction. i.e., that they possess not only the same chemical identity but also the same population of energy states. If rates happen to be wall sensitive one must also prove that both reactions are affected to the same extent. Admittedly these conditions are difficult to verify in actual practice. Since median temperatures T_m are generally high, extrapolation to 298K is required:

$$\Delta H = \Delta H(T_m) + <\Delta C_p> (298 - T_m) \qquad (7)$$

where the temperature-dependent functions of heat capacities, C_p can be estimated with sufficient accuracy.[116,151] In almost all experiments, the uncertainties in heats of formation of free radicals or the BDEs are greater than or equal to the uncertainties in the heats of formation of the parent molecules. The simplest reason is the fact that free radicals are generally short lived intermediates, both in the gas-phase and in solutions, and are therefore inappropriate subjects for conventional calorimetry.

The accuracy of heats of formation is very important for quantitatively estimating equilibrium constants of other chemical reactions. Even so called "chemical accuracy" is often not adequate. Uncertainty of ± 1 kcal/mol can give rise to changes in equilibrium constants of a factor of 5.4 at room temperature, or a change of 65% at 1000K. Despite their obvious importance, BDEs or heats of formation of polyatomic radicals lack the precision that end-users often require and they rarely have an accuracy that is better than ± 1 kcal/mol with the exception of the prototypical alkyl radicals, methyl, ethyl and tert-butyl.

1.4.2 Methods of Measurement

The experimental methods of finding the BDEs have been discussed in many important review papers, journal articles, special publications and books.[103,116,129,153-79,380] These methods can be summarized:

(1) various pyrolytic techniques for reactions of types 1 and 3;

(2) halogenation kinetics for reactions of type 2;

(3) gas-phase ion equilibria;

(4) liquid-phase radical buffers;

(5) photoacoustic calorimetry;

(6) acidity-oxidation potentials

(7) other methods.

These experimental techniques will be briefly introduced.

(1) Various pyrolytic techniques for types 1 and 3

A large number of reported values for BDEs come from direct measurement of the high pressure value of the activation energy of the dissociation step. These techniques have caused two kinds of difficulties. First, the dissociation kinetics of types 1 and 3 of even small organic molecules is recognized as very complicated. Second, the relation between

BDE and the activation energy for bond cleavage, $E_{d,T}$, involves the value of the potential barrier for combination of radicals, $E_{r,T}$, which is often not known accurately.

For the first difficulty, several techniques have been developed in the last 20 years to study the kinetics with a minimum of complications. The extent of secondary radical reactions and wall effects can be considerably limited by working either at very low pressures or by heating the system in short pulses by means of sudden compression or by pulsed irradiation with infrared lasers. For the second difficulty, it is useful to follow one of the conventions listed by McMillen and Golden,[170] i.e., (1) there does not exist a potential energy barrier at 0 K and $E_r = 0$; or (2) the Gorin rotational transition state model is used and the heat capacity change of the transition states, $\Delta C_{v,r}^*$, is - 0.5R. Then we have

$$BDE = \Delta H_{298}^o = E_{T,d} - \langle \Delta C_p^o \rangle (T - 298) + 0.5RT \tag{8}$$

This results in BDE values that are greater by 0.5RT than values based on the assumption that the activation energy for recombination (from rate constants measured in concentration units) is 0 at the reaction temperature. McMillen and Golden's second convention implicitly assumes a plausible transition state for bond dissociation reactions in which the relative motions of the separating fragments are taken as anharmonic librations having heat capacities of 0.5R per degree of freedom. However, not all reported data agree with the predictions of this convention. Use of $\Delta C_{v,r}^*$ values for transition states in which all modes are treated as vibrations leads to heats of reaction at 300K different by as much as $\pm$ 1.5 kcal/mol. This is a real weakness of pyrolytic studies in which only the forward reaction is measured.

The Carrier technique is an old one.[154] The measured rate parameters involved secondary reactions. The activation energies and A-factors were

often underestimated. Over 600 data measured by many investigators were
reviewed by O'Neal and Benson.[162]

Single-Pulse Shock Tube (SPST) Pyrolysis has been developed recently
by Tsang.[168] This is one of the simplest and most convenient techniques for
studying initial decomposition steps. Relatively fast (millisecond)
homogeneous heating and cooling is achieved by sudden expansion of an inert
gas into a mixture containing the substrate. The reaction time is generally
short enough to eliminate all secondary reactions. Surface effects are
either suppressed or kept to minimum.

One of the principal difficulties has been satisfactory temperature
definition. This difficulty appears to be essentially eliminated by use of
the SPST in the "comparative rate" mode, in which comparison of the
fractional decomposition of the substrate with that of a "temperature
standard" - a substrate whose rate parameters are well known - allows
determination of the substrate rate parameters with high precision. The
functional form of the comparative rate relation is

$$\log A - E/RT = \text{slope} \log A' - (\text{slope}) E'/RT + \text{constant} \qquad (9)$$

where A (A') and E (E') are the A-factor and activation energy,
respectively. Those with a prime belong to the reference substrate.
Extensive work in this area by Tsang and coworkers has provided a self-
consistent set of heats of formation of free radicals. However,
unexplainable differences exist between shock tube data and other BDE
sources.

Flow-tube pyrolysis. Pyrolytic reactors are constructed of cylindrical
quartz tubing. The average residence time, t, of molecules in the reactor
is obtained from the dimensions of the reactor and from the substrate flow
rate. Samples of reactor effluent are analyzed by gas chromatography and
mass spectrometry. In general, the pyrolytic process for small hydrocarbons

has been interpreted by making the steady-state approximation for the free radicals. In this way it is only possible to determine the rate constant for the initiation reaction and certain quotients of other rate constants. However, this has been improved in Pacey's laboratory.[180-1] The product yields were measured at very short reaction times when the radicals had not reached their steady-state concentration. The results enabled calculation of the concentrations of ethyl radicals and the rate constants of the forward and backward reactions, and the values of BDEs and heats formation for ethyl and methyl with high precision.

Very Low Pressure Pyrolysis (VLPP) is a versatile kinetic tool which has been developed by Benson and co-workers.[182] It was a heatable molecular flow reactor operating at very low pressures, typically 0.1 to 10 mtorr. The VLPP technique is comparable to the shock-tube technique in minimizing the impact of secondary bimolecular reactions and surface effects. Well-defined temperatures and residence times, efficient control of bimolecular radical reactions, and direct product analysis by modulated beam mass spectrometry are major assets of this technique. Improved time of flight analysis and the use of low energy electron impact ionization routinely allows unambiguous identification of primary products and the direct investigation of fast bimolecular reactions with high precision.

The principal limitation of the VLPP technique stems from the fact that, at mtorr pressures and at the temperatures required to observe substantial cleavage of 70-90 kcal/mol bonds, unimolecular reactions of small molecules are generally not at their high pressure limit. Under these conditions, VLPF does not readily provide an independent determination of both rate parameters.

Equilibration measurements lead to both forward and backward rate constants. An excellent example comes from Pilling's group.[183,319] Pilling

and co-workers describe measurements, using excimer laser flash photolysis/ resonance fluorescence, on the reaction system:

$$H + C_2H_4 \underset{b}{\overset{f}{\rightleftharpoons}} C_2H_5$$
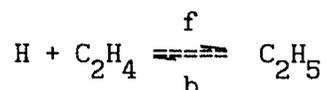
The advantage of this approach is that k_f and k_b are measured under identical conditions by a direct, time-resolved technique. By combination with a spectroscopic estimate of the entropy change of the reaction, the reaction enthalpy change and the heat of formation of the ethyl radical were determined.

(2) Halogenation kinetics for reactions of type 2

Iodination or bromination equilibria have been extensively studied during the past 45 years.[161,165,170] Today, a significant fraction of our knowledge of the thermochemistry of free radicals is still based on these experiments. In iodination or bromination processes, the mechanisms have been assumed to be

$$X_2 \rightleftharpoons 2 X$$

$$X + RH \underset{-1}{\overset{1}{\rightleftharpoons}} R + HX$$

$$R + X_2 \underset{-2}{\overset{2}{\rightleftharpoons}} X + RX$$

$$(RX \underset{-3}{\overset{3}{\rightleftharpoons}} \text{olefin} + HX)$$
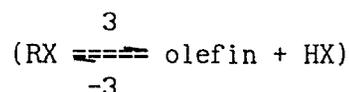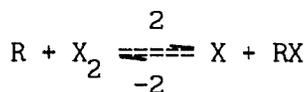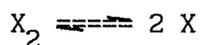
Here the measured rate constants for the forward reaction, k_1, are combined with estimated rate parameters for k_{-1} to yield ΔH and ΔS. In the case where $X = I$, most reactions (1) are very endothermic and slow. The experiments are carried out at higher temperatures and pressures. These studies have all involved determinations of the enthalpy change from the difference in the activation energies of the forward and reverse reactions.

Mechanistic complications and wall effects may have affected the kinetics. Rossi and Golden [184] have pointed out that the method has significant limitations and suggest that reliable data are best obtained by the careful measurement of rate parameters for the forward and backward reactions.

The VLPR method is a variant of the older VLPP technique applied to fast bimolecular reactions.[177] It involves a well stirred reactor operating by molecular diffusive mixing at pressures below 10 mtorr. Atoms X are generated in a microwave discharge usually of X_2 in a rare gas and allowed to flow into a Knudsen cell. A metered reactant RH also leaks into the cell where it can react with X:

$$X + RH \rightleftharpoons HX + R \qquad X = Cl, Br$$
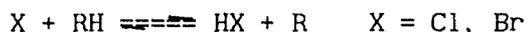
Kinetics of the reverse reaction can be easily measured by simultaneously adding HX to the system. The extreme reactivity of halogen atoms make it possible to carry out these experiments at room temperature, a condition which tends to eliminate chemical complications such as wall effects and the need for lengthy extrapolations. Thus, the VLPR technique can provide thermochemical data with great accuracy.

Its main limitation resides in the requirement that $0.1 < K < 10$ so that both k_f and k_b can be conveniently measured. Complications arise from the ever-present background traces of HX, and perhaps more seriously, from the possible participation of excited halogen atoms. All can be satisfactorily handled, however.

The Very Low Pressure Photolysis (VLPΦ) technique has been developed in Golden's group.[184-5] The precursor gases are mixed in a low-pressure Knudsen cell that is equipped with an irradiation section. The gases are formed into an effusive molecular beam leaving the Knudsen cell. The effusive molecular beam passes two differentially pumped vacuum chambers before it penetrates into the ion source of a quadrupole mass spectrometer.

The VLPΦ technique has similar advantages to the VLPR one.

Flow photolysis Halogenation reactions

$$R + HX \rightleftharpoons RH + X \qquad X = Br, \ I$$
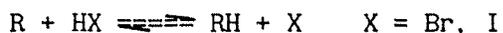
have been studied in Gutman's group.[186-8] The facility is a flow tubular reactor coupled to a photoionization mass spectrometer. Gas flowing through the tube at 5 m/s was completely replaced between laser pulses. Pulsed unfocused 193- or 248-nm radiation from an excimer laser was collimated and then directed along the axis of a heatable 1.05 cm i.d. coated Pyrex tubular reactor. Gas was sampled through a 0.4-mm-diameter hole, located at the end of a nozzle in the wall of the reactor, and formed into a beam by a conical skimmer before it entered the vacuum chamber containing the photoionization mass spectrometer. Acetone, diethyl ketone, 2-bromopropane, and 2,2,4,4-tetramethyl-3-pentanone or 4,4-dimethyl-1-pentene were methyl, ethyl, iso-propyl and tert-butyl radical sources, respectively. It is surprising that the reaction rate constants for R + HX were found to have negative activation energies. For X = I, the negative activation energies were -0.3, -0.8, -1.2 and -1.5 kcal/mol for R = methyl, ethyl, iso-propyl and tert-butyl, respectively. They have argued this was evidence for a complex mechanism involving a bound intermediate between the radical and HX.

(3) Gas-phase ion equilibria In the past 20 years, the development of pulsed ion cyclotron resonance and high pressure mass spectrometric techniques in conjunction with improved determinations of threshold energies for photoionization and photodetachment processes have led to a large body of thermochemical data for organic ions.[189,407] They can be used to derive similar information for their neutral counterparts.

With regard to negative ions, electron affinities of halogen atoms are known with great accuracy and may be used as a reference point. Bond

dissociation energies or radical heats of formation may be determined from ion cycles. The measurements of gas-phase acidities are involved in one cycle.

$$R - H \longrightarrow H^+ + R^- \qquad \Delta_{acid}H$$

$$H^+ + e \longrightarrow H \qquad - IP(H)$$

$$R^- \longrightarrow R + e \qquad EA(R)$$

$$R - H \longrightarrow R + H \qquad BDE(R-H) = \Delta_{acid}H - IP(H) + EA(R) \qquad (10)$$
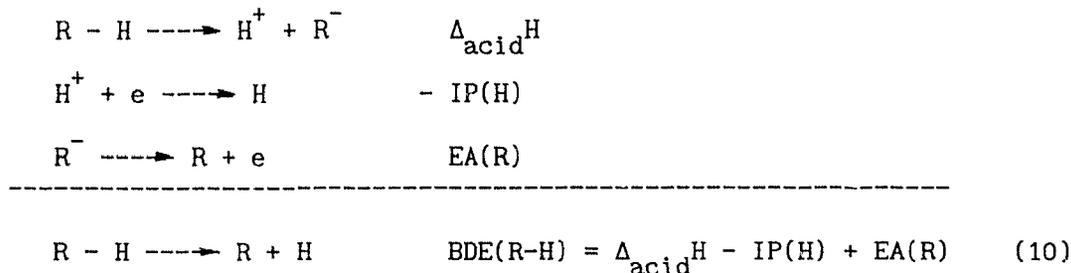
The adiabatic values for IP and EA are values of enthalpy changes for the processes at 0K. These should be adjusted by heat capacity values to 298K. The correction is small because the ion and neutral structures and frequencies are fairly similar. The neglect of this correction only results in an error less than 1 kcal/mol. This problem will be discussed in Section 1.6. In general, BDEs are usually much smaller than IP and ΔH_{acid}, and BDEs are small differences between large numbers, which is the principal source of error.

The IPs of many radicals have been measured using photoelectron and thermal electron attachments and electron impact appearance potentials. But these are difficult experiments that attempt to determine threshold energies in the range of 150-200 kcal/mol to precisions of < 1 % in order to provide values of chemical accuracy.

Very recently, Holmes and co-workers [190] derived heats of formation for alkyl radicals from appearance potential (AP) measurements. The uncertainty is within chemical accuracy. The basic principle is

$$e + AB \longrightarrow A^+ + B + 2e \qquad AP(A^+)$$

$$2e + A^+ \longrightarrow A + e \qquad - IP(A)$$

$$AB \longrightarrow A + B \qquad BDE(A-B) = AP(A^+) - IP(A)$$

or
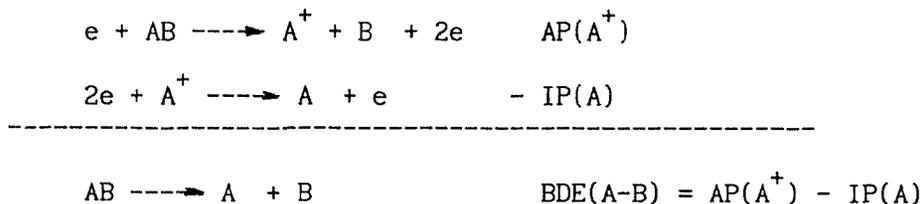
$$AP(A^+) = \Delta_f H^o(A^+) + \Delta_f H^o(B) - \Delta_f H^o(AB) \qquad (11)$$

(4) Liquid-phase radical buffers have been developed in Griller's group.[175,191,380] The iodine atom exchange reaction

$$CH_3 + RI \longrightarrow CH_3I + R$$
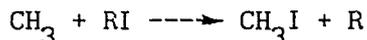
is a rapid process which, with concentrations of iodides of 1 M, can be much faster than radical-radical reactions. A true equilibrium or "radical buffer" can be established. Radicals CH_3 and R were generated thermally or photochemically by several routes in hydrocarbon solutions containing their corresponding alkyl iodides. The samples were irradiated in the cavity of an ESR spectrometer so that the spectra of the alkyl radicals could be monitored directly. The measured radical concentrations could be combined with the known concentrations of the alkyl iodides to give the values of the equilibrium constant at or near room temperature. Actual measurement of the ratios CH_3/R under these conditions combined with direct determinations of the relative heats of formation of alkyl iodides and estimated entropies of all species could be used to evaluate the differences in heats of formation between other alkyl radicals and CH_3. It has been convincingly argued that since heats of mixing of all species in hydrocarbon solvents are very small (less than 0.1 kcal/mol) and since corrections for vaporization nearly compensate, the results should be equivalent to gas-phase data,[191] even in solvents as polar as water.[321]

(5) Photoacoustic calorimetry has also been developed by Griller's group.[192-3] The technique is used to measure heats of reaction in solution where a transient species is one of the reaction products. The apparatus and experiment itself are extremely simple. The following reactions in carbon tetrachloride were initiated by a nitrogen laser:

$$t\text{-BuO-OBu-t} \longrightarrow 2 \; t\text{-BuO}$$

$$t\text{-BuO} + RH \longrightarrow t\text{-BuOH} + R$$

The release of heat into the solvent causes a shock wave which is transmitted at the speed of sound to the cell wall. When it hits the wall it causes a vibration which is detected by a sensitive piezoelectric transducer with microsecond time resolution. The sum of the heats of these reactions are accurately measured, that is

$$\Delta H_{total} = 2 \; \Delta_f H(t\text{-BuOH}) + 2 \; \Delta_f H(R) - 2 \; \Delta_f H(RH) - \Delta_f H(t\text{-BuOOBu-t}) \quad (12)$$

Heats of formation of free radicals can be estimated from this calorimeter. The BDEs of Si-H and Sn-H bonds have been measured and were in agreement with literature values.

(6) Acidity-oxidation potentials

Recently, BDEs of H-A bonds in solution have been observed.[322-9] Equilibrium acidity constant (pK_{HA}) measurements and oxidation potentials (E_{ox}) relative to the standard hydrogen electrode have enabled relative homolytic BDEs to be obtained, as follows:

$$H\text{-}A \;\rightleftharpoons\; H^+ + A^- \qquad\qquad pK_{HA}$$

$$A^- \;\rightleftharpoons\; e + A \qquad\qquad E_{ox}(A^-)$$

$$H^+ + e \;\rightleftharpoons\; H \qquad\qquad E_{red}(H^+)$$

$$\overline{\phantom{HA \;\rightleftharpoons\; H + A \qquad\qquad DH^o(H\text{-}A)xxxxxxxxxxxxxxxxx}}$$

$$HA \;=\!=\!=\!=\!=\!=\; H + A \qquad\qquad DH^o(H\text{-}A)$$
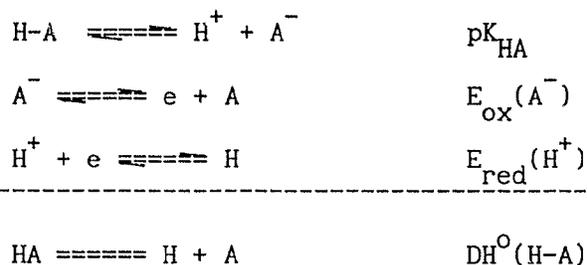
Compared with eq. (10), the solution analogues of the IPs and AEs of species are the electrochemical oxidation and reduction potentials (E_{red}). Since E_{red} for the proton is constant, the differences in the sum of the oxidation potentials of the anions and the acidity constants for their conjugate acids (pK_{HA}) can be taken as measures of relative BDEs.

$$\Delta DH^o = 2.303 \; RT \; \Delta pK_{HA} + 23.06 \; \Delta E_{ox}(A^-) \qquad\qquad (13)$$

or

$$DH^o = 2.303 \; RT \; pK_{HA} + 23.06 \; E_{ox}(A^-) + C \qquad\qquad (13a)$$

The size of the constant, C, varies slightly with the ΔS^o term. For C-H and

N-H acids, C is equal to 55.85, and for O-H and S-H acids, C = 55.39.[308] The solution BDEs observed are in agreement with gas-phase BDEs within 3 kcal/mol or less.

(7) Other methods There exist several other sources of thermochemical data for free radicals which sometimes complement the direct techniques. They include: (1) chemical activation studies,[165] and (2) energy disposal in exothermic reactions.[170]

1.4.3 Data on Heats of Formation of the Key Alkyl Radicals

The data on heats of formation of methyl, ethyl, iso-propyl and tert-butyl radicals have been selected and listed in Table 8. In this thesis, the heat of formation of the methyl radical is taken as 35.1 ± 0.1 kcal/mol from Benson's group.[152,194-5] This result has great precision, as shown in Table 8. The value has been accepted by chemists.[149,179]

The heat of formation of the ethyl radical is 28.4 ± 0.4 kcal/mol from this laboratory.[181] This value has been reproduced very well by Pilling's group,[183] and Benson's group [203-4] and is in agreement with the measurements of Tsang [168,173,205] and of Gutman's group.[187-8] From Table 8, the values of the heat of formation of the ethyl radical measured by many methods are nearly identical. $\Delta_f H^o$(ethyl) = 28.4 ± 0.4 kcal/mol can be recommended with some confidence. The strength of the primary C-H bond is no longer in doubt.[203,319]

Heats of formation of iso-propyl and tert-butyl radicals are still subject to heated dispute. The values recommended by Benson and co-workers [185,209] are adopted in this thesis for the following four reasons:

TABLE 8: Heats of Formation of the Prototypical Alkyl Radicals, in kcal/mol

Alkyls	$\Delta_f H^O(R)^a$	methods	References
CH_3	35.1+0.1	VLPR [b]	152, 194-5
	35.4±0.7	equilibrium	187
	34.4±0.7	photoionization	196
	34.8±0.2	pyrolysis	197
	35.6	photoionization	198
	35.7±0.1	photoionization	199
	34.8±0.3	equilibrium	200
	35.1±0.4	pyrolysis[c]	181
	34.8	review	201
	34.8±0.5	review	202
C_2H_5	28.4+0.4	pyrolysis	181
	28.4±0.4	laser photolysis	183, 319
	28.3±0.4	VLPR [b]	203
	28.6±0.4	VLPR [b]	204
	28.5±0.5	shock tube	168, 173, 205
	28.0±1.0	radical buffer	175, 191, 206
	28.2 [d]	equilibrium	207
	28.7±0.7	equilibrium	187
	27.8±0.6	electron impact	190
	28.3	review	201
	28.3±1.1	review	202
$i-C_3H_7$	22.3±0.6	shock tube	168, 173, 205
	19.2±1.0	radical buffer	175, 191, 206
	21.0±0.7	equilibrium	187
	19.0±1.0	pyrolysis	197

	19.1±0.6	electron impact	190
	21.0±0.5	equilibrium	208
	21.3±0.7	equilibrium	187-8
	20.0	review	201
	20.0±1.2	review	202
	<u>20.0±0.5</u>	empirical relations	209

t-C_4H_9	<u>9.9±0.6</u>	VLPΦ[e] and VLPR[b]	185
	9.2±0.5	VLPΦ [e]	185
	11.0±0.5	shock tube	168, 173, 205
	9.4±1.0	radical buffer	175, 191, 206
	11.6±0.4	equilibrium	186, 188
	11.5±0.8	equilibrium	331
	9.6±0.5	VLPR [b]	210
	9.5±0.5	VLPR [b]	177
	11.3±1.0	equilibrium	211
	9.5±0.2	electron impact	210
	10.3	review	201
	10.3±1.2	review	202

[a] The values selected in this work are underlined. [b] VLPR stands for very low pressure reactor. [c] Recalculated based on refs. 212-3. [d] The value is 28 kcal/mol in ref. 207. The value of 28.2 kcal/mol is calculated based on $\Delta H = 3.9$ kcal/mol for reaction $H + C_2H_6 \rightarrow H_2 + C_2H_5$ in ref. 207 and $\Delta_f H^o(C_2H_6) = 20.0 \pm 0.1$ kcal/mol in ref. 102. [e] VLPΦ stands for very low pressure photolysis.

(1) The entropies of formation Tsang [168,173,205] and Gutman's [186-8] groups obtained for iso-propyl and tert-butyl radicals were too large in comparison with calculated values (See Table 9).

TABLE 9: Entropies of the Prototypical Alkyls, in cal/mol.K

R	calculated	Benson, Golden	Tsang[f]	Gutman[g]
CH_3	46.4 ± 0.3[a]	46.4 ± 0.3[d]	46.4	50.9 ± 3.9
C_2H_5	59.2[b]	59.2[b]	59.3	62.1 ± 2.9
$i\text{-}C_3H_7$		66.7[e]	69.3	72.3 ± 3.1
$t\text{-}C_4H_9$	74.8 ± 2.4[c]	74.8 ± 2.4[c]	76.7	75.5 ± 1.7
		74 ± 2[h]		

[a] Ref. 106. [b] Ref. 203. [c] Ref. 185. [d] Ref. 152. [e] Ref. 116. [f] Ref. 173. [g] Ref. 187. [h] Ref. 177.

Recently, the structure, vibrational spectra and barriers for internal rotation have been determined by Pacansky and colleagues [214-22] using infrared spectra and ab initio calculations. They reported extensive restricted open-shell Hartree-Fock calculations to establish the equilibrium geometry. The results indicated that methyl is the only alkyl radical of the series with a planar radical center. As the number of hydrogen atoms in the CH_3 radical replaced by methyl groups increases, the planarity of the radical center decreases; for example, the out-of-plane bending angle for the ethyl and tert-butyl radicals is $6°$ and $25°$, respectively. The entropies of formation for the key radicals have been calculated from their results, as shown in the first column of Table 9. A very small 0.1 kcal/mol barrier to internal rotation was found for the ethyl radical; this increased to 1.1 kcal/mol and 1.2 kcal/mol barrier for the iso-propyl and tert-butyl radicals, respectively. Thus, the free rotor

model assumed by Tsang is not reasonable. Entropies of hindered rotors should be lower; consequently, the heats of formation should also be lower to maintain the observed value of the equilibrium constant.

(2) The negative activation energies measured by Gutman and co-workers cannot be explained.

Gutman and co-workers [187-9] found negative activation energies for reactions R + HI and R + HBr. For the reactions of methyl, ethyl, i-propyl and t-butyl with HI,[188] the negative activation energies were reported to be -0.3 ± 0.2, -0.8 ± 0.2, -1.2 ± 0.2 and -1.5 ± 0.3 kcal/mol, respectively.[189] For methyl, ethyl, i-propyl and t-butyl radicals reacting with HBr, they were -0.3 ± 0.3, -0.8 ± 0.3, -1.1 ± 0.4 [187] and -1.4 ± 0.3 kcal/mol,[189] respectively. Negative activation energies are unusual in metathetical reactions. Gutman [343] argued that the metathetical mechanism is a complex process involving the formation of a bound intermediate. It involves the following steps: "attraction of the $t-C_4H_9$ radical to the halogen end of the HX molecule to form a bound $t-C_4H_9 \cdot XH$ complex followed by decomposition by one of two paths, direct dissociation to reform the original reactants (via a loose transition state) or rearrangement via internal rotation of HX (followed by decomposition into the observed new products, $i-C_4H_{10}$ + X) via a tight transition state."

Which direction of attack is favorable for the reaction of an atom or radical X with a hetero-nuclear molecule YZ? Herschbach's electronegativity ordering rule [333-9] shows a reaction between a radical (or an atom) and a molecule YZ will always favor attack on the less electronegative atom of YZ. From MO theory, the HOMO and LUMO for the molecules YZ are made up primarily of the orbitals of the more electronegative atom Z. For the reaction between X and YZ, the HOMO of X correlates favorably with the LUMO of YZ. This means Herschbach's rule is understandable.[337-9] Crossed

molecular beam studies and many experimental techniques have lent evidence to support Herschbach's rule, for example, H, Br, O, or CH_3 + ICl, H + BrCl, ClF or DCl, D + HF or HCl, O + BrCl and CH_3 + BrCl. Thus, for methyl, ethyl, i-propyl or t-butyl radicals to attack the halogen end of a HX molecule is unfavorable.

Generalized treatments for the explanation of negative activation energies in terms of an intermediate complex were described by Mozurkewich and Benson.[340] Very recently, McEwen and Golden [341] made RRKM calculations to see what kind of attraction could produce a -1 kcal/mol activation energy for t-butyl + HBr and found that a well about 7.6 kcal/mol deep was needed ! Then the negative temperature dependence for the reaction observed by Dr. Gutman's group could be simulated. This also shows that it is difficult to understand the negative activation energies for R + HX reactions. Benson [342,345] has emphasized there is no basis for a negative activation energy in any of the alkyl + X_2 or HX reactions. "It is equally difficult to propose a transition state for t..c reaction of presumably an R.X.H complex to the final products RH + X that will not have a very small A-factor." [345]

The differences between laser flash photolysis (Dr. Gutman's group) [187-9] and the very low pressure reactor (Dr. Benson's group) [177,181,210] or very low pressure photolysis (Dr. Golden's group) [181] results are are clearly irreconcilable. Benson [342,345] considers that Gutman's results arise from hot radicals produced by photolysis. Gutman [343] argues that Benson and Golden's results arise from inaccuracies in assumed information in their thermochemical calculations, in particular the activation energies of the t-Bu + HX or X_2 reactions.

(3) Recalculated values

Benson [177] analyzed possible results using the VLPR experimental data

at 300 K for the reaction

Br + H-t-Bu ------► HBr + t-Bu

The results are listed in Table 10. For a contact transition state, the upper limit of the heat of formation of t-Bu radical was estimated to be 10.8 kcal/mol. A tight transition state with an angle of 135 degrees would give an upper limit of 9.9 kcal/mol. The tight transition state is more reasonable.

TABLE 10: Varied Possible Cases for $\Delta_f H^o$(t-Bu) [a]

transition state state	log A (1/mol.s)	E_f	E_b (kcal/mol)	$\Delta_f H^o$(t-Bu)
contact	11.0	7.6	0	10.8
		7.1	0.5	10.3
tight	10.4	6.7	0	9.9
		6.2	0.5	9.4

[a] $K = 5.6 (\pm1) \ 10^{-3}$ at 300 K , See ref. 30.

If zero activation energies are assumed for the alkyl + HX reactions, the values measured by Gutman and co-workers may be recalculated, as shown in Table 11. From the Table, the recalculated values of methyl, ethyl, i-propyl, n-propyl, t-butyl and s-butyl radicals are very close to those recommended by Benson and co-workers. It is interesting that the recalculated value of the heat of formation of C_2H_3, a non-alkyl radical, is also very close to that of Dobis and Benson.[345]

The values measured by Griller and co-workers[175,178,191,196] have also been recalculated. In their original work, the heat of formation of the methyl radical was taken as a reference point. They took $\Delta_f H^o$(methyl) =

34.4 kcal/mol. Now we take 35.1 kcal/mol. So, Griller's values of alkyl radicals should increase 0.7 kcal/mol. The recalculated values, including n-propyl and s-butyl radicals, have also been listed in Table 11.

TABLE 11: Recalculated Values of Heats of Formation of Alkyl Radicals, in kcal/mol

Alkyls	Benson[a]	Gutman			Griller		Doering[d]
		orig.[b]	E_a	recal.	orig.[c]	recal.	
prototypical alkyls							
methyl	35.1±0.1	35.4±0.7	-0.3	35.1	34.4[e]	35.1[e]	34.8
ethyl	28.4±0.4	28.7±0.7	-0.8	27.9	28.0±1.0	28.7	28.3
i-propyl	20.0±0.5	21.3±0.7	-1.2	20.1	19.2±1.0	19.9	20.0
		21.0±0.7	-1.1	19.9			
t-butyl	9.9±0.6	11.6±0.4	-1.5	10.1	9.4±1.0	10.1	10.3
		11.6±0.4	-1.4	10.2			
		11.5±0.8	-1.5	10.0			
disputed alkyls							
n-propyl	23.4				22.8±1.0	23.5	
s-butyl	15.0	15.9±0.7[g]	-1.2[f]	14.6	13.9±1.0	14.6	
A non-alkyl radical							
C_2H_3 [i]	66.4±0.4	66.9±0.3[h]	-0.7	66.2			

[a] Refs. 181 and 209 and Benson's group additivity based on Table VI. [b] Refs. 187-9 and 343, unless indicated. [c] Refs. 175, 178, 191 and 196. [d] Ref. 201. [e] Reference point. [f] Ref. 344. [g] Ref. 331. [h] Ref. 346. [i] Ref. 345.

The values recalculated from both Gutman's and Griller's ones are very close to those recommended by Benson and co-workers.

Data on heats of formation for n-propyl, s-butyl and other alkyl radicals are shown in Table 12. The estimation of heats of formation of alkyl radicals by Benson's group additivity (GA) will be discussed in Chapter 3.

TABLE 12: Heats of Formation of Normal and Branched Alkyls, kcal/mol

| R | $\Delta_f H^o (R)$ | | |
| | est. by GA | experiments | |
		original	recalculated [a]
disputed alkyls			
C-C-C·	23.4	22.8±1.0 [b]	23.5
		22.7 [c]	
		24.0±0.5 [d]	
C-C-C·-C	15.0	13.8±1.0 [b]	14.6
		15.3 [c]	
		17.0±0.4 [d]	
		15.9±0.7 [e]	14.6
		16.0±1.0 [f]	
rarely studied alkyls			
C C-C-C· C	8.8	7.7±2 [g]	
		10.1 [c]	
C-C·-C-C-C C	0.7	0.8±2 [h]	
C-C-C-C·	18.4	18.1 [c]	
C C-C-C·	16.4		15±3 [i]

^{a} See the text and Table 11, unless indicated. ^{b} Ref. 191. ^{c} Ref. 189.
^{d} Ref. 168. ^{e} Ref. 344. ^{f} Ref. 347. ^{g} Recalculated value based on $DH^{o}(C-H)$
$= 100\pm2$ kcal/mol and heat of formation of compound from ref. 120 and 189.
^{h} Ref. 290. ^{i} See review in ref. 102.

(4) Doering's review

Doering [201] pointed out nine years ago that all data on thermal reorganization kinetics of hydrocarbons could be explained by upwardly revising the heats of formation of the key alkyl radicals. The values adopted herein, as shown in Table 8, are near Doering's recommended values, and are also in the middle of the range of the presently available experimental results. Thus the selected values of heats of formation are reasonable.

1.4.4 Data on Homolytic Bond Dissociation Energies of X-Alkyl Bonds.

It is easy to obtain the BDEs of R-X bonds after carefully selecting heats of formation of free alkyls and combining with heats of formation of alkyl derivatives.[102] The final results have been listed in Table 13.

It was found that BDEs can be correlated very well with the new scale of electronegativity or the covalent potential, V_{x},[209] as follows: For the exchange of X,

$$CH_3 + RX \rightleftharpoons R + CH_3X$$
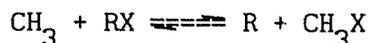
the reaction enthalpy change or the difference between the BDEs of CH_3X and R-X is given by

$$\Delta H = \Delta DH^{o}(X-CH_3/X-R) = DH^{o}(X-CH_3) - DH^{o}(X-R)$$
$$= \Delta\Delta_f H^{o}(RX/CH_3X) + \Delta\Delta_f H^{o}(CH_3/R) \qquad (14)$$

where

$$\Delta\Delta_f H^O(RX/CH_3X) = \Delta_f H^O(RX) - \Delta_f H^O(CH_3X) \tag{15}$$

$$\Delta\Delta_f H^O(CH_3/R) = \Delta_f H^O(CH_3) - \Delta_f H^O(R) \tag{16}$$

According to eq. (14), the slopes of the linear relations between $\Delta DH^O(X\text{-}CH_3/X\text{-}R)$ and V_x and $\Delta\Delta_f H^O(RX/CH_3X)$ and V_x are identical because $\Delta\Delta_f H^O(CH_3/R)$ is independent of V_x. The slopes are given by

$$b = -\frac{m}{0.67 + 0.21m} \tag{17}$$

A purely empirical equation for reproducing the BDEs of R-X bonds has been written as

$$DH^o(X\text{-}R) = DH^o(X\text{-}CH_3) - m \frac{6.33 + 0.36m - V_x}{0.67 + 0.21m} \tag{18}$$

This relation is very useful because the heats of formation of methyl radicals and methyl derivatives and the BDEs of methyl-X bonds have the best accuracy. The estimated values of BDEs based on eq. (18) are in parentheses in Table 13. For the 16 bonds involving ethyl-X and tert-butyl-X bonds, in Table 13, the average deviation between experimental and estimated values of ΔDH^O is 0.3 kcal/mol with a maximum deviation 0.9 kcal/mol. The two bonds with the maximum deviations are $C_2H_5\text{-}NH_2$ and t-$C_4H_9\text{-}Br$. As pointed out by Luo and Benson,[97] heats of formation of these two compounds have not yet been determined with better than $\pm$ 1 kcal/mol accuracy.

TABLE 13: DH^o(X-R), kcal mol^{-1} [209]

X ($\Delta_f H^o(X)^a$)	CH$_3$	C$_2$H$_5$	i-C$_3$H$_7$	t-C$_4$H$_9$
F	110.0			
(18.98)		(113.7)	(115.3)	(115.8)
OH	92.7±0.2	94.0±0.5		94.0±0.7
(9.4)		(94.3)	(94.6)	(94.3)
Cl	83.7±0.3	84.2±0.5		82.5±0.7
(28.99)		(84.1)	(83.7)	(82.8)
NH$_2$	86.5±0.3	85.6±0.5		84.7±0.7
(45.9±0.2)^b		(86.5)	(85.8)	(84.8)
Br	70.3±0.4	69.9±0.6		68.2±0.8
(26.74)		(69.7)	(68.6)	(67.3)
SH	74.6±0.6	73.5±0.7		70.1±0.9
(34.0±0.5)^c		(73.6)	(72.3)	(70.8)
I	57.1±0.4	55.7±0.6		52.6±1.0
(25.52)		(55.5)	(53.8)	(52.1)
CH$_3$	90.2±0.2	88.5±0.5		85.2±0.7
(35.1±0.1)^b		(88.5)	(86.8)	(85.1)
H	105.0±0.2	100.5±0.5		94.1±0.7
(52.10)		(100.5)	(97.0)	(94.1)

[a] From ref. 179. [b] From ref. 387. [c] From ref. 223.

In Table 13, the BDEs in the RX series are carefully compared. We can find three categories from Me to Et to i-Pr to t-Bu for R:

(1) Regular order

$$DH^o(X-Me) > DH^o(X-Et) > DH^o(X-i-Pr) > DH^o(X-t-Bu)$$
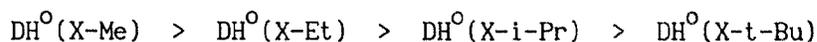
where $X = H$, CH_3, I, SH, Br and NH_2.

(2) Irregular order

$$DH^o(Cl-Me) < DH^o(Cl-Et) > DH^o(Cl-i-Pr) > DH^o(Cl-t-Bu)$$

and

$$DH^o(HO-Me) < DH^o(HO-Et) < DH^o(HO-i-Pr) > DH^o(HO-t-Bu)$$
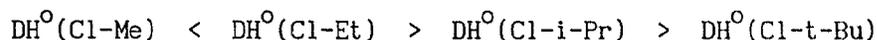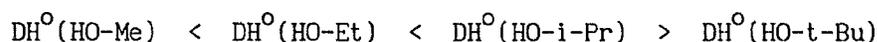
(3) Reverse order (estimated)

$$DH^o(F-Me) < DH^o(F-Et) < DH^o(F-i-Pr) < DH^o(F-t-Bu)$$
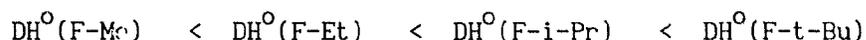
The data in Table 13 show that the location of the maximum BDE for X-R bonds is changeable, as shown in Table 14, and that it varies with the electronegativity of X. These interesting results have never previously been fully correlated.

TABLE 14: Place of Maximum and Minimum $DH^o(X-R)$ and the Classes

	Me		Et		i-Pr		t-Bu	classes
F	min	<		<		<	max	reverse
OH	min	<		<	max	>		irregular
Cl	min	<	max	>		>	min	irregular
NH_2	max	>		>		>	min	regular
Br	max	>		>		>	min	regular
SH	max	>		>		>	min	regular
I	max	>		>		>	min	regular
CH_3	max	>		>		>	min	regular
H	max	>		>		>	min	regular

One could also observe an irregular order if one took the higher values of the heats of formation of alkyl radicals, such as those from Gutman's group. As an example, for X = OH, using Gutman's values (See Table 8 or refs. 187-8), one would find

DH^{o}(HO-Me) DH^{o}(HO-Et) DH^{o}(HO-i-Pr) DH^{o}(HO-t-Bu)

93.0 ± 0.8 < 94.3 ± 0.8 < 95.6 ± 0.9 $\approx$ 95.7 ± 0.8

Some rules of the BDEs of R-X were analyzed by Griller and co-workers [178] three years ago. An unexpected result emerges when their table of BDEs is reorganized based in the order of the covalent potential, V_x. As shown in Table 15, the BDEs have an irregular order, as already reported. In Griller's work, heats of formation for methyl, ethyl, iso-propyl and tert-butyl were taken as 34.4, 28.0, 19.2 and 9.4 kcal/mol, respectively. Thus his values of BDEs are lower than those in this thesis.

Pacey and Wimalasena,[181] and Nicholas and Arnold [224] reported seven years ago the following order, unlike H-C bonds:

DH^{o}(HO-Me)   < DH^{o}(HO-Et)

Anyway, the three orders of the values of the BDEs are real, although only two orders have been proved by experiments. A new problem is how to understand the orders. All available theories, semiempirical and non-empirical, do not and cannot explain and predict these orders. To understand and describe them quantitatively is one of the targets in this thesis.

TABLE 15: The BDEs for Compounds R-X, based on Ref. 178, in kcal/mol [a]

X	H-X	Me-X		Et-X		i-Pr-X		t-Bu-X
F	136.3	108.3		107.9		108.3		
O-centered groups								
HO	119.3	92.0		93.6		93.8		93.5
HO_2	88.1							71.7
CH_3O	105.1	83.2	<	84.5	≈	84.2	>	82.0
$OC(O)CH_3$	105.9	83.2		84.5		84.7		
Cl	103.1	82.9	<	83.7	>	82.8	>	81.8
N-centered groups								
NH_2	107.4	84.2	>	83.6	>	83.4	>	82.6
Br	87.5	69.6		69.5		69.7	>	67.7
S-centered groups								
HS	90.1	73.0		72.2		70.5		68.7
CH_3S	91.8	77.6	>	76.4	>	75.0	>	72.6
PhS	82.0	67.9		66.4				
I	71.3	56.4	>	55.3	>	54.3	>	52.1
C-centered groups								
Me	104.3	88.8		87.4		85.7		84.0
Et	100.1	87.4		86.0		83.9		81.9
i-Pr	96.3	85.7		83.9		81.0		77.5
t-Bu	93.6	84.0		81.9		77.5		72.7
$c-C_5H_9$	95.5	84.9		83.4				
$c-C_6H_{11}$	95.5	85.3		82.9				
C_2H_3	103.0	93.0		91.4		89.2		87.3
C_3H_5	86.8	73.9	>	72.6	>	71.0	>	68.4
$PhCH_2$	87.9	75.1		73.9		72.6		
C_2H	129.6	122.2		120.5				
Ph	110.0	101.0		99.5		96.8		93.4
HC(O)	88.3	84.4		82.7		81.1		
$CH_3C(O)$	87.3	81.8		80.6		77 4		74.4
$C(O)OCH_3$	96.7	92.4						87.1
CN	125.3	118.2		114.9		112.8		109.2
Sn-centered group								
Me_3Sn	74.0	64.0	>	60.0	>	55.4	>	50.4
H	104.2	104.3	>	100.1	>	96.3	>	93.6

[a] $DH^o(R-F)$ are not considered here because the heats of formation of fluorides are unknown at present.

1.4.5 Correlations of Bond Dissociation Energies

(1) Evans-Polanyi Correlations

This is the most popular correlation. The correlated parameters may be activation energies, reaction enthalpies, rate constants (absolute, relative or competitive ones) or equilibrium constants. The correlation is useful and convenient, but not unambiguous for determining the BDEs. The usefulness, pitfalls and limitations of Evans-Polanyi relationships have been extensively tested.[156,165,168,170,179] Evans-Polanyi relationships are most reliable for interpolation only within a series of closely related compounds.

(2) Stretching Frequency Correlations

A linear correlation has been very recently proposed[225] between isolated stretching frequencies from IR and the BDEs of H-C bonds in hydrocarbons, fluorocarbons and CHO compounds. But the uncertainties in the correlation cannot be predicted and explained.

(3) Rotational Barrier Correlations

An empirical correlation has been reported[226] between C-H bond energies in molecules of the type RCH_2-H and the corresponding barriers to internal rotation about the $R-CH_2$ bonds. The barriers to internal rotation were determined in hydrocarbon solutions by ESR spectroscopic techniques.

(4) Substituent Constant Correlation

This topic will be addressed in Section 1.5.

1.4.6 Estimation of Bond Dissociation Energies

(1) Semenov and Szabo's Methods

About 40 years ago, Voevodskii[227] suggested a formula for estimating the BDEs of C-H bonds in hydrocarbons. It was described as

$$DH^o(C-H) = A + B\,\alpha^n \tag{19}$$

where A and B are constants, n is the number of carbon atoms between a methyl group and the bond in question, and α is the reduction factor per intervening atom.

Soon, the equation was rewritten by Semenov [156] as

$$DH^o(R-H) = D^o - V(R) \tag{20}$$

Semenov imagined that the process RX $\longrightarrow$ R + X occurs in two steps:

(1) The R - X bond breaks while maintaining in the radicals R and X the same distribution of electron density and the same atom spacing as in the molecule R - X. According to the rule of bond additivity, and within the approximation of this rule, the expenditure of energy is always the same D^o and does not depend on the structure of either R or X.

(2) The radicals R and X relax to their characteristic shape and electron distribution. The energy V(R) is thereby evolved, determined solely by the individual properties of R. The quantity V(R) was called the resonance energy of the 'free' electron in the radical: it characterized the energy of interaction of the 'free' electron with the electrons and nuclei of radical R.

Because the bond dissociation energy does not depend on its path, eq. (20) must apply.

Vedeneev and Voevodskii [228-9] used eq. (20) and the Evans-Polanyi relations for estimating the BDEs of H-R and Cl-R.

Szabo [158,230] made the following proposal. He postulated that the BDE of a bond between two atoms is influenced by the adjacent atoms and groups in a manner which can be expressed in the form of independent and constant contributions. Conventional basic values, D^o, and decrements for atomic and radical groups, V(R), were given. Szabo and Berces [231] suggested that the influence of neighboring atoms and radicals on BDEs is constant from one molecule to another.

(2) Sanderson's Method

Sanderson [36,39-40] offered an equation for estimating BDEs. It was presented as

$$DH^o(R_1-R_2) = CBE + E_R(1) + E_R(2) \qquad (21)$$

where CBE is the contributing bond energy which is only dependent on the two bonding atoms, and $E_R(i)$ is the reorganizational energy of the radicals and i is 1 or 2. The reorganizational energies are explained as the energies required when the free radicals rearrange to their most stable form. The reorganizational energy of a given radical was assigned as a constant. For example, the reorganizational energies of methyl, ethyl, iso-propyl and tert-butyl radicals were assigned to be 3.9, 2.0, 0.9 and -1.7 kcal/mol, respectively.

(3) The Challenge to Semenov, Szabo and Sanderson's methods

The constancy of V(R) is the core of Semenov, Szabo and Sanderson's theories. Benson and Shaw [232] first found that V(R) was dependent on the polarizability of R-X bonds. In other words, V(R) should not be a constant.

Egger and Cocks [164] evaluated critically the BDE data for more than 50J bonds. For hydrocarbons the ratio of $DH^o(R^+-X^-)/ DH^o(R-X)$ was dependent on X. They did not give any explanation.

A powerful challenge came from Ruchardt.[163] He found that the differences between $DH^o(Me-X)$ and $DH^o(R-X)$, as measures of the stabilization of R, were strongly dependent upon the nature of X and pointed out the importance of steric strain in the parent R-X molecules.

Nicholas and Arnold [224] developed the idea that electronic interactions between X and the alkyl groups, R, would vary as a function of alkylation in R and the electronegativity (EN) of X. On this basis, it follows that variations in the BDEs along the series, R-X, should be sensitive to the EN of X. But they did not answer which is the best

correlation with so many scales of EN.

Griller and co-workers [178] investigated this situation further for 29 X substituents. They found that for some X substituents such as halogen atoms, O- and N-centered radicals, the C-X bond decreased little or not at all along the radical series, but for others, particularly H, C- and Sn-centered radicals, the decrease was large. Holmes, Lossing and Maccoll said [190] that Griller's data did not support the suggestion that this difference in behavior is entirely a function of the EN of X.

As pointed out previously (See Section 1.4.4), the rules have become clear only after reorganizing Griller's table based on our new scale of EN, V_x. In Table 13, O, Cl, N and Br are atoms with higher or middle EN. But S, I, C, Sn and H are atoms with low EN. Consequently, they have different behaviors. Pauling's, Mulliken's, Allred-Rochow's, Sanderson's, and Gordy's scales of EN do not give good correlation with the BDEs of R-X bonds.

V(R) is not a constant, independent of the nature of X. It can be simply explained. On cleaving R-X bonds, R is affected by X, but X is also affected by R. The nature of R, clearly, should not be constant when X has been changed. As an example, it is impossible that the electron distribution is the same for the ethyl group in fluoroethane, chloroethane, bromoethane, iodoethane, ethanol or ethane. Since it is not, one cannot find a constant $V(C_2H_5)$. $V(C_2H_5)$ is a variable depending on the EN or the covalent potential of X.

1.4.7 Theoretical Calculations

(1) Ab initio calculations. [233] Hartree-Fock theory with any basis set gives poor results for the direct calculation of a homolytic BDE, as is widely recognized. The correlation energy correction for the electrons forming the bond is a significant fraction of the total bond energy. If

correlation is omitted, the errors will be greater for the bonded system R-X than for separated R and X, and calculated BDEs will be too small.

Very recently, Boyd and co-workers [234] studied the change in homolytic BDEs on conversion of A-B to A-B$^+$H using Moller-Plesset perturbation theory with the 6-31G** basis set. It was shown that protonation increases the C-N BDE in methylamine and that this observation can be explained in terms of Pauling's original ideas which lead to his EN scale. Thus, the EN difference in $CH_3-NH_3^+$ is greater than in CH_3-NH_2 and hence the bond is stronger. Conversely it was shown that decreasing the EN difference, by protonating the less EN atom, weakens the bond.

(2) Direct SCF calculations by Leroy. In Leroy's theory,[235-9,390-1] the BDEs are expressed as

$$DH^o(R-X) = E(C-X) + SE(RX) - SE(R) - SE(X) \tag{22}$$

where SE is the stabilization energy of the respective species, namely,

$$SE = \Delta_{at}H - \Sigma N_{AB} E_{AB} \tag{23}$$

in which the first term is the heat of atomization of the species under consideration; E and E_{AB} are standard bond energy terms, very similar to Laidler's terms,[240-1] derived from the heats of atomization of reference compounds. N_{AB} is the number of the bond energy terms. The total energies were calculated at the ab initio 6-31G RHF or UHF level, with full geometry optimization. They yielded very impressive results, reproducing some measured heats of formation of free radicals and predicting others still unknown.

(3) Semi-empirical calculations

Del Re and colleagues [243-4] developed a semi-empirical method for estimating the effective Hamiltonian, H_{eff}. They used some adjustable parameters in the calculation of charge distributions in the bonds. The calculated values of the BDEs were well related with values available in

the 1970's.

Dotdaev and Bopusov [245-6] calculated the atomization energies by a semi-empirical equation which is described as

$$\Delta_{at}H = \Sigma \; n_i(2-n_i)E_i \; - \; \Sigma \; n_i n_j \Delta_{ij} \tag{24}$$

where n_i is the number of bonds of a given type, and E_i and Δ_{ij} are semi-empirical parameters determined from the observed BDEs by means of least squares. The average deviation of the calculated BDFs from values available in the 1970's is $\pm$ 1.4 kcal/mol. But the deviations from the BDEs of CH_3-X bonds, where X = H, methyl, ethyl and OH, are as much as 5 or 9 kcal/mol.

1.4.8 Summary: the Factors Which Moderate the BDEs of Alkyl-X Ronds

A useful conclusion may be drawn from the empirical equation (18) and the above discussion. There are four factors which moderate the BDEs of alkyl-X bonds as follows:

(1) the electronegativity or the covalent potential of X, V_x;

(2) the degree of methyl substitution at the radical center, m;

(3) interactions between the radical center and distant atoms; and

(4) the steric compression relief due to bond cleavage.

A problem is how to quantitatively correlate the BDEs with the four factors. The problem has now been resolved within chemical accuracy. The new approach involves the electronegativity of the bonding atom in X plus the inductive effect and the steric effect. In our procedure, V(R), substituent constants and group electronegativities are not fixed. The new procedure will be described quantitatively in Chapters 3 to 7

1.5 Substituent Effect

Since Hammett's and Taft's equations were established, interest in understanding and predicting the effects of substituents on a variety of physical and chemical properties, sucn as spectra, equilibria, and

reactivities of organic molecules has continued unabated.[52-4,247-9] We must introduce this topic to understand the rules for the BDEs of alkyl-X bonds, where both R and X may be regarded as substituents.

1.5.1 Types of Substituent Effects

According to updated opinions,[52-4] substituent electronic effects are considered as four separate primary or principal effects:

(1) Electronegativity or the inductive effect;

(2) The field effect;

(3) The resonance effect; and

(4) The polarizability effect.

Parameterized scales for the four primary substituent effects have been presented.[52] The four types differ in their origin. Their symbols, transmission modes, whether or not significant substituent charge transfer occurs, the sign of the interaction energy and the relative range of the effects are indicated in Table 16.

TABLE 16: Four Types of Substituent Effects

Effect	Symbol	Transmission Mode	Substituent Transfer of Charge	Interaction Energy	Range
Electronegativity or Inductive	X	sigma-bonds	yes	stabilizing or destabilizing	short
Field	F	space (r^{-2})	no	destabilizing	long
Resonance (pi-electron transfer)	R	pi-bonds	yes	stabilizing (in an extended pi system)	long
Polarizability	P	space $(r^{-4} \text{ or } r^{-6})$	no	stabilizing	short

Various secondary effects can occur, but these four are the most important.

The features of each of the four primary types of substituent effects and the idealized interactions that cause them have been summarized as follows:[52]

(1) Electronegativity or the inductive effect

This effect originates from the partial ionic character of the sigma bond between the substituent and its bonding atoms in the molecular framework. The transmission occurs through the sigma bonds of the molecular framework. The interaction range is short, not operative beyond three bonds. There is transfer of charge from the substituent, either positive or negative sigma-electronic charge. The interaction energy is either stabilizing or destabilizing.

(2) The field effect

This effect originates from charge-charge, charge-dipole, or dipole-dipole interactions between the substituent, the polarized bonds of the framework, and the reaction or probe center. Its transmission occurs via a through-space electrostatic effect on the probe. Simple electrostatics now allows calculation of the expected effect. The range of the interaction energy is long (directly proportional to $1/r^2$), but no transfer of charge occurs from the substituent. The interaction energy is either stabilizing or destabilizing, depending on the sign of the charges or the dipole orientation.

(3) The resonance effect

This effect originates from pi-electron bonding and delocalization between the substituent and the framework. The transmission mode is through the pi-bonds of the framework and the probe center. The interaction range is long in an extended pi-electron system. There is transfer of pi-electronic charge to or from substituent. The interaction energy is pi-electron delocalization energy which only stabilizes molecules.

(4) The polarizability effect

This effect originates from charge-induced dipole or dipole-induced dipole interactions between the substituent and the reaction or probe center. The transmission mode is through space (with an effective dielectric constant, D). The interaction range is short, but there is no transfer of cnarge from the substituent. This effect drops off rapidly with distance, proportional to $1/r^4$ if the probe is charged, or $1/r^6$ if it is a dipole. The interaction energy can only stabilize molecules.

In general, tne substituent effects in aliphatic systems are described as the sum of the inductive and field effects, and those in aromatic systems as the sum of field, resonance and pi polarization effects. The systems to be studied herein are aliphatic. Here, R represents alkyls only

and there is no charge on X. Thus, there are also no charge-charge or charge-dipole, or dipole-dipole interactions. For this reason, the field, resonance and polarizability effects will not be considered in this thesis. The inductive effect is operative for the R-X system.

1.5.2 The Inductive Effect and Taft's Constants

The concept of the inductive effect was first introduced as a through-sigma-bond effect by Robinson[306] and Ingold.[307] The inductive effect originates in the difference in electronegativity between the substituent (or more accurately, the first attached atom of the substituent) and the carbon atom to which it is joined. The effect should thus be a function of the electronegativity of X. Such effects are transmitted by a progressive but diminishing relay of polar effects along a chain of carbon atoms depicted as

$$\overset{\delta-}{X} ---- \overset{\delta+}{CH_2} ---- \overset{\delta\delta+}{CH_2} ---- \overset{\delta\delta\delta+}{CH_2}$$
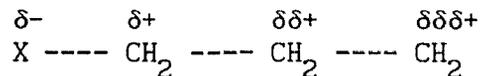
STO-3G calculations for 1-fluorobutane have given substituent-induced changes in electron populations at carbon atoms, as compared to butane itself, as shown in electron units below[52]

$$F ---- CH_2 ---- CH_2 ---- CH_2 ---- CH_3$$
$$0.208 \quad\quad 0.016 \quad\quad 0.000 \quad\quad 0.001$$
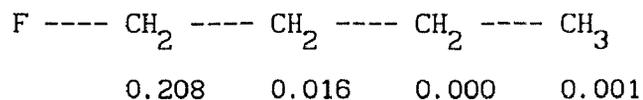
The charges on individual carbons were measured by ^{13}C-NMR chemical shifts.[250] It was shown that the inductive effect is rapidly attenuated so that a slight reversal of charge is apparent on successive carbons.

The magnitude of the inductive effects obviously depends on the number and length of the chains of atoms connecting the substituent to the probe site. While there is no theory for predicting the absolute magnitude of the sigma inductive effect in a given system, relative magnitudes in related systems have been predicted by eq. (1).[51]

$$\text{sigma inductive effect} \propto \sum_m P^n \tag{1}$$

where P is the propagator or transmission coefficient per bond, i.e., the decrease in magnitude of the sigma inductive effect from bond to bond along the molecular framework, n is the number of bonds between the substituent and the probe center, and m refers to the number of pathways for transmission of the sigma inductive effect. This formula should be equally applicable for sigma inductive effects on acidity, reactivity, nuclear magnetic screening constants, bond dissociation energies, etc.

The effect is difficult to detect experimentally beyond the first bond. There is no general agreement concerning the value of P. Values between 0.2 and 0.7 have been employed for carbon atoms of different hybridization, but most empirical values are near 0.4.[251,320]

Following a suggestion by Ingold, about 40 years ago Taft examined the difference between the substituent effects on base-catalyzed and acid-catalyzed esterification and ester hydrolysis. Taft's equation has been established since then. In general, Hammett- and Taft-like correlations are based on the so-called linear free energy principle (LFEP). If a member of a particular series is chosen as a reference, then, the substituent constants can be determined.[252-3] We can find various kinds of substituent constants.[101] These substituent constants are used to correlate with the energetic properties of molecular systems, such as Gibbs' free energy, various reaction enthalpies and energies (including homolytic and heterolytic BDEs), ionization potentials, equilibrium constants and rate constants, infrared frequencies and intensities, NMR chemical shifts, ESR results, charge densities and related properties.

Finding a correlation of Taft's constants, $\sigma(R)$, with acidity constants of the α-substituted acetic acids, XCH_2COOH, Taft then defined an

inductive substituent constant, $\sigma_I(R)$, which was related to $\sigma(XCH_2)$ by eq. (2).

$$\sigma_I(X) = 0.45 \; \sigma(XCH_2) \qquad\qquad (2)$$

Taft's constants used in this thesis are as shown in Table 17, from a review.[48] $\sigma_I(R)$ is probably a reliable measure of the substituent effect of group X relative to H.[254] Updated Taft's constants are available for many substituents.[379]

TABLE 17:   Taft's Constants of Some Alkyls [a]

R	$- \sigma(R)$	$-\sigma_I(R)$
H	$- 0.490$	0.000
Me	0.000	0.046
Et	0.100	0.055
n-Pr	0.115	0.058
i-Pr	0.190	0.064
n-Bu	0.130	0.060
i-Bu	0.125	0.064
s-Bu	0.210	0.068
t-Bu	0.300	0.074
n-Am	0.16	0.064
neo-Pt	0.165	0.065
t-Am	0.33	0.078

[a] From ref. 48.

1.5.3 Inductive Effects from MO Theory Calculations

It is difficult to conceive of an experimental method capable of measuring inductive effects directly, but recently a scale has been derived by Taft and co-workers[80] from ab initio MO calculations at the 6-31G*

level with geometry optimization. The inductive substituent constant, σ, defined as

$$\sigma = 1 - q_H \tag{3}$$

or [52-4]

$$\sigma = 2 [q_H(CH_4) - q_H(HX)] \tag{4}$$

where q_H is the excess electronic charge on hydrogen in compounds H-X and is a measure of the pure inductive effect of group X. This scale differs significantly from the experimental scale of Taft's constants.

1.5. Datta's Group Method for Estimating BDEs -- A New Failure

Very recently, Datta and Singh [374] tried to establish a scheme of group ENs by Pauling's thermochemical method. They found that the EN of t-butyl (2.65) was closer to that of methyl (2.68) than to those of ethyl (2.59) and i-propyl (2.54). This is an unexpected order for the inductive effect. As a general rule, every scale of EN based on observed BDEs should reproduce well the values of BDEs. However, Datta and Singh's scale of group EN cannot predict BDEs in organic compounds. The author has commented upon this work and has pointed out a basic reason for this new failure.[375]

In this author's opinion, one could not predict, explain and/or understand the rules of the BDEs for alkyl-X bonds with a single set of values of substituent constants for either groups X or R. The reason is very simple. You would only obtain one fixed order of substituent constants for groups X or R. But there are three orders for the BDEs, as pointed out in Section 1.4. This opinion has been accepted by Drs. Datta and Singh.[397]

From basic principles, the concepts of constant V(R), fixed substituent constants and fixed group EN are equivalent. In this thesis it is proposed to jump beyond this cycle and open up a new path by introducing a procedure with variable parameters.

1.6 Heterolytic Bond Dissociation Energies of Alkyl-X Bonds

1.6.1 Thermochemistry of Gas-Phase Ions

In the past 20 years, the progress in gas-phase ion chemistry has been dramatic, almost explosive.[255-61,279,407] Data on the thermochemistry of gaseous ions has been critically evaluated, presented and compiled.[262-6] Quantum chemical calculations of very high accuracy on the thermochemical properties of ions, especially small ions, have been published.[267-8] Two sets of empirical schemes for estimating ionization energies and/or heats of formation of organic molecular cations have been put forward.[266,269-72, 279] No simple method has been available so far, however, for estimating the heterolytic bond dissociation energies and heats of formation of alkyl cations.

For the thermochemistry of gas-phase ions, the following quantities are very important.

(1) The adiabatic ionization potential of a species, M, IP(M)

This is defined as the enthalpy change at 0 K in the ionization process, i. e.

$$M \longrightarrow M^+ + e \qquad (1)$$

$$IP(M) = \Delta_f H(M^+) + \Delta_f H(e) - \Delta_f H(M) \qquad (2)$$

where $\Delta H(e)$ is the heat of formation of an electron and will be discussed later.

(2) The electron affinity of a species, M, EA(M)

This is defined as the negative of the enthalpy change at 0 K for the electron attachment reaction:

$$M + e \longrightarrow M^- \qquad (3)$$

$$- EA(M) = \Delta_f H(M^-) - \Delta_f H(e) - \Delta_f H(M) \qquad (4)$$

(3) The proton affinities or gas-phase basicities of a species, M, PA(M)

This is the negative of the enthalpy change for the hypothetical protonation reaction:

$$M + H^+ \longrightarrow MH^+ \tag{5}$$

$$- PA(M) = \Delta_f H(MH^+) - \Delta_f H(M) - \Delta_f H(H^+) \tag{6}$$

The term proton affinity, as universally used, is a quantity defined at 298.15 K , not strictly analogous to the adiabatic ionization potential and electron affinity, which are the enthalpy changes at 0 K.

(4) Gas-phase acidity (or acidity) of species, AH.

The gas-phase acidity of a molecule AH, $\Delta_{acid}G(AH)$, is the Gibbs energy change for the reaction:

$$AH \longrightarrow A^- + H^+ \tag{7}$$

usually defined at 298.15 K . The enthalpy change of reaction 7, $\Delta_{acid}H$, is, of course, the proton affinity of the anion. From thermochemistry,

$$\Delta_{acid}H(AH) = \Delta_f H(A^-) + \Delta_f H(H^+) - \Delta_f H^o(AH)$$

or

$$= DH^o(A-H) - EA(A) + IP(H) \tag{8}$$

The Gibbs energy change of the reaction:

$$AH + B^- \longrightarrow BH + A^- \tag{9}$$

is called the relative acidity of species AH and BH.

(5) Hydrogen atom affinity of ions, RX^+, $HA(RX^+)$

This is the enthalpy change at 298.15 K for the reaction:

$$RXH^+ \longrightarrow RX^+ + H \tag{10}$$

From thermochemistry, the enthalpy change

$$\Delta H_{10} = HA(RX^+) = DH(RX^+-H)$$

$$= \Delta_f H(RX^+) + \Delta_f H(H) - \Delta_f H(RXH^+) \tag{11}$$

or

$$= IP(RX) + PA(RX) - IP(H) \tag{12}$$

(6) Appearance potential of ions, A^+, $AP(A^+)$

This is the enthalpy change at 298.15 K for the ionization reaction:

$$AB + e \longrightarrow A^+ + B + 2e \tag{13}$$
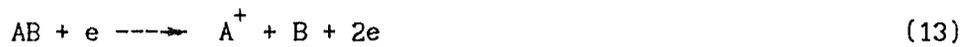
$$AP(M^+) = \Delta_f H(A^+) + \Delta_f H(B) + 2\Delta_f H(e) - \Delta_f H(AB) \tag{14}$$

The auxiliary thermochemical information required for any species is most often available only at 298.15 K. Thus, a rigorously correct treatment of heats of formation of ions requires explicit treatment of the differences in thermochemical values at 0 K and at higher temperatures.

There are two conventions for dealing with the thermochemistry of the electron, one used predominantly by thermodynamicists, for example in the JANAF Tables,[106] and one adopted by scientists studying ion physics and chemistry, for example in refs. 189 and 262-5. The thermodynamicists' convention, or (thermal) electron convention, defines the electron as a standard chemical element and treats its thermochemistry accordingly. The mass spectrometrists' convention, or stationary electron convention or ion convention, defines the electron as a sub-atomic particle. The enthalpy difference between quantities in these two definitions is 5RT/2, which is the integrated heat capacity of an ideal Boltzmann gas and equal to 1.481 kcal/mol at 298.15K. The values from the ion convention are lower for positive ions and higher for negative ions. In this thesis, the ion convention will be adopted.

Consider two thermochemical cycles

$$
\begin{array}{ccccc}
M_{0\ K} & \longrightarrow & M^+_{0\ K} & + & e_{0\ K} \\
\downarrow A & & \downarrow B & & \downarrow C \\
M_{298\ K} & \longrightarrow & M^+_{298\ K} & + & e_{298\ K}
\end{array}
$$

and

$$
\begin{array}{ccccc}
M_{0\ K} & +\ e_{0\ K} & \longrightarrow & M^-_{0\ K} \\
\downarrow A & \downarrow C & & \downarrow D \\
M_{298\ K} & +\ e_{298\ K} & \longrightarrow & M^-_{298\ K}
\end{array}
$$
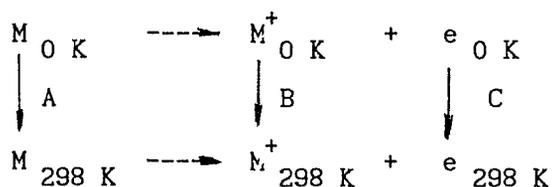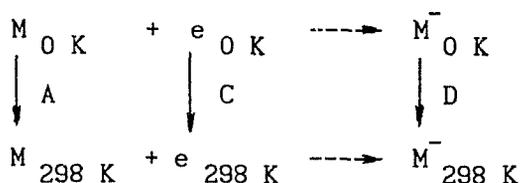
where A, B, C and D are the integrated heat capacities for the various indicated species. Under the ion convention C = 0 and we have

$$\Delta_f H(M^+)_{298} = \Delta_f H(M)_{298} + [IP(M) + B - A] \qquad (15)$$

$$\Delta_f H(M^-)_{298} = \Delta_f H(M)_{298} + [- EA - A + D] \qquad (16)$$

It has been shown from Lias and Ausloos's analysis [274] that (1) there will be no discernible differences between the translational and rotational heat capacities of M and M^+; (2) that differences arising from a splitting of degenerate energy levels in multiplet ground states of M or M^+ will never be larger than 0.009 ev (or 0.21 kcal/mol), and (3) when the frequency of a particular vibration changes upon ionization, there will be a difference between the integrated heat capacities of M and M^+. However, even the latter contribution will usually be sufficiently small that a significant error will be not be introduced if it is ignored. For example, the lowest ionization potential of ethylene corresponds to removal of an electron from the C-C pi bond, which leads to a lowering of the frequency of the symmetric C-C stretch from 1623 to 1230 cm^{-1} and a reduction in the frequency for the twisting motion around the C-C bond from 1027 to 430 cm^{-1}. Although these differences in vibrational frequencies are significant, the predicted effect on the enthalpy of ionization at 298.15 K is to raise it above the value for the adiabatic ionization potential by only 0.0069 ev (or 0.16 kcal/mol). Only the most accurate experimental measurements would detect an increment of this size. Consequently, the simplifying assumption that

$$A = B = D \qquad (17)$$

will not introduce significant errors in the heats of formation of species at 298 K. Then we have

$$\Delta_f H^o(M^+) = \Delta_f H^o(M) + IP(M) \qquad (18)$$

$$\Delta_f H^o(M^-) = \Delta_f H^o(M) - EA(M) \qquad (19)$$

This means that to determine heats of formation of gas-phase ions is equivalent to finding ionization potentials and electron affinities. This applies for molecules, atoms and free radicals.

Using eqs. (18) and (19), data for free radicals important in this thesis have been calculated. They are listed in Tables 18 and 19.

TABLE 18: Thermochemistry of R and R^+ [a]

R	$IP(R^+)$ [b]	$\Delta_f H^o(R)$ [c]	$\Delta_f H^o(R^+)$
	(ev)	(kcal/mol)	(kcal/mol)
CH_3	9.84 ± 0.01	35.1 ± 0.1	262.0 ± 0.3
C_2H_5	8.13	28.4 ± 0.4	215.9 ± 1.0
$i\text{-}C_3H_7$	7.36 ± 0.02	20.0 ± 0.5	189.7 ± 0.7
$t\text{-}C_4H_9$	6.70 ± 0.03	9.9 ± 0.6	164.4 ± 1.0

[a] The conversion factors for energies are 1 ev = 23.06 kcal/mol = 96.48 kJ/mol; 1 kcal/mol = 4.184 kJ/mol. The IP and EA and heats of formation and the BDE are usually reported in ev and kcal/mol, respectively. [b] From ref. 189. [c] See Table 13 in Section 1.4.

TABLE 19: Thermochemistry of X and X$^-$

X	EA(X$^-$)^a	$\Delta_f H^O(X)^b$	$\Delta_f H^O(X^-)$
	(ev)	(kcal/mol)	(kcal/mol)
F	3.399$\pm$0.003	18.98	-59.4$\pm$0.1
OH	1.828	9.4	-32.8$\pm$0.1
Cl	3.617$\pm$0.003	28.99	-54.4$\pm$0.1
NH$_2$	0.75$\pm$0.06	45.9$\pm$0.2	28.6$\pm$1.5
Br	3.365$\pm$0.003	26.74	-50.9$\pm$0.1
SH	2.32$\pm$0.10	34.0$\pm$0.5	-19.5$\pm$2.4
I	3.059	25.52	-45.0$\pm$0.1
CH$_3$	0.08$\pm$0.03	35.1$\pm$0.1	33.3$\pm$0.8
H	0.754209	52.10	34.71$\pm$0.01

^{a} From ref. 189. ^{b} See Table 13 in Section 1.4.

1.6.2 Data on Some Heterolytic Bond Dissociation Energies

Based on equation (4) in Section 1.1 and Tables 18 and 19, the values of some heterolytic BDEs have been calculated and are listed in Table 20.

These are the fundamental data needed to establish a new approach to heterolytic BDEs in Chapter 4.

1.6.3 Bond Homolysis and Heterolysis Energies in Solution

The electron donor and acceptor properties of a molecule in the gas phase are characterized by its ionization potential and electron affinity. However, these properties are not directly relevant to the liquid phase where solvation of ions becomes important. The solution analogues of the ionization potential and electron affinity of a molecule are the electrochemical oxidation and reduction potentials [275-6] which, for the vast majority of persistent molecules, are easily measured by standard

techniques.

Some correlations for solution thermochemistry of molecules, radicals, and ions have been found.[193,277-8,329,389,400] These interesting topics will not be discussed because they go beyond the scope of this thesis.

TABLE 20: Heterolytic Bond Dissociation Energies, $DH^o(X^--R^+)$, in kcal/mol[a]

| X^- | R^+ | | | |
	CH_3^+	$C_2H_5^+$	$i-C_3H_7^+$	$t-C_4H_9^+$
F^-	258.5±0.6			
		(228.8)	(206.6)	(191.9)
OH^-	277.4±0.4	239.4±1.1	222.0±0.8	206.3±1.1
		(239.6)	(222.2)	(206.6)
Cl^-	227.2±0.4	188.3±1.1	169.9±0.8	153.6±1.2
		(188.2)	(170.0)	(153.9)
NH_2^-	296.1±1.5	255.8±1.7	238.3±1.6	221.9±1.7
		(256.7)	(238.2)	(222.0)
Br^-	219.6±0.5	179.8±1.1	162.6±1.0	145.1±1.1
		(179.6)	(160.8)	(144.2)
SH^-	248.0±2.5	207.5±2.7	188.4±2.6	171.1±2.7
		(207.5)	(188.5)	(171.8)
I^-	213.5±0.5	172.7±1.2	154.3±1.3	136.6±1.3
		(172.5)	(153.0)	(136.1)
CH_3^-	315.3±0.9	274.2±1.3	255.1±1.2	237.9±1.3
		(274.2)	(254.7)	(237.8)
H^-	314.5±0.4	270.6±1.1	249.4±0.8	231.2±1.1
		(270.6)	(249.4)	(231.2)

[a] The values in parentheses are estimated (See Section 4.1).

1.7 Thermochemistry of Gas-Phase Molecular Cations

The thermochemistry of gas-phase molecular cations includes two important quantities : the adiabatic ionization potentials and heats of formation. In general, heats of formation of odd-electron molecules are known well. We have

$$\Delta_f H^o(RX^+) = IP(RX) + \Delta_f H^o(RX) \qquad (1)$$

Ionization potentials of molecules and heats of formation of molecular cations are complementary quantities, just like the relationship between the heats of formation of radicals and the BDEs of R-X bonds.

In general, the experimentally-determined IPs display widely varying uncertainties, ranging from 0.0001 to 1 eV.[189] For polyatomic systems, IPs can be measured with good accuracy, 0.05 eV, only with the aid of specialized apparatus.[409] Acceptable IPs values, c. 0.1 to 0.2 eV, may be obtained using conventional analytical mass spectrometers, but their use for the measurement of appearance potential is generally highly unsatisfactory, giving results which may be in error by up to 0.5 eV.

1.7.1 Ionization Potentials of Organic Molecules

Within the past ten years, reliable information on ionization potentials of neutral molecules has become available.[189] Chemists, of course, seek relationships between IPs and molecular structures.

Levitt and Widing [48,376] showed that IPs of n-alkanes and haloalkanes were linear functions of Taft's inductive substituent constant or a revised scheme, calculated from the structure of the alkyl group according to delocalization, inductive and field effects. The author has tested their functions. The average deviations are always larger. Secondly, these functions cannot be extended to more compounds.

Better correlations were obtained by four French chemists. Bachiri,

I

Mouvier, Carlier and DuBois [309] advanced a scheme for estimation of the ionization potentials of alkenes, alkynes, aldehydes, ketones, alcohols, ethers, mercaptans and thioethers. Their empirical equation took the form:

$$\log \frac{IP(R_1 X R_2) - IP^*}{IP_o - IP^*} = 0.106[I(R_1) + I(R_2)] \qquad (2)$$

Here X is a functional group, such as $-CH=CH-$ or $>C=CH_2$ for alkenes, $-O-$ for alcohols and ethers, $-C=O$ for aldehydes and ketones and so on; R_1 and R_2 are the attached alkyl groups; IP_o is the ionization potential of the reference compounds for which R_1 and R_2 are H atoms; IP^* is a constant for each type of compound.

This complex empirical correlation has been modified recently. [310] The modification can be written as:

$$\log \frac{IP(RX) - IP(RX)^*}{IP(R_o X) - IP(RX)^*} = \Phi(R) \qquad (3)$$

Here X is the substituent, $IP(R_o X)$ and $IP(RX)^*$ represent the IPs for the initial and limiting member of a suitable set of 1-substituted alkanes and Φ is a universal function of the alkyl group R. Eqs (2) and (3) work well, except when X represents hydrogen or halogen atoms. Note that eqs. (2) and (3) do not lend themselves to a simple graphical representation. [311]

Holmes and Lossing [269-72,279,311] have found that the IP is a function of the total number, N, of atoms in a molecule. Here N represents simply the molecular size. They have pointed out that a straight line results when the IPs for a homologous series are plotted against the reciprocal of N. The equation of the straight line is given by

$$IP(RX) = A + B/N \qquad (4)$$

However, there are some interesting exceptions for methane and methyl chloride, in which N = 5.

1.7.2 Heats of Formation of Molecular Cations

Holmes's group has advanced two schemes for estimating the heats of formation for homologous series.

The first is a logarithmic function with two parameters:

$$\Delta_f H^O(RX^+) = A + B \log N \qquad (5)$$

Here A and B are constants for the series.

The second is a reciprocal function with four parameters:

$$\Delta_f H^O(RX^+) = A + BN + C/N + Dn_b \qquad (6)$$

Here A, B and C are constants derived from the experimental data for any particular series without branched structures. The last term in eq. (6) is necessary for correction of chain-branching effects.

Holmes and Lossing emphasized that the A + BN part of the eq. (6) is analogous to the thermochemical additivity system of Benson et al. (See Section 1.3.3), which accurately reproduces the linear decrease in $\Delta_f H(RX)$ with increasing size of homologue. The third term, C/N, on the right side of eq. (6) reflects the fact that IP is not linear in molecular size, but falls at a decreasing rate (See eq. (4)).

In general, eq. (6) works well when the steric effect in molecules is negligible. We will discuss this problem in Chapter 7. Holmes' equation will be improved by considering steric effects.

Chapter II Theoretical Support for the Covalent Potential

2.1 Introduction

Contrary to expectations, the covalent potential, the simplest scale of EN, gave the least scatter and the highest correlation coefficient for heats of formation of alkyl derivatives,[96,97,144] ionization potentials[280] and Lewis acid strengths.[305] The new scale has also been used very satisfactorily for estimating group parameters,[131] heats of formation of silicon-containing compounds,[145-7] and ho⟩ ⟨tic bond dissociation energies.[209] In this thesis, it has been extenued to the propagator of the sigma inductive effect (See Chapter 3.), to heterolytic bond dissociation energies (See Chapter 4.), to bond energies of silicon compounds (See Chapter 5.), and to a theoretical model of bond cleavage. (See Chapter 6.) When it was used to correlate with homolytic and heterolytic bond energies, the agreement of most estimated values with experiment was within experimental accuracy (± 1 kcal/mol). The covalent potential was also used by Walsh[312] to correlate the divalent state stabilization energies of SiX_2. Surprisingly, the simplest scale always gave the best results. Is there any reason for this ?

The author has found that a powerful theoretical support for the new scale of electronegativity comes from the absolute electronegativity theory of Parr an⟩ ⟨Pearson,[12,330] Firstly, the dimension of V_x is energy divided by charge, (See page 23) like electronegativity in Parr and Pearson's theory. Secondly, the value of n_x/r_x is a "global" atomic property, which is consistent with Parr and Pearson's theory. Thirdly, the value of n_x/r_x is dependent on the valence state, charge and ligand number of the central atom. This means it is general, as is Parr and Pearson's theory. The fourth and most important point, will be discussed in Section

2.2.

2.2 V_x: a Measure of the Valence-State EN

First, we have found there are good linear correlations between V_x and Parr's electronic chemical potential, μ, and the central electrostatic potential, V_Q, at r_μ, for the 21 free atoms of main-group 'ements listed in ref. 33, as shown in Fig. 2. Here μ was calculated as the Mulliken electronegativity of a ground state atom,

$$\mu = X_M = (IP + EA)/2 \tag{1}$$

where IP and EA are the ionization potential and the electron affinity, respectively; r_μ is the radial distance at which the total electrostatic potential, $V(r_\mu)$, of a ground-state atom exactly equals its chemical potential, μ. V_Q is defined as Q/r_μ, where Q is the total electronic and nuclear charge inside a sphere of radius r_μ. The correlation coefficients have been determined, as shown in the second-last column of Table 21.

Table 21: Correlation Coefficients for Linear Relations Between Measures of Electronegativity for 21 Main Group Elements.[a]

	ground-state in atoms		valence-state in molecules	
	μ	V_Q	V_x	X_M
ground-state μ	1	.985	.964	.931
V_Q		1	.967	.945
valence-state V_x			1	.989
X_M				1

[a] μ and V_Q are from ref. 33; V_x, from ref. 96; X_M, from ref. 20.
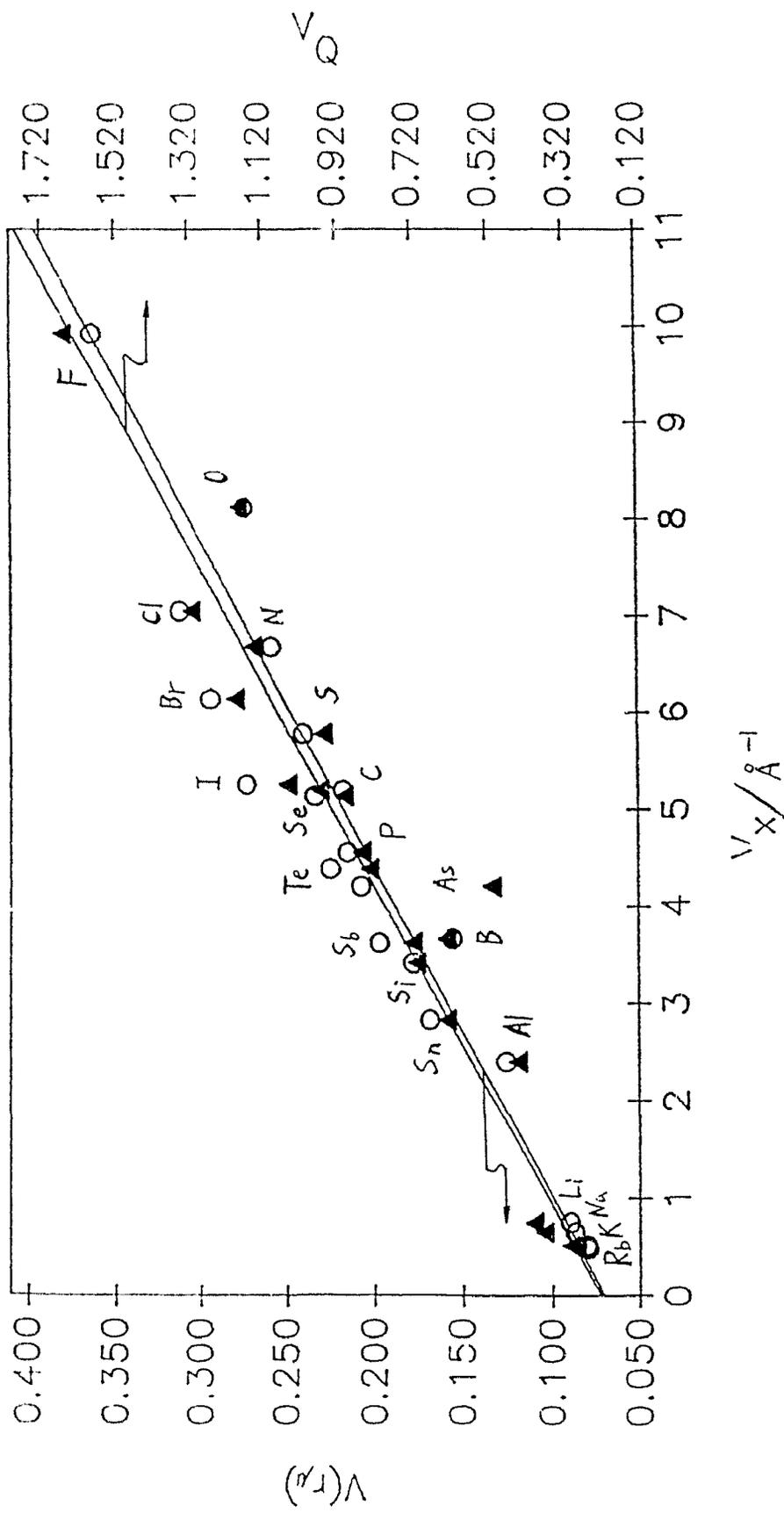
Fig. 2:

Relation between V_x and $V(r_\mu)$ and V_Q

A close linear relation between r_μ and the covalent radius has been noted previously.[33,313,332] Mulliken's scale of electronegativity, μ, for free atoms in the ground-state was found to be strongly correlated with V_Q.[33]

Any atom in a molecule is in its energetically optimum valence state, not in the free ground state. Unfortunately, this important fact has not been remembered by many chemists who studied electronegativity.[396] The covalent radius is a particular measure of the size of an atom in a molecule[313] and is thus a valence state property. Consequently, the covalent potential, V_x, should be a most basic parameter for the contribution of atoms to molecular properties.[305,378]

The parameters, μ, $V(r_\mu)$, r_μ and V_Q of atoms in valence states have been too difficult so far to calculate by absolute electronegativity theory. But valence-state ionization potentials, electron affinities and Mulliken electronegativities have recently been calculated[20] by the semi-empirical method of Hinze and Jaffe.[22] According to absolute electronegativity theory, the inherent valence-state Mulliken electronegativity scale, X_M, the valence-state electronic chemical potential, μ, and Huheey's parameter, a,[63-4], are all approximately the same.

We have calculated the correlation coefficients for linear relations between four measures, μ, V_Q, V_x and X_M, of electronegativity for the 21 main group elements considered in ref. 33. They are listed in Table 21 on page 91.

It is interesting to note in Table 21 that the two ground-state measures, μ and V_Q, correlate well with each other, but less well with the valence-state measures, V_x and X_M.
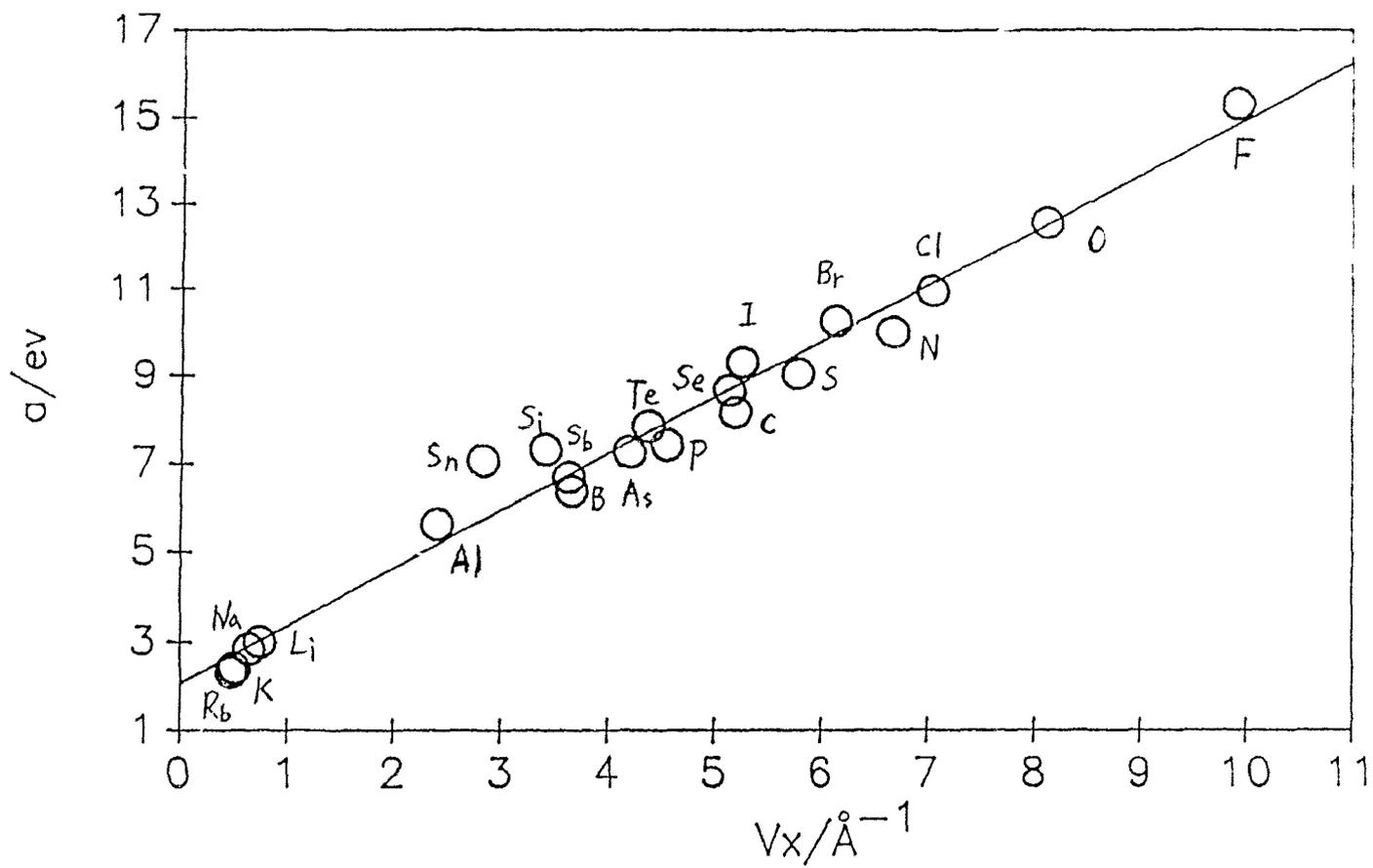
Fig. 3:

Relation between V_x and Chemical Potentials at the Valence States

The simple V_X is strongly linked with X_M, as shown in Figure 3; the correlation coefficient is 0.989. This comparison means the new scale, V_X, is theoretically reasonable and a good measure of the valence-state electronegativity. This explains the good correlations between V_X and bonding properties.

Parr and Pearson's absolute electronegativity theory is sophisticated and Hinze and Jaffe's method is advanced. Our new scale is not only theoretically reasonable and scientifically useful, but it is also so simple that beginning chemistry students know the two parameters, n_X and r_X. Based on previous work [96,97,131,144-7,209,280,305,312] and this work the authors [105] predict that there is a good possibility (a) of using the new scale to simply correlate energetics of polyatomic systems, and (b) of introducing and teaching the new scale in introductory classes.

Chapter III Homolytic Bond Dissociation Energies of Alkyl X Bonds

In Section 1.4.4, an empirical equation for the BDEs for $X-C(CH_3)_m H_{3-m}$ was introduced, that is

$$DH^o(X-C(CH_3)_m H_{3-m}) = DH^o(X-CH_3) - m \frac{6.33 + 0.36m - V_x}{0.67 + 0.21m} \quad (1)$$

This equation provides a convenient manner of estimating the homolytic BDEs of X-R bonds.

For the next-nearest methyl substituent effect on the homolytic BDEs of alkyl-X bonds, the following approximation is suggested by most chemists:[116,162,189,344,352]

$$DH^o(X-alkyl) \approx DH^o(X-C(CH_3)_m H_{3-m}) \quad (2)$$

Is this approximation acceptable? Is the next-nearest methyl substituent effect on homolytic BDEs negligible within experimental uncertainty? The approximation has not been investigated in detail in previous work. We have now found that the number of next nearest neighbours affects homolytic BDEs in a systemic manner. If eq. (2) is acceptable homolytic BDEs of alkyl-X bonds may be estimated well using only two equations, i.e. eqs. (1) and (2). Therefore, this work will be of significance for the prediction of homolytic BDEs.

3.1 Inductive Effect

In physical organic chemistry, the inductive or electronegativity effect refers to the influence of substituents through bonds on equilibria and rates of reactions. According to updated theory,[52-4,247-9,251] the inductive effect is one of four primary electronic effects. Others are field, resonance and polarizability effects. The four effects have different propagation or transmission modes, interaction energies and ranges. For example, in the inductive model, the influence of a substituent

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is propagated by successive polarization through the bonds along the molecular framework. In both of the field and polarizability models, the substituent influences are propagated by the electrostatic field through space. The system in our work is alkyl-X, in which there is only one substituent. We postulate that the inductive effect is the most prominent. This will proved intuitive advantages.

When the steric effect is negligible and the popular concept of inductive propagation with additivity is accepted, the BDE(X-R) can be described by the following equations:[156]

$$DH^o(X-CH_3) = D^o(X-C) - 3\ V_{C-H}$$
$$DH^o(X-C_2H_5) = D^o(X-C) - 2\ V_{C-H} - 3\ V_{C-H}P_{X-C} \qquad (3)$$
$$DH^o(X-i-C_3H_7) = D^o(X-C) - V_{C-H} - 2\ 3\ V_{C-H}\ P_{X-C}$$
$$DH^o(X-t-C_4H_9) = D^o(X-C) - 3\ 3\ V_{C-H}\ P_{X-C}$$

where $D^o(X-C)$ is a constant which depends only on the type of X-C bond, V_{C-H} represents the effect caused by an adjacent, C-H bond and P_{X-C} is the propagator or the transmission coefficient for X-C bond. The contribution, V_{C-C}, from a homonuclear bond, C-C, has been assumed to be zero. The three parameters, $D^o(X-C)$, V_{C-H} and P_{X-C}, are all unknown. Eq. (3) may be replaced by a simple equation:

$$DH^o(X-R) = DH^o(X-CH_3) + m\ V_{C-H}\ (1 - 3\ P_{X-C}) \qquad (4)$$

Clearly, an important behavior may be predicted from eq. (4)

$$DH^o(X-CH_3) > DH^o(X-R) \qquad \text{if } P_{X-C} > 1/3$$
$$DH^o(X-CH_3) = DH^o(X-R) \qquad \text{if } P_{X-C} = 1/3 \qquad (5)$$
$$DH^o(X-CH_3) < DH^o(X-R) \qquad \text{if } P_{X-C} < 1/3$$

Comparing eqs. (1) and (4) , we derive

$$P_{X-C} = \frac{1}{3} + \frac{6.33 + 0.36m - V_x}{3\,V_{C-H}\,(0.67 + 0.21m)} \qquad (6)$$

In fact, there is only one independent variable among the three unknown parameters, D^o(X-C), V_{C-H} and P_{X-C}, in eq. (3).

Assignment of any of the three parameters in eq. (3) can exactly reproduce the values of the BDEs fitted by eq. (1). If chemical significance is to be obtained, the three parameters cannot be assigned arbitrarily. In Chapter 6, we will find that D^o(X-C) can be determined from the valence-state energy for sp^3 hybridization of a carbon atom. Using eq. (3) and the observed value of DH^o(X-CH$_3$),[209] we obtain

$$V_{C-H} = [D^o(X-C) - DH^o(X-CH_3)_{obs}]/3 \qquad (7)$$
$$= 14.0 \text{ kcal/mol}$$

Consequently, the P_{X-C} may be calculated from eq. (6). In other words, eq. (3) can be used to estimate the BDE of X-R bonds.

The P_{X-C} of 36 bonds have been calculated using eq. (6) for various values of m and V_x. The values are listed in Table 22. The values vary from 0.246 to 0.441. The average value for hydrocarbons is 0.40. The average value for all compounds in Table 22 is 0.36. Many chemists would accept that propagators in organic compounds are about 0.2 to 0.7 [251] or 0.3 to 0.5.[320] The average value is near 0.4.[251,320] Thus eq. (6) is acceptable.

Eq. (4) is a function of the same variables as eq. (1). However, eq. (1) is purely empirical. Eq. (4) is a semi-theoretical expression in which the empirical terms are partially replaced by terms which may be related to the inductive effect. Eq. (4) demonstrates that the number of next nearest methyl groups affects C-X BDEs in a systematic fashion which can be predicted.

TABLE 22: P_{X-C} Calculated from eq. (6) with $V_{C-H} = 14.0$ kcal mol^{-1} [a]

| X | V_X | P_{X-C} | | |
		m =1	m = 2	m = 3
F	9.915	.246	.271	.287
OH	8.11	.295	.310	.321
Cl	7.04	.324	.334	.340
NH_2	6.67	.334	.342	.347
Br	6.13	348	.353	.357
SH	5.77	.358	.361	.363
I	5.25	.372	.373	.373
CH_3	5.19	.374	.374	.374
PH_2	4.55	.391	.388	.386
SiH_3	3.41	.422	.413	.407
GeH_3	3.27	.426	.416	.409
H	2.70	.441	.428	.420

[a] The values are taken from ref. 96.

3.2 Group Language and Heats of Formation of Higher Alkyls

Benson's group additivity rule for estimating thermochemical properties of organic and organometallic compounds has been widely adopted.[116-7,119,131] The additivity rules have been extended to free radicals.[165,289] There are two questions to be discussed. Firstly, the values of the group parameters for free radicals should be updated. Secondly, the reliability of the application of the group additivity rule to alkyl radicals should be re-examined.

First, using the group language and eq. (1), we obt...in

$$\Delta_f H^o(C(CH_3)_m H_{3-m}) = \Delta_f H^o(CH_3) + (0.9 - 1.5m(m-1))$$

$$- m \frac{6.33 + 0.36m}{0.67 + 0.21m} \qquad (8)$$

This implies that heats of formation of C_2H_5, $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$ radicals are only a function of m, independent of V_x, as expected. We will report that relations similar to eqs.(1) and (8) are good for the heterolytic BDEs of X-R bonds and the ionization potentials of the prototypical radicals.

TABLE 23: The Group Parameters of Carbon-Centered Radicals

Group	$\Delta_f H^o$ / kcal mol^{-1}	
	updated	old [a]
[C-(C)(H)$_2$]	38.5±0.4	35.8
[C-(C)$_2$(H)]	40.2±0.5	37.5
[C-(C)$_3$]	40.1±0.6	38.0

[a] From ref. 135.

Substituting the heat of formation of methyl into eq.(7), we have

$$\Delta_f H^o[C-(C)_m(H)_{3-m}] = 36.0 + m (11.58 - 1.5m - \frac{6.33 + 0.36m}{0.67 + 0.21m}) \qquad (9)$$

Values estimated from equation (9) are listed in Table 23. In Table 23 old values dating from 1973 [165] are listed for comparison. The updated values, in general, are 2.1 to 2.7 kcal/mol greater than the old ones.

Second, let us discuss the heats of formation of higher alkyl radicals by means of the concept of the inductive effect.

An attractive advantage of group additivity is that it includes second order interactions. This method works well for stable organic compounds and for C_2H_5, $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$ radicals. For radicals with more complicated

structures, such as C-Ċ-C-C and C-Ċ(C)-C-C, it is necessary to consider whether third and higher order interactions are significant. The group additivity rule, of course, will work well if those interactions are small.

The order of interactions we take during the dissociation of X-R bonds is as shown in Fig. 4(a). Here arrows indicate the direction and magnitude of the electron shifts or of the propagation of the inductive effect.

The first order interaction is the strongest. The second order interaction is less. By analogy, the third order should be weak and the fourth order, weaker. Using this principle, we will estimate the BDEs of X-alkyl bonds in straight chain molecules first.

For normal alkyls, as shown in Fig. 4(b), the BDEs can be described by

$$DH^o(X-CH_3) = D^o(X-C) - 3\ V_{C-H}$$

$$DH^o(X-C_2H_5) = D^o(X-C) - 2\ V_{C-H} - 3\ V_{C-H}\ P_{X-C}$$

$$DH^o(X-n-C_3H_7) = D^o(X-C) - 2\ V_{C-H} - 2\ V_{C-H}\ P_{X-C} - 3\ V_{C-H}\ P_{X-C}\ P_{C-C}$$

$$DH^o(X-n-C_4H_9) = D^o(X-C) - 2\ V_{C-H} - 2\ V_{C-H}\ P_{X-C} - 2\ V_{C-H}\ P_{X-C}\ P_{C-C} -$$
$$- 3\ V_{C-H}\ P_{X-C}\ P_{C-C}\ P_{C-C} \tag{10}$$

$$DH^o(X-n-C_5H_{11}) = D^o(X-C) - 2\ V_{C-H} - 2\ V_{C-H}\ P_{X-C} - 2\ V_{C-H}\ P_{X-C}\ P_{C-C} -$$
$$- 2\ V_{C-H}\ P_{X-C}\ P_{C-C}^2 - 3\ V_{C-H}\ P_{X-C}\ P_{C-C}^3$$

The above equation may be expressed by a generalized one:

$$DH^o(X-R) = D^o(X-C) - V(R) \tag{11}$$

or

$$DH^o(X-R) = DH^o(X-CH_3) + [V(CH_3) - V(R)] \tag{12}$$

For all R

$$V(R) = \sum_{i>2} N_{CH}\ V_{C-H} \prod_{(i-2)} P_k \tag{13}$$

where i is the number associated with the interaction, that is, first order, second order, etc.; N_{CH} is the number of C-H bonds at the ith position, k is the type of given bonds.

$$X - \xi - C_1 \Longleftarrow C_2 \Longleftarrow C_3 \longleftarrow C_4 \dashleftarrow C_5$$

Ist   2nd   3rd   4th

$$X - \xi - C + C + C + C +$$
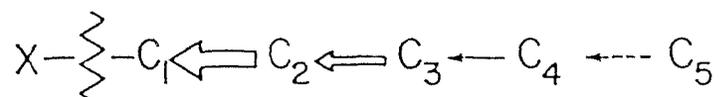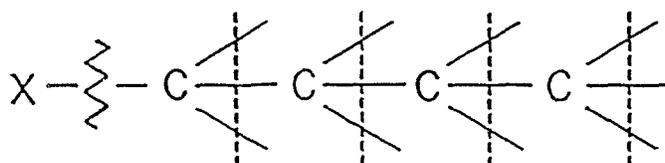
i = 0   1   2   3   4

Fig. 4:

The Interaction Orders

Now we can estimate the BDEs of bonds involving higher alkyl radicals because all of the terms in eqs. (10) to (12) are known and available.

Our interest is to study the influence of the second and higher order interactions on the BDEs of alkyl-C bonds by means of the concept of the inductive effect. From the inductive effect, the difference between $DH^O(X-CH_3)$ and $DH^O(X-C(CH_3)_m H_{3-m})$ represents the contribution from the second order interaction or the influence of the methyl group at the β-position. It has been described in eq. (1). From F with high electronegativity to H with low electronegativity, the effect of the first methyl, i.e. $DH^O(X-methyl) - DH^O(X-ethyl)$, varies between -3.7 to 4.5 kcal/mol; the effect of three methyls, i.e. $DH^O(X-methyl) - DH^O(X-t-butyl)$, varies between -5.8 to 10.9 kcal/mol, as shown in Table 13. For each methyl in t-butyl, the average value is -1.9 to 3.6 kcal/mol. Clearly, these values are of great importance to chemical reactions.

The difference between $DH^O(X-C(CH_3)_m H_{3-m})$ and $DH^O(X-C(CH_3)_{m-1}(CH_2 CH_3)H_{3-m})$ or the influence of a methyl at the γ-position comes from the third order interaction. Using the above-mentioned model, the difference is given by

$$\Delta DH^O = V_{C-H} \ (3 \ P_{C-C} - 1) \ P_{X-C}$$
$$= 0.42 \ (for \ F) \ to \ 0.75 \ (for \ H) \ kcal/mol \qquad (14)$$

The average value is 0.6 kcal/mol. Compared with the second order effect, it is a small, positive quantity.

The difference between $DH^O(X-C(CH_3)_{m-1}(CH_2 CH_3)H_{3-m})$ and $DH^O(X-C(CH_3)_{m-1}(CH_2 CH_2 CH_3)H_{3-m})$ or the influence of a methyl at a δ-position comes from the fourth order interaction. Based on the above model, the difference may be described as:

$$\Delta DH^O = V_{C-H} \ P_{C-C} \ (3 \ P_{C-C} - 1) \ P_{X-C} = 0.16 \ to \ 0.28 \ kcal/mol \qquad (15)$$

This is less than the uncertainty in most experimental values. The difference between $DH^O(X-C(CH_3)_{m-1}(CH_2CH_2CH_3)H_{3-m})$ and $DH^O(X-C(CH_3)_{m-1}(CH_2CH_2CH_2CH_3)H_{3-m})$ comes from the fifth order interaction or the influence of a methyl at the ε-position. The difference is given by

$$\Delta DH^O = V_{C-H} \, P_{C-C}{}^2 \, (3 \, P_{C-C} - 1) \, P_{X-C} = 0.0 \text{ to } 0.1 \text{ kcal/mol} \qquad (16)$$

It is negligible. These results are consistent with the popular idea that inductive effects fall off rapidly with distance and are generally thought to be exhausted with three bonds. The idea has been supported by ^{13}C NMR studies of paraffinic hydrocarbons.[350] It was also supposed[351] that the regular BDEs for alkyl-X bonds decrease with the increase of the n-alkyl chain length. But, in the absence of important steric effects, further increases of the chain length will not significantly affect the BDEs of alkyl-X bonds.

From most experiments in gas- or liquid-phase chemical kinetics, the uncertainty is about 1 to 2 kcal/mol or more. Therefore it may be considered that all influences of methyl groups at the γ-, δ- and ε-positions on the BDEs of alkyl-C bonds could be negligible. For example, it is usually assumed that

$$DH^O(X-C_4H_9) \approx DH^O(X-n-C_3H_7) \approx DH^O(X-C_2H_5)$$

and

$$DH^O(X-s-C_4H_9) \approx DH^O(X-i-C_3H_7)$$

We are, therefore, faced with the choice of accepting one of the three following assumptions: (1) methyl effects at the γ-, δ-, and ε-positions are neglected, as done by B. son,[116,165] Seetula and Gutman,[344] Tsang[352] and Holmes and co-workers;[189] (2) methyl effects at the γ-position only are considered; (3) methyl effects at all positions are considered. The BDEs of alkyl-X bonds may be correspondingly described as:

(1) $DH^o(X\text{-alkyl})_{est} \approx DH^o(X\text{-}C(CH_3)_m H_{3-m})$ (17)

or

$= \Delta_f H^o(X) + \Delta H^o[C\text{-}(C)_m(H)_{3-m}] - \Delta_f H^o[C\text{-}(X)(C)_m(H)_{3-m}]$ (17a)

(2) $DH^o(X\text{-alkyl})_{est} = DH^o(X\text{-}C(CH_3)_m H_{2-m}) - 0.6\ \gamma$ kcal/mol (18)

(3) $DH^C(X\text{-alkyl})_{est} = DH^C(X\text{-}C(CH_3)_m H_{3-m}) -$ all interactions (19)

Here γ is the number of carbon atoms or alkyl substituents at the γ-position in the alkyl, and γ = 0, 1, 2 or 3. Two terms in eq. (17a) can be known from Table 23 and ref. 116.

The three choices can be expressed by means of Benson's group language, that is, we have three different paths to estimate the heats of formation of higher alkyl radicals. They may be described as:

(1) $\Delta_f H^o(alkyl)_{est} \approx \Delta_f H^o(alkyl)_{GA}$ (20)

(2) $\Delta_f H^o(alkyl)_{est} = \Delta_f H^o(alkyl)_{GA} - 0.6\ \gamma$ kcal/mol (21)

(3) $\Delta_f H^o(alkyl)_{est} = \Delta_f H^o(alkyl)_{GA} +$ all higher interactions (22)

Here the subscript "GA" means this term is from the values estimated by Benson's group additivity rule.

Eqs.(18) and (21) express a small correction (about 0.6 to 1.8 kcal/mol) to Benson's group additivity rules for the third order inductive effect. This second assumption (or eqs. (18) and (21)) is a compromise. However, we will still accept the first assumption, that is eqs. (17) and (20). There are two important reasons. First, the observed uncertainty of most kinetic, mass-spectrometric and other experiments is $\pm$ 1 to 2 kcal/mol or more. Second, heats of formation of most alkyl radicals have been studied rarely, as shown in Tables 11 and 12. The accuracy of the experimental evidence is not yet sufficient to support a change to the potentially more accurate eqs. (18) and (21).

In general, Benson's group additivity rules with steric corrections for alkyl radicals are acceptable to within 1 to 2 kcal/mol. For example,

the BDEs of primary, secondary and tertiary C-H bonds may be taken as 100 ± 1, 97 ± 1 and 94 ± 1 kcal/mol, respectively. The heats of formation of many alkyls have been estimated by group additivity rules and have been compared with observed values, as shown in Table 29 in Chapter 4. The reliability of the application of group additivity rules, or eqs (17) and (20), to alkyl radicals is good.

3.3 Bond Dissociation Energies for R-C, R-N and R-O Bonds

As pointed out in eq.(4), P_{X-C} is a function only of m and V_x when V_{C-H} has been fixed. The bonding atom in carbon-centered groups, such as CH_3, C_2H_5, $i-C_3H_7$, $t-C_4H_9$, other alkyls, CN, CH_3CO and RCO, is carbon. Those groups have the same P_{X-C} for a given X and m. For oxygen-centered groups, such as OH, OCH_3, OR, ONO and ONO_2, and nitrogen-centered groups, such as NH_2, NHR, NR_1R_2, NO and NO_2, there are two other sets of values of P_{X-C}. This suggests that the BDEs should follow similar patterns. Consider the observed values of the BDEs of R-C, R-N and R-O bonds in Table 24. Heats of formation of the compounds are taken from refs. 102, 106, 169, 170, and 176. The estimated BDEs, which are in parentheses, are from eq. (3). As predicted, the estimated and observed BDEs of R-C, R-N and R-O bonds are in good agreement.

TABLE 24: BDEs of R-C, R-N and R-O Bonds, kcal mol^{-1} [a]

group center	X	CH$_3$	C$_2$H$_5$	i-C$_3$H$_7$	t-C$_4$H$_9$
	CH$_3$	90.2±0.2	88.5±0.5	87.2±0.6	85.2±0.7
	(35.1±0.1)		(88.5)	(86.8)	(85.1)
	C$_2$H$_5$	88.5±0.5	86.8±0.5	85.1±0.8	82.8±1.0
	(28.4±0.4)	(88.5)	(86.8)	(84.3)	(81.8)
C –	CN	121.5±2.1	120.1±0.7	118.4±0.7	114.5±0.8
	(104±2)		(119.8)	(118.1)	(116.4)
	CH$_3$CO	81.2±0.5	79.7±0.6	76.9±0.7	73.6±0.8
	(-5.8±0.4)		(79.5)	(77.0)	(74.5)
	OH	92.7±0.2	94.0±0.5	94.5±0.6	94.0±0.6
	(9.4)		(94.3)	(94.6)	(94.3)
O –	ONO	59.1	60.5	59.8	58.8
	(7.9±0.2)		(60.7)	(60.2)	(59.1)
	i-C$_3$H$_7$O	82.9±0.6		83.9±0.8	83.0±1.6
	(-12.4±0.5)		(84.5)	(83.2)	(82.9)
	H$_2$N	86.5±0.3	85.6±0.5	85.9±0.6	84.7±0.7
	(45.9±0.2)		(86.5)	(85.9)	(84.8)
N –	ON	40.9±0.9		38.9±3.1	35.5-41.0
	(21.6)		(40.0)	(39.3)	(38.3)
	O$_2$N	60.8±0.4	60.8±0.6	61.2±0.8	60.1±0.8
	(7.9±0.2)		(60.8)	(60.1)	(59.1)

[a] $\Delta_f H^o$ of free radicals, listed under X, are from refs 149, 176 and Table 13.

3.4   X = SiH$_3$, GeH$_3$ and PH$_2$

Luo and Benson[209] did not estimate BDE(X-R), where X = SiH$_3$, GeH$_3$ and PH$_2$, because data for heats of formation of these compounds RX were not available. From the concept of the inductive effect, eq. (3) is valid for more compounds wherein X = SiH$_3$, GeH$_3$ and PH$_2$. Therefore, we may estimate the the BDEs for X-R from those of X-CH$_3$, as shown in Table 25.

TABLE 25: Estimated BDEs of Si-C, Ge-C and P-C Bonds, in kcal mol^{-1}

	CH$_3$	C$_2$H$_5$	i-C$_3$H$_7$	t-C$_4$H$_9$
SiH$_3$ (46.1±1)	88.5±1.5[a]	84.8	81.8	79.1
GeH$_3$ (52.1±1.2)c	82.6[b]	78.7	75.7	73.1
PH$_2$ (33.3)d	73.0±2.5[b]	70.6	68.4	66.4

[a] Observed value from refs.103 and 147.   [b] Based on ref. 144.   [c] Ref. 348.
[d] Ref. 349.

The heats of formation of these compounds, further, may also be estimated. Based on the definition of the BDE and eq. (4), we have

$$\Delta_f H^o(RX) = \Delta_f H^o(CH_3 X) - \Delta_f H^o(CH_3) + \Delta_f H^o(R) - m\, V_{C-H}(1 - 3\, P_{X-C}) \quad (23)$$

The estimated values of $\Delta_f H^o(RX)$ have been listed in Table 26.

TABLE 26: Heats of Formation of Si-, Ge- and P-Containing Compounds

(in kcal mol^{-1})

|	CH$_3$	C$_2$H$_5$	i-C$_3$H$_7$	t-C$_4$H$_9$
SiH$_3$	-7.0±1.0[a]	-10.0	-15.4	-22.8
GeH$_3$	4.6±2.0[b]	1.8	-3.6	-11.1
PH$_2$	-4.6±1.5[b]	-8.9	-15.1	-23.2

[a] Observed value from refs. 103 and 147.   [b] Based on ref. 144.

The heats of formation of these compounds, of course, can also be estimated by the group additivity rules. The group parameters were estimated in ref. 131. Clearly, both results should be identical. There, $\Delta_f H^o$ of the terminal groups Si-(C)(H)$_3$, Ge-(C)(H)$_3$ and P-(C)(H)$_2$ are recommended in our work as -3.1, 14.5 and 5.5 kcal, respectively. The thermochemistry of silicon compounds will be discussed in Chapter 5.

3.5 Discussion

In eq. (3), D^o(X-C) is an interesting quantity related to the so-called "valence state energy".[114,285] We will discuss it in Chapter 6 when we try to establish a new model of the bond dissociation process. In this way, the original ideas of Semenov,[156] Szabo,[158] and Sanderson[36,39,40] will be updated and the work of Luo and Benson[209] will be extended from methyl-, ethyl, -isopropyl and -tertbutyl bonds to methyl-alkyl bonds and alkyl- alkyl bonds. Thus, the new parameters will enrich our understanding of the strong interaction in homolytic cleavage processes.

The substituent effect for the classical alkyls has been studied by MO theory.[233] Recently, the atomic charge densities on the hydrogen atom in compounds HR, where R = CH$_3$, C$_2$H$_5$, i-C$_3$H$_7$ and t-C$_4$H$_9$, have been calculated by means of ab initio MO calculation at the 6-31G* level with geometry optimization.[80] The order of charge density found was

$$CH_3 > C_2H_5 > i\text{-}C_3H_7 < t\text{-}C_4H_9$$
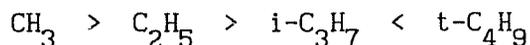
Clearly, this order does not correlate with that of the BDEs for H-R bonds.

The perturbation method has been applied to study the inductive effect.[286] The predicted changes in bond energies for a series , such as X-CH$_3$, X-C$_2$H$_5$, X-i-C$_3$H$_7$ and X-t-C$_4$H$_9$, were predicted to be monotonic. This prediction is not supported by the data on the chlorides in Table 13. It has also been suggested[286-7] that replacing H by a more electronegative

substituent would strengthen and shorten the other bonds in the molecule. Thus replacing H by CH_3 should strengthen X-C bonds. We see in Table 13 that this is true for HO-C bonds, but not for the bonds lower in the Table. A semi-theoretical calculation[274] showed a different result. For X = H, I, Cl and F, the BDEs of X-C bonds were predicted to always decrease in the order R = CH_3 > C_2H_5 > $i-C_3H_7$ > $t-C_4H_9$. Clearly, this result is not now in agreement with experiments.

Larson, Epiotis and Shaik[288] discussed bond energies in terms of a competition between overlap or resonance contributions and inductive effects. The $t-C_4H_9$ radical would be capable of less overlap with the orbitals of X than would the CH_3 radical, because the frontier orbital in the former case is less strongly focused on the central carbon atom. On the other hand, $t-C_4H_9$ has a lower ionization energy and is thus more electropositive. It would form a more polar bond (and hence a stronger bond) with OH but a less polar, and weaker, bond with H. These two factors could predict behavior qualitatively similar to that recorded in Table 13. However, the method cannot explain the irregular order observed with the chlorides or alcohols, where the maximum BDE occurs for C_2H_5 or $i-C_3H_7$.

Chemists like to use so-called "substituent constants", e. g. Taft's constant,[48] and "group electronegativities" to describe chemical processes. However, the traditional idea of a fixed substituent constant is not tenable. The concepts of a fixed substituent constant, a constant V(R) and a fixed group electronegativity, in fact, are related. They are all at a similar level of approximation and correlate with each other very well. None of them can explain all the trends now observed in the homolytic and heterolytic BDEs.

As we have seen, any theory based on substituent constants or group electronegativities cannot explain and predict the three orders of the

BDEs. The method we take is different from the traditional one. We accept the concept of a "fixed" substituent constant and group electronegativity. The propagator of the inductive effect should a variable, not a constant. It can be simply explained. For cleaving X-R bonds, R is affected by X, but X is also affected by R. The nature of R, clearly, is not a constant when X has been changed. In other words, the idea of fixed substituent constants and group electronegativities has its limitations. This opinion has been supported and demonstrated.[397]

A few research groups,[163,178,224,232] in fact, have already pointed out the limitations of such concepts. In mathematical form, Semenov and coworkers[156] found eq. (11) 30 years ago. They took P_{X-C} as a constant and estimated $V(R)$. They also found a linear relation between $V(R)$ and the substituent constant. Soon afterwards, Szabo[158] also used eq. (6) for estimating BDEs. Semenov and Szabo suggested that $V(R)$ was practically independent of the nature of the substituent X.

After a few years, Benson and Shaw[232] pointed out that $V(R)$ is not only dependent on R, but is also dependent on the polarity of X-C bonds. The idea of a constant $V(R)$ for a given R has been challenged many times. Ruchardt,[163] Arnold,[224] Griller[178] and coworkers found $V(R)$ should be sensitive to the electronegativity of X. Nobody, however, has given a quantitative method to estimate the relationship between $V(R)$ and X. Therefore, estimation of BDEs has been an unresolved problem. Today, the problem of X-alkyl bonds is approaching a resolution.

Chapter IV Heterolytic Bond Dissociation Energies of Alkyl-X Bonds

In this chapter, we will discuss heterolytic cleavages. We will find that methods similar to those in ref. 209 and Chapter 3 are suitable to study heterolytic BDEs. A few simpler methods for estimating the ionization potentials of alkyl radicals and heats of formation of alkyl cations and heterolytic BDEs of X-alkyl bonds will be established.

4.1 Reproduction of the Heterolytic BDEs of Alkyl-X Bonds

As shown in Section 1.6, heats of formation of positive and negative ions and heterolytic BDEs of alkyl-X bonds have been calculated and are listed in Tables 18-20, respectively. Here we will try to find methods of reproducing them.

Following the path of ref. 209, we will study the enthalpy change in the displacement reaction below

$$CH_3^+ + RX \quad \text{------→} \quad R^+ + CH_3X \tag{1}$$
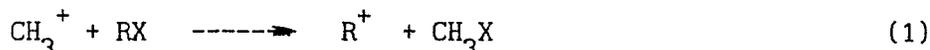
The enthalpy change or the difference in the heterolytic BDEs of X-R and X-CH_3 is given by

$$
\begin{aligned}
- \Delta H_1 &= \Delta DH^o(X^--CH_3^+ \, / \, X^--R^+) = \\
&= DH^o(X^--CH_3^+) - DH^o(X^--R^+) \\
&= \Delta\Delta_f F^o(RX/CH_3X) + \Delta\Delta_f H^o(CH_3^+ \, /R^+)
\end{aligned}
\tag{2}
$$

where

$$\Delta\Delta_f H^o(RX/CH_3X) = \Delta_f H^o(RX) - \Delta_f H^o(CH_3X) \tag{3}$$

$$\Delta\Delta_f H^o(CH_3^+/R^+) = \Delta_f H^o(CH_3^+) - \Delta_f H^o(R^+) \tag{4}$$

Substituting eq. (18) in Section 1.6 into eq. (2), we obtain

$$
\begin{aligned}
\Delta DH^o&(X^--CH_3^+ \, /X^--R^+) = \\
&= \Delta\Delta_f H^o(RX/CH_3X) + \Delta\Delta_f H^o(CH_3/R) + \Delta IP(CH_3^+/R^+) \\
&= \Delta DH^o(X-CH_3/ \, X-R) + \Delta IP(CH_3/ \, R)
\end{aligned}
\tag{5}
$$

where

$$\Delta DH^{o}(X-CH_3/X-R) = DH^{o}(X-CH_3) - DH^{o}(X-R)$$

$$= \Delta\Delta_f H^{o}(RX/CH_3X) + \Delta\Delta_f H^{o}(CH_3/R) \qquad (6)$$

$$\Delta\Delta_f H^{o}(CH_3/R) = \Delta_f H^{o}(CH_3) - \Delta_f H^{o}(R) \qquad (7)$$

$$\Delta IP(CH_3/R) = IP(CH_3) - IP(R) \qquad (8)$$

For $R = C(CH_3)_m H_{3-m}$, some good linear relations between $\Delta\Delta_f H^{o}(RX/CH_3X)$ and V_X have been described in Section 1.3. Clearly, three linear relations are expected between $\Delta DH^{o}(X^- - CH_3^+/X^- - R^+)$ and V_X because $\Delta\Delta_f H^{o}(CH_3/R)$, $\Delta\Delta_f H^{o}(CH_3^+/R^+)$ and $\Delta IP(CH_3/R)$ are all independent of the nature of X. This important relationship is the starting point in this Chapter.

TABLE 27: The Relation between $\Delta DH^{o}(X^- - CH_3^+/X^- - R^+)$ and V_X

|		$\Delta DH^{o}(X^- - CH_3^+/X^- - R^+)$, kcal/mol		
X	$V_X{}^{a}$	$R = C_2H_5$	$R = i-C_3H_7$	$R = t-C_4H_9$
F	9.915			
OH	8.11	38.0±1.2	55.4±0.9	71.1±1.2
Cl	7.04	38.9±1.2	57.3±0 9	73.6±1.3
NH$_2$	6.67	40.3±2.3	57.8±2.2	74.2±2.3
Br	6.13	39.8±1.3	57.0±1.2	74.5±1.3
SH	5.77	40.5±3.7	59.6±3.7	76.9±3.7
I	5.25	40.8±1.3	59.2±1.4	76.9±1.4
CH$_3$	5.19	41.1±1.6	60.2±1.5	77.4±1.6
H	2.70	43.9±1.2	65.1±0.9	83.3±1.2

^{a} From Table 2.
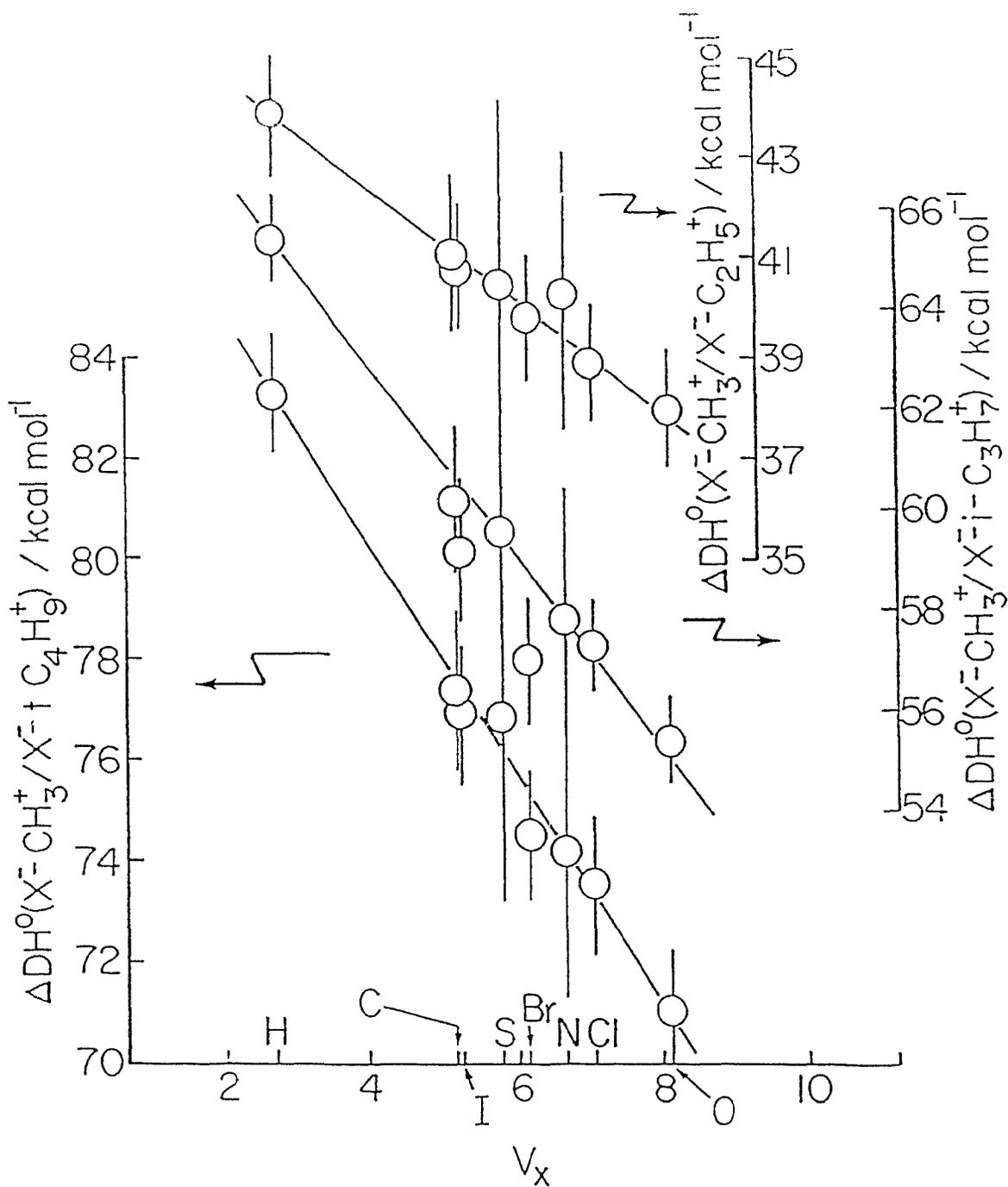
Fig. 5:

Relation between $\Delta DH^o(X^--CH_3{}^+/X^--R^+)$ and V_x

Based on the heterolytic BDEs in Table 20, the differences in the heterolytic BDEs, $\Delta DH^O(X^--CH_3^+/X^--R^+)$ have been calculated and are listed in Table 27. In Fig. 5, it can be seen that $\Delta DH^O(X^--CH_3^+/X^--R^+)$ and V_x are linearly related. The values of the intercepts and the slopes for the lines are in Table 28. According to eq. (5), the linear relations between $\Delta DH^O(X^--CH_3^+/X^--R^+)$ vs. V_x, $\Delta DH^O(X-CH_3/X-R)$ vs. V_x and $\Delta\Delta_f H^O(RX/CH_3X)$ vs. V_x must have the same values of the slopes. The slope equation is as follows

$$S_m = -m/(0.67 + 0.21m) \tag{9}$$

As shown in Sections 1.3 and 1.4 in Table 28 below, the estimated and observed values of the slopes derived from eq. (9) are in excellent agreement with each other. The following equation has been fitted to the intercepts in Fig. 5.

$$I_m = S_m f^+(m)$$

$$= \frac{m}{0.67 + 0.21m} f^+(m) \tag{10}$$

where

$$f^+(m) = 27.91 + 2.38m + 11.07/m \tag{11}$$

The estimated and observed values of the intercepts have been compared in Table 28. They are also consistent.

TABLE 28: Values of the Intercepts (I_m) and Slopes (S_m) in Fig. 5

m and R	I_m/kcal mol^{-1}		S_m/kcal A mol^{-1}	
	exptl	est.(eq.10)	exptl	est.(eq.9)
R = $C(CH_3)_m H_{3-m}$				
m = 1, CH_3CH_2	47.0±0.8	47.0	-1.14±0.04	-1.14
m = 2, $(CH_3)_2CH$	70.1±0.8	70.1	-1.84±0.04	-1.83
m = 3, $(CH_3)_3C$	89.4±0.8	89.4	-2.30±0.04	-2.30

In summary, we have found the purely empirical equation below, which is similar to eq. (18) in Section 1.4, for reproducing the heterolytic BDEs of alkyl-X bonds, where R is ethyl, iso-propyl and tert-butyl.

$$DH^o(X^--R^+) = DH^o_o(X^--CH_3^+) - m \frac{f^+(m) - V_x}{0.67 + 0.21m} \quad (12)$$

The experimental values for the methyl radical, the methyl cation and methyl derivatives, such as $\Delta_f H^o(CH_3)$, $IP(CH_3^+)$, $\Delta_f H^o(CH_3X)$ and $DH^o(X-CH_3)$ have been determined experimentally with very high precision. So, equation (12) can be used to estimate the heterolytic BDEs of R-X bonds. Values estimated using eq. (12) were listed in parentheses in Table 20 on page 86. As can be seen, the estimated BDEs are in agreement with those calculated directly from experiments within their uncertainties. The average deviation for all 24 bonds is only ± 0.3 kcal/mol with a maximum deviation of 1.8 kcal/mol for Br-i-C_3H_7. Luo and Benson [97] pointed out that the experimental uncertainties of $\Delta_f H^o(C_2H_5NH_2)$, $\Delta_f H^o(i-C_3H_7Br)$, $\Delta_f H^o(i-C_3H_7I)$ and $\Delta_f H^o(t-C_4H_9Br)$ are larger than the quoted values.

4.2 Estimations of the IPs of Alkyl Radicals and Heats of Formation of Alkyl Cations

Equation (5) is of importance to our discussion. Substituting eq. (1) in Chapter 3 and eq.(12) into it, we have

$$IP(R^+) = IP(CH_3^+) - m \frac{21.58 + 2.02m + 11.07/m}{(0.67 + 0.21m) 23.06} \quad (13)$$

where the IP is in ev. The IPs of R, where R = $C(CH_3)_m H_{3-m}$, are only a function of m.

The values of the IPs of larger alkyl radicals are listed in Table 29. Estimation of the IPs of these alkyls is an unresolved problem. Thus we have tried to find a new method for estimating the IPs of alkyl radicals.

TABLE 29: Values of the IPs and Heats of Formation of Alkyl Radicals and of Heats of Formation of Alkyl Cations

Radicals or Cations	γ^+	IP/eV obs.[a]	est.[b]	$\Delta_f H^o$/kcal mol^{-1} R rev.[a]	est.[c]	R$^+$ rev.[a]	est.[d]
C$^+$		9.84±0.01		34.8±0.3		261.3±0.4	262.0
Primary							
C-C$^+$		8.13	8.13	28	28.4	215.6±1.0	215.9
C-C-C$^+$	1	8.09±0.01	8.07	24.0±0.5	23.4	211	209.5
C-C-C-C$^+$	2	8.02	8.01	18	18.4	(203)	203.1
C-C-C-C-C$^+$	3	(7.85)	7.95	13	13.4	(194)	196.7
C-C-C-C-C-C$^+$	4	7.92±0.06	7.89	8	8.4	(191)	190.3
C-C-C-C-C-C-C$^+$	5		7.83		3.4	(183)	184.0
C-C-C$^+$ / C	2	7.93	8.01	16	16.4	(199)	201.1
C / C-C-C$^+$ / C	3	7.88±0.05	7 95	8	8.8	(190)	192.1
C-C-C-C$^+$ / C	3		7.95		12.2		195.5
C-C-C-C$^+$ / C	3		7.95		12.2		195.5
Secondary							
C-C$^+$-C		7.36±0.02	7.36	21.0±0.7[f]	20.0	190.9	189.7
C-C$^+$-C-C	1	7.25±0.02	7.30	15.9±0.7[g]	15.0	183	183.3
C-C$^+$-C-C-C	2	(7.1); 7.41	7.24	12	10.0	(175)	177.0
C-C-C$^+$-C / C	2		7.24		8.9	(176)[e]	175.9
C-C-C$^+$-C-C	2		7.24		10.0		177.0
C-C$^+$-C-C-C-C	3	7.0	7.18	7	5.0	(168)	170.6
C-C-C$^+$-C-C-C	3		7.18		5.0		170.6

C-C⁺-C-C-C-C-C 4 (6.95) 7.12 0.0 (162) 164.2

Tertiary

C-C⁺-C C		6.70	6.70	11.6±0.8[f]	9.9	165.8	164.4

C-C⁺-C
    C   6.70   6.70 11.6±0.8[f] 9.9 165.8 164.4

C-C⁺-C-C
    C   1 6.65 6.64 6.5 5.7 158±1 158.8

C-C⁺-C-C-C
    C   2 6.58 0.8±2.0[h] 0.7 152 152.4

C-C-C⁺-C
    C C   2 6.58 -0.5 150 151.2

C-C-C⁺-C-C
      C   2 6.58 1.5 152 153.2

C-C⁺-C-C-C-C
    C   3 6.52 -4.3 147 146.1

C-C-C⁺-C-C
    C-C   3 6.52 -2.7 150.6 147.7

C-C⁺-C-C-C
    C   C   3 6.52 -5.5 148.4 144.9

     C
C-C⁺-C-C
    C C   3 6.52 -6.6 144.5 143.8

C-C⁺-C-C-C-C-C
    C   4 6.46 -9.3 139 139.7

C-C⁺-C-C-C-C
C-C-C   5 6.40 -13.5 133 134.1

[a] from ref. 189, unless noted. The values in the parentheses have not been established or evaluated, see ref. 4. [b] Estimated based on eqs.(14) or (15). [c] Including the gauche correction. [d] Estimated based on eq. (16). [e] Estimated in ref. 295. [f] From Tables 11 and 12.

The resulting empirical equation for estimating the IPs of all alkyl radicals is very simple. Following eq. (13), we obtain

$$IP(\text{alkyl radical}) = IP(CH_3) - m \frac{21.58 + 2.02m + 11.07/m}{(0.67 + 0.21m)\ 23.06} - 0.06\ \gamma^+ \quad (14)$$

or

$$= IP(C(CH_3)_m H_{3-m}) - 0.06\ \gamma^+ \quad (15)$$

where γ^+ is the total number of carbon atoms at and beyond the γ-position, relative to the radical center. We have introduced the term in γ^+ in order to account for higher order interactions in cations. The factor, 0.06 eV, was found to give the best fit to the most accurate IPs. The values estimated using eq. (15) have been compared with the updated observed ones in Table 29.[189] The average deviation is only 0.05 eV for 14 alkyl radicals.

So, the heats of formation of alkyl cations are given by

$$\Delta_f H^o(\text{alkyl cation})_{est} = \Delta_f H^o(\text{alkyl})_{est} + 23.06\ IP(C(CH_3)_m H_{3-m}) -$$
$$- 1.4\ \gamma^+\ \text{kcal/mol} \quad (16)$$

The estimated values have also been listed in the last column of Table 29. They are in good agreement with values from a recent compilation.[189] The average deviation is 1.3 kcal/mol for 25 alkyl radicals.

From thermochemistry, thus, the heterolytic BDEs of all X-alkyl bonds can be estimated:

$$DH^o(X^- - R^+)_{est} = \Delta_f H^o(\text{alkyl cation})_{est} + \Delta_f H^o(X^-) - \Delta_f H^o(RX) \quad (17)$$

Here the first term on the right is estimated from eq. (16), and the other two terms are taken from experimental results. Values estimated by eq. (17) have been listed in Table 30 for the special case where X is hydrogen. The estimates are in good agreement with observed values. The average deviation is 1.3 kcal/mol for 25 alkyl cations. These observed values are calculated using the observed heats of formation of radicals, cations (See Table 29),

and compounds (See ref. 102).

4.3 A Simpler Method

From eq. (5), a new method for estimating the heterolytic BDEs of X-R bonds has been obtained. It is given by

$$DH^O(X^--R^+) = DH^O(X^--CH_3^+) - \Delta DH^O(X-CH_3/ X-R) - \Delta IP(CH_3^+/R^+) \qquad (19)$$

Every term in the right side of eq. (16) can be estimated well. Furthermore we have a new equation. It is represented by the equation

$$DH^O(X^--alkyl\ cation) = DH^O(X^--CH_3^+) - m\ \frac{f^+(m) - V_x}{0.67 + 0.21m} - $$

$$-1.4\ \gamma^+ \qquad (19)$$

or

$$= DH^O(X^--C^+(CH_3)_m H_{3-m}) - 1.4\ \gamma^+ \quad kcal/mol \qquad (20)$$

where energy is in kcal/mol. In eq. (19), only the first term on the right side is taken from experiments. The values of the first term on the right side of eq. (20) are listed in Table 20. Thus, the heterolytic BDEs of X-alkyl bonds can be estimated using both eqs. (17) and (20). Comparisons in Table 31 between the values estimated by eqs. (17) and (20) and the observed values show that eq. (20) is not only simple, but also dependable.

Eq. (20) may be derived by another path. From thermochemistry, we obtain the following

$$DH^O(X^--alkyl\ cation) = DH^O(X-alkyl) + EA'X) + IP(alkyl) \qquad (21)$$

Using Benson's group additivity scheme and eq. (15), we obtain

$$DH^O(X^--R^+) = \Delta_f H^O(X^-) + IP(C(CH_3)_m H_{3-m}) + [C-(C)_m(H)_{3-m}] -$$

$$- [C-(X)(C)_m(H)_{3-m}] - 1.4\ \gamma^+\ kcal/mol \qquad (22)$$

$$= DH^O(X^--C^+(CH_3)_m H_{3-m}) - 1.4\ \gamma^+\ kcal/mol \qquad (20)$$

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TABLE 30: Heats of Formation of RH and Heterolytic Bond Dissociation
Energies of Alkyl-H Bonds, Energy in kcal/mol

R^+	$\Delta_f H^o$(RH) obs.[a]	$DH^o(R^+-H^-)$ obs.[b]	est. eq(28)	est. eq(30)
n=1 C^+	-17.8±0.1	313.8	314.5[c]	
Primary				
n=2 $C-C^+$	-20.0±0.1	270.3	270.6	270.6
n=3 $C-C-C^+$	-25.0±0.1	270.7	269.2	269.2
n=4 $C-C-C-C^+$	-30.0±0.2	267.7	267.8	267.8
			1.9	0.1
$C-C-C^+$ / C	-32.1±0.2	265.8	267.9	267.8
n=5 $C-C-C-C-C^+$	-35.1±0.3	263.8	266.5	266.4
C / $C-C-C^+$ / C	-40.2±0.2	264.9	267.0	266.4
			1.1	0.5
$C-C-C-C^+$ / C	-36.7±0.3		266.9	266.4
$C-C-C-C^+$ / C	-36.7±0.3		266.9	266.4
n=6 $C-C-C-C-C-C^+$	-39.9±0.2	265.6	264.9	265.0
n=7 $C-C-C-C-C-C-C^+$	-44.9±0.4	262.6	263.6	263.6
Secondary				
n=3 $C-C^+-C$	-25.0±0.1	250.6	249.4	249.4
n=4 $C-C^+-C-C$	-30.0±0.2	247.7	248.0	248.0
n=5 $C-C^+-C-C-C$	-35.1±0.3	244.8	246.8	246.6
$C-C-C^+-C$ / C	-36.7±0.3	247.4	246.9	246.6
			2.6	0.1
$C-C-C^+-C-C$	-35.1±0.3		246.8	246.6
n=6 $C-C^+-C-C-C-C$	-39.9±0.2	242.6	245.2	245.2
				0.0
$C-C-C^+-C-C-C$	-39.9±0.2		245.2	245.2

n=7 $C-C^+-C-C-C-C-C$ -44.9±0.4 241.6 243.8 243.8

Tertiary

n=4 $C-C^+-C$
⠀⠀⠀⠀⠀C -32.1±0.2 232.6 231.2 231.2

n=5 $C-C^+-C-C$
⠀⠀⠀⠀⠀C -36.7±0.3 229.4 230.2 229.8

n=6 $C-C^+-C-C-C$
⠀⠀⠀⠀⠀C -41.8±0.3 228.5 228.9 228.4

⠀⠀⠀⠀$C-C^+-C-C$
⠀⠀⠀⠀C C -42.6±0.3 227.3 228.5 228.4

⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀1.2⠀⠀⠀⠀⠀0.5
⠀⠀⠀⠀$C-C-C^+-C-C$
⠀⠀⠀⠀⠀⠀⠀C -41.1±0.3 227.8 229.0 228.4

n=7 $C-C^+-C-C-C-C$
⠀⠀⠀⠀⠀C -46.5±0.3 228.2 227.3 227.0

⠀⠀⠀⠀$C-C-C^+-C-C$
⠀⠀⠀⠀⠀C-C -45.3±0.3 230.6 227.7 227.0

⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀3.2⠀⠀⠀⠀⠀0.5
⠀⠀⠀⠀$C-C^+-C-C-C$
⠀⠀⠀⠀⠀C⠀⠀⠀C -48.2±0.3 231.3 227.8 227.0

⠀⠀⠀⠀⠀⠀⠀C
⠀⠀⠀⠀$C-C^+-C-C$
⠀⠀⠀⠀⠀C⠀⠀C -48.9±0.4 228.1 227.4 227.0

n=8 $C-C^+-C-C-C-C-C$
⠀⠀⠀⠀⠀C -51.5±0.4 225.2 225.9 225.6

n=9 $C-C^+-C-C-C-C$
⠀⠀⠀⠀⠀C-C-C -55.6[d] 223.3 224.4 224.2

a Ref. 102, unless indicated. b See text, the observed uncertainty of most heterolytic BDEs is within 2 kcal/mol or more. c Calculated using $\Delta_f H^o(CH_3)$ = 35.1±0.1 kcal/mol, see text. d Based on Benson's group additivity rule and including two gauche corrections. Therefore the value in this work is 1.6 kcal/mol higher than that in ref. 272.

4.4 Summary of the Thermochemistry of Alkyl Radicals and Cations

Now we can estimate the thermochemistry of any kind of saturated hydrocarbon radical and cation in the gas-phase at $25^{\circ}C$. The e methods have been summarized in Table 31. The estimated quantities include heats of formation of organic and organo-metallic compounds, $\Delta_f H^{\circ}(RX)$, heats of formation of free alkyl radicals, $\Delta_f H^{\circ}(R)$, heats of formation of alkyl cations, $\Delta_f H^{\circ}(R^+)$, ionization potentials of alkyl radicals, IP(R), the homolytic bond dissociation energies, $DH^{\circ}(X-R)$, and the heterolytic bond dissociation energies, $DH^{\circ}(X^--R^+)$. The thermochemistry of radicals and cations with cyclic and unsaturated structures have not been studied in this work. The V_{nb} and ΔV_{nb} in this Table represent the non-bonded steric interactions and the steric compression relief due to bond cleaving, respectively. The steric effect will be discussed quantitatively in Chapter 6.

TABLE 31: Summary of Methods for Estimating Thermochemical Properties

of Alkyl Radicals and Cations [a]

Terms	Estimation Method	References
1. Heats of Formation of Organic and Organo- Metallic Compounds, $\Delta_f H^o(RX)$	Benson's Group Additivity (GA) Rules in kcal/mol	102, 116, 125, 131
2. Heats of Formation of Free Alkyl Radicals, $\Delta_f H^o(R)$	$= \Delta_f H^o{}_{GA} + V_{nb}$ in kcal/mol	116 this work
3. Ionization Potentials of Alkyl Radicals, $IP(R)$	$= IP(C(CH_3)_m H_{3-m})$ $- 0.06\ \gamma^+$ in eV.	this work
4. Heats of Formation of Alkyl Cations, $\Delta_f H^o(R^+)$	$IP(R) + \Delta_f H^o(R)$ in kcal/mol	this work
5. Homolytic BDEs, $DH^o(X-R)$	$= DH^o(X-C(CH_3)_m H_{3-m})$ $+ \Delta V_{nb}$ in kcal/mol	this work
6. Heterolytic BDEs, $DH^o(X^- -R^+)$	$= DH^o(X^- -C^+(CH_3)_m H_{3-m})$ $- 1.4\ \gamma^+ + \Delta V_{nb}$ in kcal/mol	this work

[a] Here $X = F$, Cl, Br, I, H, CH_3, SiH_3, GeH_3, OH, SH, SeH, NH_2 and PH_2.

The reliability of the methods in Table 31 is almost within experimental uncertainty, i.e. $\pm$ 1 - 2 kcal/mol or 0.05 - 0.1 eV. The examples of two tertiary radicals are presented below.

(a) 2-methyl-2-butyl

(1) $\Delta_f H^o(\overset{\bullet}{C}-\underset{C}{\overset{|}{C}}-C-C) = 3 \; [C-(C)(H)_3] + [C-(C)_2(H)_2] + [C-(C)_3] + 1$ gauche =

$$= 3 \; (-10.08) + (-5.0) + 40.1 + 0.8 = 5.7 \text{ kcal/mol}$$

There is no observed value for comparison.

(2) $IP(C-\underset{C}{\overset{|}{\overset{+}{C}}}-C-C)_{est} = IP(C-\underset{C}{\overset{|}{\overset{+}{C}}}-C)_{est} - 0.06 \text{ eV} =$

$$= 6.70 - 0.06 = 6.64 \text{ eV}$$

$$\text{obs.} = 6.65 \text{ eV} \; [189].$$

(3) $\Delta_f H^o(C-\underset{C}{\overset{|}{\overset{+}{C}}}-C-C)_{est} = IP(C-\underset{C}{\overset{|}{\overset{+}{C}}}-C)_{est} + \Delta_f H^o(\text{s-Bu})_{est} =$

$$= 6.64 \times 23.06 + 5.7 = 158.8 \text{ kcal/mol}$$

$$\text{obs.} = 158 \pm 1 \text{ kcal/mol} \; [189].$$

(4) $DH^o(H^- - \overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{\overset{+}{C}}}-C-C)_{est} = DH^o(H^- - \overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{\overset{+}{C}}}-C)_{est} - 1.4 =$

$$= 231.2 - 1.4 = 229.8 \text{ kcal/mol}$$

$$\text{obs.} = \Delta_f H^o(H^-) + \Delta_f H^o(R^+) - \Delta_f H^o(RH) =$$

$$= 34.7 + 158(\pm 1) - (-36.7 \pm 0.3) = 229.4 \pm 1.1 \text{ kcal/mol}$$

(5) $DH^o(Cl^- - \overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{\overset{+}{C}}}-C-C)_{est} = DH^o(Cl^- - \overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{\overset{+}{C}}}-C)_{est} - 1.4 =$

$$= 153.9 - 1.4 = 152.5 \text{ kcal/mol}$$

$$\text{obs.} = \Delta_f H^o(Cl^-) + \Delta_f H^o(R^+) - \Delta_f H^o(RCl)$$

$$= -54.4 + 158(\pm 1) - (-48.3 \pm 2.0) = 151.9 \pm 2.3 \text{ kcal/mol}$$

(6) $DH^o(HS^- - \overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{\overset{+}{C}}}-C-C)_{est} = DH^o(HS^- - \overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{\overset{+}{C}}}-C)_{est} - 1.4 =$

$$= 171.8 - 1.4 = 170.4 \text{ kcal/mol}$$

$$obs. = \Delta_f H^o(HS^-) + \Delta_f H^o(R^+) - \Delta_f H^o(RSH) =$$

$$= -19.5(\pm 2.4) + 158(\pm 1) - (-30.4\pm 0.3) = 168.9\pm 2.6 \text{ kcal/mol}$$

(7) $DH^o(HO^- \overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{C}}{}^{+}\text{-C-C})_{est} = DH^o(HO^- \overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{C}}{}^{+}\text{-C})_{est} - 1.4 =$

$$= 206.6 - 1.4 = 205.2 \text{ kcal/mol}$$

$$obs. = \Delta_f H^o(HO^-) + \Delta_f H^o(R^+) - \Delta_f H^o(ROH)$$

$$= -32.8(\pm 0.1) + 158(\pm 1) - (- 79.1\pm 0.4) = 204.3\pm 1.1 \text{ kcal/mol}$$

(b) 2-methyl-2-heptyl

(1) $\Delta_f H^o(R)_{est} = 3 [C-(C)(H)_3] + 4 [C-(C)_2(H)_2] + [C-(C)_3] + 1 \text{ gauche} =$

$$= 3 (-10.08) + 4 (-5.0) + 40.1 + 0.8 = -9.3 \text{ kcal/mol}$$

There is no observed value for comparison.

(2) $IP(R)_{est} = 6.70 - 4 \times 0.06 = 6.46 \text{ eV}$

There is no observed value for comparison.

(3) $\Delta_f H^o(R^+)_{est} = 6.46 \times 23.06 + (-9.3) = 139.7 \text{ kcal/mol}$

$$obs. = 139 \text{ kcal/mol }^{189}$$

(4) $DH^o(H^- - R^+)_{est} = 231.2 - 4 \times 1.4 = 225.6 \text{ kcal/mol}$

$$obs. = \Delta_f H^o(H^-) + \Delta_f H^o(R^+) - \Delta_f H^o(RH) =$$

$$= 34.7 + 139 - (-51.5 \pm 0.4) = 225.2 \pm 1 \text{ kcal/mol}$$

(5) $DH^o(HO^- - R^+)_{est} = 206.6 - 4 \times 1.4 = 201.0 \text{ kcal/mol}$

There is no observed value for comparison.

In general, the time needed to estimate each thermochemical parameter is only about one or two minutes without a computer. It goes without saying that these methods are of considerable interest for the theory and the practice of chemistry and physics.

4.5 Discussion

Lossing and Holmes [272] found that the heterolytic BDEs of H-alkyl bonds are a linear function of the logarithm of the number of atoms in

the alkyl cation. Beauchamp and co-workers [353-4] found a qualitative correlation between the IPs of primary, secondary, and tertiary alkyl radicals and the number of carbon atoms. The two groups, however, did not give an expression for estimating the heterolytic BDEs of H-alkyl bonds and the IPs of alkyl radicals. From the third column in Table 30, the observed values of the heterolytic BDEs of H-alkyl bonds with the same numbers of atoms and the same types (primary, secondary and tertiary) of C-H bonds are scattered by 1.1 to 3.2 kcal/mol. The values estimated by eq. (17) are scattered by 0.5 kcal/mol. Eq. (20) gives no scatter and is a good representation of eq. (17). Eqs. (15), (17) and (20) are consistent with the opinions expressed by both Holmes' and Beauchamp's groups. Eq. (20) is more strongly recommended than eq. (17) because it is simpler but has the same reliability. According to eqs. (15) and (20), the average deviation between the estimated and experimental values are 0.05 eV for the IPs of 14 alkyl radicals and 1.3 kcal/mol for the BDEs of 25 H-alkyl bonds, respectively. In other words, the qualitative and semi-quantitative descriptions of both research groups have been quantified very well in this work.

Eq.(20) is valid not only for H-alkyl bonds, but also for more general X-alkyl bonds, as the above-mentioned examples have already demonstrated. This implies that the heterolytic BDEs of X-alkyl bonds are sensitive to the size of alkyl radicals, but insensitive to the structure. The homolytic BDEs of the same types (primary, secondary and tertiary) are insensitive to the size of the fragments and the structure. This important difference originates from the different interaction mechanism between the radical center or formal charge center and distant atoms in radicals and cations. This topic will be discussed in Chapter 7.

The empirical formulas in Table 31 are made up of two parts. The first

is the strong interaction term and the second is the weak interaction or correction term. The parameter γ^+ represents such corrections in alkyl cations. All valence electrons in the sa'urated hyJrocarbons are paired. The interactions between the electron pairs are short range, extending about 1-3 Å. The third order or higher order interactions, thus, can be neglected except for some steric effects. This is why Benson's group additivity rules work so well for hydrocarbons. In a free alkyl radical, the third order interaction is considered as a small quantity, negligible compared to the observed uncertainty (± 1 to 2 kcal/mol).

For alkyl cations, we must include the third, fourth, and higher order interactions between the positive, formal charge and the paired electrons. As pointed out by Lossing and Holmes,[272] the ionic charge is not localized at the formal charge site and must be distributed over the whole ion. From the updated values of IPs and heats of formation of alkyl radicals in Table 29, the attenuation with increasing size of the alkyl cations is gradual. Eq. (15) has been established as a simple correlation. The group additivity rule cannot be applied to estimate the heats of formation of alkyl cations because the third and higher order interactions in cations cannot be neglected.

The interactions between the formal charge center and the carbon atoms at and beyond the γ-positions are very important for the energetics of organic cations. These interactions will be called the "γ effect" for convenience. We will address the γ effect in hydrocarbon, chloro-, bromo- and iodo-alkane cations in Chapter 7. The IPs for these classes of molecules may be estimated using expressions similar to eq. (15).

The effect of methyl substitution on the heterolytic BDE of X-R bonds has been paid some attention.[164,270,272,293-4] The methyl substitution effect at the α-position is a second order or strong interaction. It has

been quantitatively represented by eq.(5). The values of the three terms in eq. (5) have been listed in Table 32, respectively. The methyl substitution effect at the α-position is a function of V_x and m. The decrease in the heterolytic BDEs upon methyl substitution, thus, is not a constant for different atoms and alkyl groups. A simple example is given in Table 32, where R = ethyl and X = halogen, H, CH_3, NH_2, OH and SH. They show again that $\Delta\Delta_f H^\circ(C_2H_5X/CH_3X)$, $\Delta DH^\circ(X-CH_3/X-C_2H_5)$ and $\Delta DH^\circ(X^- -CH_3^+/X^- -C_2H_5^+)$ are linearly dependent on V_x. An exception is $C_2H_5NH_2$. The value of this heat of formation may be in error, by about $\pm$ 1 kcal/mol.[97]

We always find

$$\Delta_f H^\circ(C_2H_5X) \quad < \quad \Delta_f H^\circ(CH_3X)$$
$$DH^\circ(X^- -C_2H_5^+) \quad << \quad DH^\circ(X^- -CH_3^+)$$
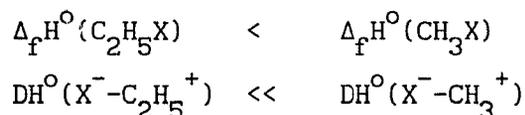
There is a different rule for the homolytic BDEs. When X has low or middle electronegativity (EN), such as H, I, Br, CH_3, SH and NH_2, $DH^\circ(X-methyl)$ is greater than $DH^\circ(X-ethyl)$, but when X has higher EN, such as Cl and OH, $DH^\circ(X-methyl)$ is less than $DH^\circ(X-ethyl)$, as in the third column of Table 32 on page 130.

There have been controversies involving some groups, such as those of Arnold,[224] Griller [178] and Holmes [190], regarding the extent to which these trends can be explained by EN. Such controversies can be resolved using our new scale of EN.

In summary, there are four factors which moderate the heterolytic BDEs of X-alkyl bonds. They are:

(1) the new scale of electronegativity or the covalent potential of X, V_x;

(2) the degree of methyl substitution on the radical center or formal charge center, m;

(3) the interactions between the formal charge center and distant

atoms, which is called the γ effect; and

(4) steric compression relief due to bond cleaving.

The importance of the four factors was announced in Section 1.4.8. The four factors and a similar method will be extended to systems of organic molecular cations in Chapter 7.

TABLE 32: The Methyl Substitution Effect at the α-Position, an Example, Energy in kcal/mol

X	$V_x{}^a$	$\Delta\Delta_f H^o$ $(CH_3X/C_2H_5X)^b$	ΔDH^o $(X\text{-}CH_3/X\text{-}C_2H_5)^c$	ΔDH^o $(X^-\text{-}CH_3{}^+/X^-\text{-}C_2H_5{}^+)^d$
F	9.915			
OH	8.11	8.1±0.2	-1.4±0.6	38.0±1.2
Cl	7.04	7.2±0.4	-0.5±0.7	38.9±1.2
NH_2	6.67	5.8±0.3	0.9±0.6	40.3±2.3
Br	6.13	6.3±0.5	0.4±0.8	39.8±1.3
SH	5.77	5.6±0.3	1.1±0.6	40.5±3.7
I	5.25	5.3±0.5	1.8±0.8	40.8±1.3
CH_3	5.19	5.0±0.2	1.7±0.6	41.1±1.6
H	2.70	2.2±0.2	4.5±0.6	43.9±1.2

[a] From Table 2. [b] From Table 5. [c] From Table 13. [d] From Table 27.

Chapter V Silicon-Containing Compounds

5.1 Introduction

It has been found [103,167,193,299-301,355] that Si-H, Si-C and Si-Si bond dissociation energies do not appear to be sensitive to alkyl substitution, unlike C-H bonds. For example, an approximate constancy or "uniformity" of the BDEs of Si-H bonds has been emphasized:

$$DH^{o}(H-Si(CH_3)_m H_{3-m}) \approx 90 \pm 2 \text{ kcal/mol}$$

here m represents the degree of methyl substitution, and m = 0, 1, 2 or 3. But carbon-hydrogen bonds, $DH^{o}(H-C(CH_3)_m H_{3-m})$, have a different pattern. The BDEs are equal to 105.0 ± 0.1, 100.5 ± 0.5, 97.0 ± 0.6 and 94.1 ± 0.7 kcal/mol for CH_3-H, C_2H_5-H, i-C_3H_7-H and t-C_4H_9-H bonds, respectively. (See Chapter 3.) This comparison is fascinating since the factors which influence carbon-hydrogen bonds are now reasonably well understood. Why is there the lack of substituent effect for Si-H bonds ? Chemists are puzzled by this problem. Some have commented, "there is hardly any information",[279] and "the reasons are not yet clear."[225]

In this Chapter, we will study and answer this interesting problem. Our method is simple, only extending a few results in Chapter 3. It will be predicted that BDEs of Si-X bonds, where X is an atom or group with low or moderate electronegativity, such as, H, CH_3, SiH_3, SH and NH_2, are also not sensitive to alkyl substitution; but BDEs of Si-X bonds, where X is a halogen atom or group with high electronegativity, such as OH, are sensitive to alkyl substitution. In other words, there is no "uniformity".

5.2 Values of BDEs and Group Parameters

Almost all of the available thermochemical data on silicon compounds and alkylsilyl radicals are due to the pioneering work of Walsh and his colleagues.[103,167] Benson's group additivity (GA) rules, which are

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valuable for hydrocarbons, were first introduced into silicon-containing compounds by Doncaster and Walsh four years ago.[292] These rules were extended to more silicon-containing compounds last year.[298] The determination of the values of group parameters has been a key problem.

Recently, Luo and Benson [131] put forward an equation for estimating the group parameters for carbon-centered groups. It is given by

$$\Delta_f H^o[C-(C)_m(X)(H)_{3-m}] = 0.9 + (m-1)(10.08 - 1.5m) - \frac{mV_x}{0.67 + 0.21m} \quad (1)$$

Here m = 1, 2 and 3. The energy unit is kcal/mol. X represents all polyvalent atoms, both nonmetallic and metallic, in the periodic table, for example, Zn, Cd, Hg, B, Al, Ga, C, Si, Ge, Sn, Pb, Ti, N, P, As, Sb, O, S, Se, Cr, Pd and others. V_x is the covalent potential of X. The estimated values from eq. (1) are in agreement with those from experimental data on heats of formation of organic and organometallic compounds. Examples for silicon-containing groups are listed in the first line of Table 33. The values in parentheses were obtained directly from experimental data on heats of formation of hydrocarbons [125] and alkylsilanes.[103,292] It has been reported that estimated heats of formation based on group additivities are consistent with ab initio heats of formation based on second-order Moller-Plesset theory (MP2) and 6-31G(d) basis sets at self-consistent field geometries.[131-2]

TABLE 33: Estimated and Derived Values of Group Parameters for Compounds Containing Si, C and H Atoms [a], in kcal/mol

Central atom	X	$[C-(X)(H)_3]$	$[C-(X)(C)(H)_2]$	$[C-(X)(C)_2(H)]$	$[C-(X)(C)_3]$
C	Si		-3.0	1.7	4.2
		(-10.08)	(-4.0)[c]		
	C		-5.0	-1.5	0.1
		(-10.08)	(-5.0)[c]	(-1.9)[c]	(0.5)[c]

		$[Si-(X)(H)_3]$	$[Si-(X)(C)(H)_2]$	$[Si-(X)(C)_2(H)]$	$[Si-(X)(C)_3]$
Si	C		-2.3	-8.8	-15.3
		(3.1 ± 1.0)[b]	(-2.2)[d]	(-8.4)[d]	(-14.8)[d]
	Si		2.4	-3.8	-9.9
		(7.8 ± 1.0)[b]			

[a] The values in parentheses are calculated directly from experimental data. The experimental values for hydrocarbons are from refs. 116 and 125. Those for silicon-containing compounds are from refs. 103 and 292, unless otherwise indicated. Values without parentheses for C-centered groups are from eq.(1) and ref. 131. Values without parentheses for Si-centered groups are from ref. 147. [b] Ref. 147. [c] Ref. 131. [d] Ref. 292.

5.3 Empirical Relations for X-Si Bond Dissociation Energies

According to thermochemistry, the difference between $X-Si(CH_3)_mH_{3-m}$ and $X-SiH_3$ bond strengths is dependent on the heats of formation of the relevant compounds and free radicals. That is

$$\Delta DH^o(X-Si(CH_3)_mH_{3-m}/X-SiH_3) = \Delta\Delta_f H^o(Si(CH_3)_mH_{3-m}/SiH_3) -$$
$$- \Delta\Delta_f H^o(Si(CH_3)_mH_{3-m}X/SiH_3X) \qquad (5)$$

Here

$$\Delta DH^o(X\text{-}Si(CH_3)_mH_{3-m}/X\text{-}SiH_3) = DH^o(X\text{-}Si(CH_3)_mH_{3-m}) - DH^o(X\text{-}SiH_3) \quad (6)$$

$$\Delta\Delta_fH^o(Si(CH_3)_mH_{3-m}X/SiH_3X) = \Delta_fH^o(Si(CH_3)_mH_{3-m}X) - \Delta_fH^o(SiH_3X) \quad (7)$$

$$\Delta\Delta_fH^o(Si(CH_3)_mH_{3-m}/SiH_3) = \Delta_fH^o(Si(CH_3)_mH_{3-m}) - \Delta_fH^o(SiH_3) \quad (8)$$

Thermochemical data on SiH_3X have not been determined with high precision and are relatively scarce. Luo and Benson [145-7] took another path to avoid uncertainties when estimating heats of formation of silicon-containing compounds. Heats of formation of CH_3X compounds were better known, so they studied the relations between $\Delta\Delta_fH^o(Si(CH_3)_mH_{3-m}X/CH_3X)$ and the covalent potential, V_x.

$$\Delta\Delta_fH^o(Si(CH_3)_mH_{3-m}X/CH_3X) = \Delta_fH^o(Si(CH_3)_mH_{3-m}X) - \Delta_fH^o(CH_3X) \quad (9)$$

All of the relations were reported to be linear. The relations between $\Delta\Delta_fH^o(Si(CH_3)_mH_{3-m}X/SiH_3X)$ and V_x can be determined from $\Delta\Delta_fH^o(Si(CH_3)_mH_{3-m}X/CH_3X)$

$$\Delta\Delta_fH^o(Si(CH_3)_mH_{3-m}X/SiH_3X) = \Delta\Delta_fH^o(Si(CH_3)_mH_{3-m}X/CH_3X) -$$
$$- \Delta\Delta_fH^o(SiH_3X/CH_3X) \quad (10)$$

Here

$$\Delta\Delta_fH^o(SiH_3X/CH_3X) = \Delta_fH^o(SiH_3X) - \Delta_fH^o(CH_3X) \quad (11)$$

The first term on the right hand side of eq.(10) was given in eq.(4) of ref. 125 for X equal to H, CH_3 and SiH_3 and with different parameters for F, Cl, Br, I, OH, SH and NH_2. The need for different parameters was believed to be caused by p-d pi backbonding from lone pairs on the electronegative atoms to vacant d orbitals on Si. The final term in eq.(10) was given in eq.(4) of ref. 145 for X equal to H, F, Cl, Br and I. We have assumed that the same relations also apply to the polyatomic groups. Combining these terms we obtain eq.(12):

$$
\Delta\Delta_f H^O(Si(CH_3)_m H_{3-m}X/SiH_3X) = \begin{cases} -16.0m + 0.9 \quad kcal/mol \\ \quad \text{if } X = H \\ -(15.5m + 9.8) - (0.2m - 1.06)V_X \quad (12) \\ \quad \text{if } X = \text{halogen} \\ -(15.5m - 0.4) - (0.2m - 0.1)V_X \\ \quad \text{if } X = CH_3, \; SiH_3, \; OH, \; SH \text{ and } NH_2 \end{cases}
$$

Appropriate values of V_X have been substituted to obtain the expressions listed in the third column of Table 34.

Taking the preferred values for heats of formation of alkylsilyl radicals [103,167], the differences, $\Delta\Delta_f H^O(Si(CH_3)_m H_{3-m}/SiH_3)$, are equal to -15.9±1.4, -32.1±1.4 and -47.2±1.4 kcal/mol for m = 1, 2 and 3, respectively. By linear regression we obtain an approximate relation

$$\Delta\Delta_f H^O(Si(CH_3)_m H_{3-m}/SiH_3) = -0.4 - 15.7 \, m \quad kcal/mol \qquad (13)$$

$$\approx -16 \, m \qquad (13a)$$

The differences in the BDEs of X-Si bonds, thus, can be estimated by substituting eq.(13) into eq.(5). These values have been listed in the last three columns of Table 34. As shown in this Table, the differences for X-Si bonds, where X = H, CH_3, SiH_3, SH and NH_2, are about zero within ± 2 kcal/mol, which is the experimental uncertainty for silicon compounds today. For X = H, SiH_3 and CH_3, the differences are especially small. This reflects the observation that the methyl substitution effects for H-Si, Si-Si and Si-C bonds are negligible within the present experimental uncertainty. But Si-halogen and Si-OH bonds have a different pattern. The estimated BDEs of Si-Si bonds have been listed in the last column of Table 36. There is experimental evidence [167] that methyl substitution slightly increases the strength of Si-Si bonds. The following order of BDEs applies to almost all the ligands which we have studied:

$$DH^O(X-SiH_3) \leqslant DH^O(X-Si(CH_3)H_2) \leqslant DH^O(X-(CH_3)_2H)$$
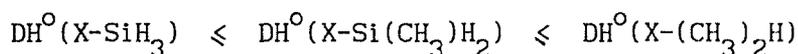
$$\leqslant \quad DH^o(X\text{-}Si(CH_3)_3) \qquad\qquad (14)$$

TABLE 34: Differences in Heats of Formation of Silicon Compounds and in the BDEs of Si-X Bonds, in kcal/mol

X	V_x^a	$\Delta\Delta_f H^o$ $(Si(CH_3)_m H_{3-m} X/SiH_3 X)$	$\Delta DH^o(X\text{-}Si(CH_3)_m H_{3-m}/X\text{-}SiH_3)^b$		
			m = 1	m = 2	m = 3
F	9.915	-17.5m + 0.7	0.9	2.2	4.6
OH	8.11	-17.1m + 1.2	0.0	0.3	2.9
Cl	7.04	-16.9m - 2.3	3.3	4.0	5.8
					(4.9±3.0)
NH_2	6.67	-16.8m + 1.1	-0.2	0.4	2.1
Br	6.13	-16.7m - 3.4	4.2	4.7	6.3
					(7.6±2.9)
SH	5.77	-16.7m + 1.0	-0.2	0.3	1.9
I	5.25	-16.5m - 4.3	4.9	5.2	6.6
					(5.2±2.9)
CH_3	5.19	-16.5m + 0.9	-0.3	0	1.4
			(-0.3±2.1)	(0.0±2.1)	(1.5±2.0)
SiH_3	3.41	-16.2m + 0.8	-0.5	-0.5	0.6
H	2.70	-16.0m + 0.9	-0.8	-1.0	-0.1
			(-0.7±1.9)	(-1.3±1.9)	(0.1±1.9)

[a] From Table 2. [b] Values in parentheses were calculated directly from experimental results; see ref. 147.

The fact that the average Me-for-H replacement enthalpies in the methylmonosilanes and methyldisilanes are about -16.0 (or -15.8 to -17.7) kcal/mol and -15.3 kcal/mol has also been noted by Walsh[103,356], O'Neal[357], Pilcher[355] and co-workers. They, however, did not express the

replacement enthalpies as a function of m and did not use it to correlate the BDEs. The average Me-for-H replacement enthalpies they noted are reproduced by both eq.(12) and Table 34.

Based on the linear relation between $\Delta\Delta_f H^O (Si(CH_3)_m H_{3-m}/CH_3 X)$ and V_x and on the covalent radius of the silicon atom, heats of formation of four disilanes, $SiH_3 SiH_3$, $SiH_3 SiH_2(CH_3)$, $SiH_3 SiH(CH_3)_2$ and $SiH_3 Si(CH_3)_3$, were estimated by Luo and Benson.[147] They were 15.5, 0.1, -16.1 and -32.3 kcal/mol, respectively. Using the assigned value $\Delta_f H^O[C-(Si)(H)_3]$ = $\Delta_f H^O[C-(C)(H)_3]$ = -10.08 kcal/mol,[111] the group parameters of Si-centered groups may be determined. The parameters have been listed in the last row of Table 33. These parameters will be used to estimate heats of formation of the methylated disilanes and to compare with the results from kinetic experiments and ab initio calculations in Section 5.5.

5.4 Group Parameters of Carbon- and Silicon-Centered Radicals

Values of group parameters for silicon-centered radicals have been calculated from the experimental heats of formation of refs. 103 and 167. The equation needed for this calculation is as follows:

$$\Delta_f H^O[Si-(C)_m(H)_{3-m}] = \Delta_f H^O(Si(CH_3)_m H_{3-m}) - m\Delta_f H^O[C-(Si)(H)_3)] =$$
$$= \Delta_f H^O(Si(CH_3)_m H_{3-m}) - 10.08m \qquad (15)$$

The results are listed in the first four lines of Table 35. The group parameters of carbon-centered radicals are also shown for comparison.

It is interesting to note that the differences between group parameters in successive lines for silicon-centered groups are nearly the same (-5 to -6 kcal/mol) within the present experimental uncertainty. It is very easy to estimate the BDE of any kind of X-alkylsilyl bond and the heat of formation of any free alkylsilyl radical using Table V in ref. 147, Tables 34 and 35 in this thesis and refs. 103 and 116.

It is also possible to estimate group parameters for radicals with silicon atoms at other positions. Recently Walsh and his co-workers[308] have measured the enthalpy change for the reaction

$$I + Si_2H_6 \longrightarrow Si_2H_5 + HI \qquad (16)$$

to be 15.3 kcal/mol. According to the first law of thermodynamics we can then obtain

$$DH^o(H-Si_2H_5) = 15.3 + DH^o(H-I) = 86.8 \text{ kcal/mol.}$$

Using the revised value of the heat of formation of Si_2H_6, 15.5 kcal/mol,[147] the heat of formation of Si_2H_5 can be calculated

$$\Delta_f H^o(Si_2H_5) = 50.2 \text{ kcal/mol.}$$

Taking the assigned value of the group $Si-(Si)(H)_3$, from Table 33, we obtain

$$\Delta_f H^o[Si-(Si)(H)_2] = 42\ 4 \pm 1.0 \text{ kcal/mol.}$$

TABLE 35: Group Parameters of C- and Si-Centered Radicals, in kcal/mol

Si-Centered			C-Centered		
Groups	$\Delta_f H^{oa}$	$\Delta\Delta$	Groups	$\Delta_f H^{ob}$	$\Delta\Delta$
$[Si-(H)_3]$	46.4 ± 1.0 [c]		$[C-(H)_3]$	35.1 ± 0.1 [d]	
		-5.8 ± 1.4			3.4 ± 0.5
$[Si-(C)(H)_2]$	40.6 ± 1.0		$[C-(C)(H)_2]$	38.5 ± 0.4	
		-6.1 ± 1.4			1.7 ± 0.7
$[Si-(C)_2(H)]$	34.5 ± 1.0		$[C-(C)_2(H)]$	40.2 ± 0.5	
		-5.1 ± 1.4			-0.1 ± 0.8
$[Si-(C)_3]$	29.4 ± 1.0		$[C-(C)_3]$	40.1 ± 0.6	
$[Si-(H)_3]$	46.4 ± 1.0 [c]		$[C-(H)_3]$	35.1 ± 0.1 [d]	
		-4.0 ± 1.4			2.1 ± 2.1
$[Si-(Si)(H)_2]$	42.4 ± 1.0		$[C-(Si)(H)_2]$	37.0 ± 2.0 [a]	
		-6.1 ± 1.4 e			
$[Si-(Si)(C)(H)]$	36.3 ± 1.0				
		-5.1 ± 1.4 e			
$[Si-(Si)(C)_2]$	31.2 ± 1.0				

[a] This work, see text. [b] Calculated based on ref. 131, unless otherwise indicated. [c] $\Delta_f H^o(SiH_3)$ from ref. 103 and 167. [d] $\Delta_f H^o(CH_3)$ from Table 8. [e] Assumed, see text.

In order to agree with the observed uniformity of the BDEs of H-Si bonds we may assume that

$$\Delta\Delta_f H^O[Si-(Si)(C)_m(H)_{2-m}/Si-(Si)(C)_{m-1}(H)_{3-m}]$$

$$= \Delta\Delta_f H^O[Si-(C)_{m+1}(H)_{2-m}/Si-(C)_m(H)_{3-m}] \qquad (17)$$

Here m = 1 or 2. This leads to estimated values for

$$\Delta_f H^O[Si-(Si)(C)(H)] = 36.3 \pm 1.0 \text{ kcal/mol.}$$

$$\Delta_f H^O[Si-(Si)(C)_2] = 31.2 \pm 1.0 \text{ kcal/mol.}$$

In terms of group language, the BDE of $H-CH_2Si(CH_3)_3$ may be expressed as

$$DH^O(H-C) = \Delta_f H^O(H) + \Delta_f H^O[C-(Si)(H)_2] - \Delta_f H^O[C-(Si)(H)_3]$$

Taking the experimental value of $DH^O(H-C)$ as 99.2 $\pm$1.0 kcal/mol,[167] we obtain

$$\Delta_f H^O[C-(Si)(H)_2] = 37.0 \pm 2 \text{ kcal/mol.}$$

These group parameters have also been summarized in Table 35.

An example of a calculation of a BDE for ethyl silane and of $\Delta_f H^O$ for an ethylsilyl radical follows.

$$DH^O(H-SiH_2CH_2CH_3)_{est} \approx DH^O(H-SiH_2CH_3)_{est} = 89.5 \text{ kcal/mol}$$

$$\Delta_f H^O(SiH_2CH_2CH_3)_{est} \approx [Si-(C)(H)_2] + [C-(Si)(C)(H)_2] + [C-(C)(H)_3]$$

$$= 40.6 - 3.0 - 10.08 = 27.5 \text{ kcal/mol}$$

No experimental data are available for this system at present.

5.5 Discussion

From eq. (5), the difference between the BDEs, $\Delta DH^O(X-Si(CH_3)_m H_{3-m}/X-SiH_3)$, is dependent on two terms. The first is the difference in the heats of formation of the silicon radicals, which is a function of m, as in eq. (12). The second is the difference in the heats of formation of the silicon compounds, which is a function of V_x and m, as shown in the third column of Table 34. The last three columns in Table 34 give the total contribution of

these two terms. The results show that the electronegativity of X has a significant effect on the trend of BDEs of X-Si bonds with increasing m.

Why do the differences in the BDEs of H-Si bonds approach zero ? There are two opposing contributions. The first contribution is the difference in the heats of formation of alkylsilyl radicals, $\Delta\Delta_f H^o(Si(CH_3)_m H_{3-m}/SiH_3)$, which is approximately -16m, as in eq.(13a). Secondly, the heats of formation of the alkylsilanes are a linear function of m, as shown in Fig.6 on page 141.

$$\Delta_f H^o(Si(CH_3)_m H_{4-m}) = - 16.0(\pm 0.2)m + 0.9(\pm 0.4) \text{ kcal/mol} \qquad (18)$$

The correlation coefficient is 0.9998. This is equivalent to the first line in eq.(12). Substituting eqs. (13a) and (18) into eq.(5), we can see that the differences of the BDEs of H-Si bonds are almost independent of m because the coefficients, i.e. 16, almost cancel out.

Heats of formation of hydrocarbons, also shown in Fig. 6, have a nonlinear pattern, which was described quantitatively in refs. 97 and 144.

From Table 34, the differences in heats of formation of halogen and OH derivatives of alkylsilanes have a stronger dependence on m. Their pattern, thus, is different from that of the H atom. On the basis of similar analyses, we can also interpret the behavior of Si-C and Si-Si BDEs.

Our relation for the trend in the H-Si BDEs is based on thermochemical information, the electronegativity, V_x, and the degree of substitution by methyl, m. This approach reproduces the uniformity of the BDEs of Si-H and Si-C bonds, and the trends in bond strengths between Si and other atoms.

Our approach is empirical, and is independent of any particular theoretical approach. However the important role of V_x is consistent with the suggestion of Walsh [167] that inductive effects can explain these observed trends. Coolidge and Borden [301] also emphasized the importance of
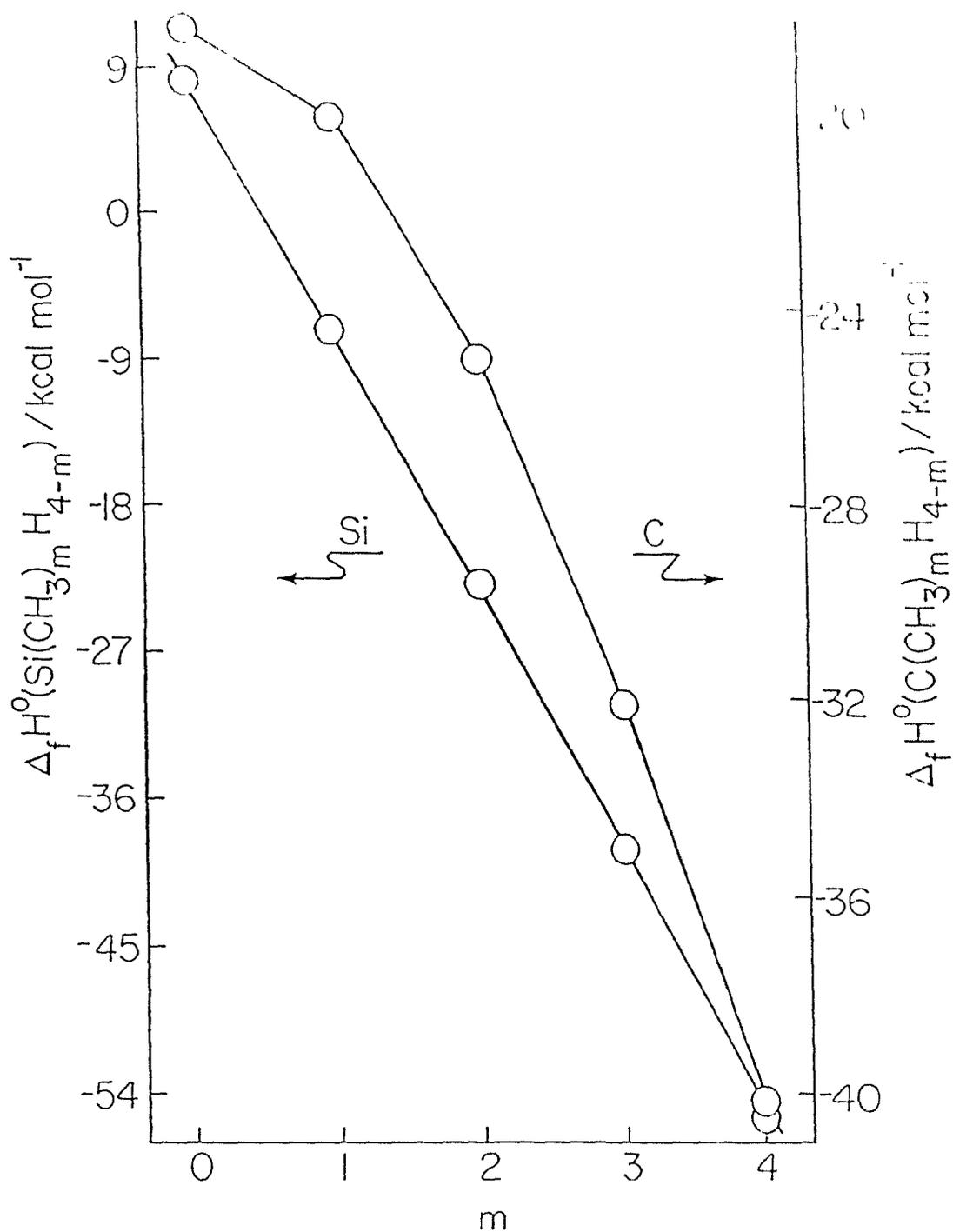
Fig. 6:

Relation between $\Delta_f(X(CH_3)_m H_{4-m})$, where X - Si and C

electronegativity, on the basis of ab initio calculations. Their scale of electronegativity reversed the order of Si and H compared to the V_x scale, but the differences were so small they should not affect the overall results.

Based on structural information for free alkylsilyl and alkyl radicals,[300] Brauman and his colleagues thought the modest changes in geometry between silanes and the corresponding silyl radicals would result in smaller substitutent effects than for alkanes, which change to almost planar radicals. Another potential explanation (hyperconjugation in the radicals) has not been accepted, as noted previously by Walsh.[167]

The BDEs of Si-H bonds may not be uniform when dissociation relieves steric compression in silicon compounds. This problem has been emphasized by Griller[321] and Walsh,[356] but a quantitative description has not yet been offered. Steric compression relief in the bond cleavage of organosilicon compounds will be studied quantitatively in Chapter 6.

The heats of formation of methylated disilanes have been the subject of heated dispute. The upper limit, lower limit and preferred values of Walsh[356] and the values estimated in this work are listed in Table 36. The Table also contains the values of O'Neal et al.[357] from kinetic experiments.

The largest differences between Walsh's preferred values and our values occur for disilane and hexamethyldisilane. Walsh has given $\Delta_f H^o(Si_2(CH_3)_6) = -83 \pm 3$ kcal/mol, which is, in fact, based on $\Delta_f H^o(Si_2H_6)$ = 19.1 kcal/mol and a reexamination of kinetic data. As pointed out earlier,[147] the value of the heat of formation of Si_2H_6 may be in error. This means there is a shift in the reference point for the thermochemistry of methylated disilane compounds. We feel that the preferred value of Walsh for hexamethyldisilane (-83.0 kcal/mol) is subject to similar uncertainty.

TABLE 36: Heats of Formation of the Methyldisilanes and the Estimated BDEs of Si-Si Bonds, kcal/mol

Compounds	$\Delta_f H^o$									BDE[h]
	Walsh[a]			This work		Kinetics		Ab initio		
	upper	lower	prefer.	GA[c]	BA[d]	kinet.[b]	rev.[e]	theo.[g]	rev.[e]	
H₃Si-SiH₃	19.1	19.1	19.1	15.6	15.5	19.1	15.5	19.1	15.5	77.2
C-Si-Si[i]	3.4	1.5	2.1	0.1	-0.5	5.0	1.4	4.3	0.7	76.8
C-Si-Si C	-12.3	-16.2	-14.9	-16.1	-16.5	-11.0	-14.6	-11.6	-15.2	76.8
C-Si-Si-C	-12.3	-16.2	-14.9	-15.4	-16.5	-9.0[f]	-12.6	-10.5	-14.1	76.4
C C-Si-Si C	-27.9	-33.8	-31.9	-32.3	-32.4	-26.9	-30.5	-27.8	-31.4	77.9
C-Si-Si-C C	-27.9	-33.8	-31.9	-31.5	-32.4	-25.0[f]	-28.6	-26.3	-29.9	76.3
C C-Si-Si-C C	-43.6	-51.5	-49.0	-47.8	-48.4	-41.3	-44.9	-42.2	-45.8	77.5
C-Si-Si-C C C	-43.6	-51.5	-49.0	-47.7	-48.4	-40.9	-44.5	-41.8	-45.5	76.3
C C-Si-Si-C C C	-59.3	-69.1	-66.0	-64.0	-64.4	-57.5	-61.1	-58.5	-62.1	77.5
C C C-Si-Si-C C C	-75.0	-86.8	-83.0	-80.3	-80.4	-75.0	-78.6	-75.0	-78.6	78.7

[a] Ref. 356. [b] Ref. 357 and $\Delta_f H^o(Si_2H_6)$ = 19.1 kcal/mol as reference point. [c] Group additivity, see Table 33. [d] Bond additivity, see text. [e] The values to the left minus 19.1 kcal/mol plus 15.5 kcal/mol, see text. [f] Assumed in ref. 357. [g] Theoretical values, see ref. 363. [h] Heats of formation of silicon-centered radicals are taken from ref. 103 and heats of formation of the disilanes are from the additivity scheme in Table 33. [i] C represent CH_3; H is not shown.

Firstly, using the estimated value of Luo and Benson for $\Delta_f H^O(Si_2H_6)$ (15.5 kcal/mol)[147] and a constant increment for Me-for-H replacement, about - 16.0 kcal/mol, the heat of formation of hexamethyldisilane may be estimated simply as:

$$\Delta_f H^O(Si_2(CH_3)_6)_{est} \approx 15.5 - 16.0 \times 6 = -80.5 \text{ kcal/mol}$$

Secondly, taking group parameters from Table 33 and using group additivity (GA), we obtain (as in the fifth column of Table 36)

$$\Delta_f H^O(Si_2(CH_3)_6)_{est} = 6 (-10.08) + 2 (-9.9) = -80.3 \text{ kcal/mol}$$

Thirdly, simple bond additivity (BA) works quite well with organosilicon compounds, especially where no polar groups are involved.[103, 147, 292, 356-7] Based on heats of formation of CH_4, SiH_4, Si_2H_6 and $Si(CH_3)_4$ (-17.8,[102] 8.2,[103] 15.5, revised by Luo and Benson,[147] and -55.7 [103] kcal/mol), the bond additivity parameters are -4,45, 2.05, 3.2 and -0.58 kcal for C-H, Si-H, Si-Si and Si-C bonds, respectively. Consequently, these parameters can be used to estimate the heats of formation of methylated disilane compounds, as in the eighth column of Table 36. For example, the heat of formation of hexamethyldisilane is given by

$$\Delta_f H^O_{est} = 18 (-4.45) + 6 (-0.58) + 3.2 = -80.4 \text{ kcal/mol}$$

Fourthly, the bond dissociation energy of the $Me_3Si-SiMe_3$ bond was reexamined by Walsh.[167,358] Most probably, it was 80.5,[167,359] 77.4, 75.5 or 75.3±3 [174] kcal/mol. Taking Walsh's value of the heat of formation of the radical Me_3Si, -0.8 kcal/mol ± 1 kcal/mol,[103] we have

$$\Delta_f H^O(Si_2(CH_3)_6)_{est} = -82.1, -79.0, -77.1 \text{ or } -76.8 \pm 2 \text{ kcal/mol}$$

The values of the heat of formation of hexamethyldisilane from various sources have been listed in Table 37. There are two groups in this Table: observed and calculated or estimated.

Table 37: The Heat of Formation of Hexamethyldisilane from Various Sources

$\Delta_f H^o$	Methods	Refs
(1) Observed		
-85.8 ±2.6	combustion calorimetry	365-6
-82.9 ±2.2	combustion calorimetry	367
-83.4 ±3.6	kinetics of dissociation and recombination	356
-72.6 ±1.3	reaction-solution calorimetry	355
(2) Calculated or Estimated		
-78.5	molecular mechanics (MM2)	357
-79.6	MO calculation (Dewar AM1 method)	357
-77.9	Benson and Luria scheme (EECBA)	357, 360-2
-75.0	Ab initio calculation + homodesmic reactions	363
-75	analysis of kinetic data	357
-77 o -82	from the observed BDE of $Me_3Si-SiMe_3$ bond	this work
-80.3	group additivity	this work
-80.4	bond additivity	this work

From Table 37, the values observed are scattered from -72.6±1.3 kcal/mol to -85.8±2.6 kcal/mol. But the values estimated are near -75 kcal/mol to -80 kcal/mol. All estimated values for hexamethyldisilane are different from those of combustion calorimetry.

Using the values of heats of formation in Table 36 from group additivity rules, the bond dissociation energies of Si-Si bonds may be estimated, as shown in the last column of this Table. The BDEs of the ten Si-Si bonds, clearly, are almost constant, like Si-H and Si-C bonds. The average BDE of an Si-Si bond is 77.1±1.0 kcal/mol. In general, it is acceptable that BDEs of Si-H, Si-C and Si-Si bonds for silicon-containing compounds without steric effects are taken as 90, 89 and 77 ± 2 kcal/mol,

respectively.

From Table 36, both the kinetic values of O'Neal et al.[357] and the ab initio values at the MP2/6-31G(d)//RHF/3-21G* level of Boatz and Gordon[363] are systematically higher than the values estimated in this work. There is a simple explanation. These two articles are based on $\Delta_f H^o(Si_2H_6)$ equal to 19.1 kcal/mol as the reference point for the thermochemistry of the methylated disilanes. The values in these two articles could be revised by shifting the reference point to 15.5 kcal/mol.[147] The revised values are 3.6 kcal/mol (i.e. 19.1 -15.5 kcal/mol) lower. It is interesting to find that the revised values of heats of formation for methylated disilanes are close to the values estimated by both bond and group additivity from this work.

Strictly speaking, however, "heats of formation of methylated disilanes are not 'known'".[357] The heat of formation of hexamethyldisilane, a key compound, "cannot yet be taken as reliably established".[356] The reason is that the calorimetric methods used in measuring heats of formation are often plagued by incomplete combustion of the disilanes.[103,365,357,363,364] So, this dispute can only be settled by accurate, future experiments.

Chapter VI   The Cleaving-Relaxation Model for Homolysis of C-X Bonds

6.1 Introduction

Most available data on heats of formation of free alkyl radicals and on bond dissociation energies have been obtained from gas kinetic measurements of high precision (± 0.1 to 1.0 kcal/mol). This technique is restricted to volatile or low molecular weight compounds. The number of chemical bonds and free radicals are so many, it is impossible to measure them one by one. We have to develop new, simple and dependable methods for estimating BDEs and heats of formation of free radicals.

Of course, we wish to establish a generalized theory or method soon. To achieve this objective is difficult. We have to work steadily and make solid progress. In previous work,[209] (See Section 1.4.4) the BDEs of X-$C(CH_3)_m H_{3-m}$ bonds were described quantitatively, where X represents halogen, H, CH_3, OH, SH and NH_2; and m, the degree of methyl substitution and m = 1, 2 or 3. In Chapter 3, the propagator of the inductive effect was inferred from these BDEs. It is a function of V_x and m and given by

$$P_{x-c} = \frac{1}{3} + \frac{6.33 + 0.36m - V_x}{42.0 \ (0.67 + 0.21m)} \qquad (1)$$

where V_x is the covalent potential or a new scale of electronegativity. (See Chapter 2). For any alkyl, a simpler equation is described as

$$DH^o(\text{X-alkyl}) \approx DH^o(\text{X-}C(CH_3)_m H_{3-m}) \qquad (2)$$

The method was also extended to the heterolytic BDEs of X-alkyl bonds (See Chapter 4), the homolytic BDEs of X-Si bonds (See Chapter 5) and the ionization potentials of organic molecules (See Chapter7), respectively. In fact, three factors have already been considered:

(1) the covalent potential or a new scale of the electronegativity, V_x;

(2) the degree of methyl substitution, m;

(3) the nature of the third order and higher order interactions in alkyl radicals and in alkyl and molecular cations, which was called the γ effect in Chapter 4.

These methods are strongly different from the traditional ones. The concepts of atomic electronegativity and the inductive effect have been accepted, but not the concepts of fixed substituent constants and group electronegativities.

As emphasized in Chapter 3, the second order interaction in free alkyl radicals is a very important quantity, the third order interaction is a small quantity (0.6 kcal/mol) relative to "chemical accuracy" ($\pm$ 1 kcal/mol). The fourth order and higher order interactions may be neglected. But, we have not described well the first order interaction. This interaction will be addressed in this Chapter.

Can we also estimate the BDEs of alkyl-alkyl, alkoxy-alkyl, RS-alkyl, R_1R_2N-alkyl, and alkylsilyl-alkyl bonds ? CH_3, SiH_3, OH, SH and NH_2 of Chapter 3 could be replaced by C-, Si-, O-, S- and N-centered groups. In this Chapter, we will study the BDEs of C-C or alkyl-alkyl bonds. The topic of the Si-, O-, S- and N-centered groups will discussed separately in future work. A new semi-empirical model, the cleaving-relaxation model, for describing bond dissociation processes will be established. The fourth factor to influence BDEs -- the steric effect will be described quantitatively.

6.2 An Empirical Relation for the BDEs of X-Methyl Bonds

We can give accurate values for the BDEs of X-methyl bonds, where X represents F, Cl, Br, I, H and CH_3, because the heats of formation of these atoms, the methyl radical and methyl derivatives have been determined with

very high precision. They are listed in Table 38.

Table 38: Enthalpies of CH_3 Compounds, in kcal/mol

X [a] ($\Delta H_f(X)$)	$\Delta_f H^o(CH_3X)$ [c]	$DH^o(X-CH_3)$	$\bar{D}(X-C)$ [e]	$DH^o - \bar{D}(X-C)$
H (52.10)	-17.8±0.1	105.0±0.2	99.37	5.6
F (18.98)	-55.9 [d]	110.0±0.6	104.4	5.6
Cl (28.99)	-19.6±0.1	83.7±0.3	78.1	5.6
Br (26.74)	- 8.5±0.3	70.3±0.4	64.7	5.6
I (25.52)	3.5±0.3	57.1±0.4	51.5	5.6
CH_3 (35.1±0.1)b	-20.0±0.1	90.2±0.2	79.0	2x5.6

[a] From ref. 149, unless indicated. [b] From Table 8. [c] From ref. 102. [d] From ref. 141. [e] According to eq. (5) and $\Delta_f H^o(C) = 171.29±0.11$ kcal/mol.[149]

The third column in this Table lists the observed BDEs of X-methyl bonds. They are given by

$$DH^o(X-CH_3) = \Delta_f H^o(X) + \Delta_f H^o(CH_3) - \Delta_f H^o(CH_3X) \qquad (3)$$

The fourth column lists the average bond energies determined from the atomization energy, $\Delta_{at} H^o$, of methyl derivatives, CH_3X. It is interesting to note that the differences between the observed BDEs and the average bond energies are a constant, independent of the nature of X when X represents univalent atoms. The difference is a doubling of this constant when X is methyl itself.

The constant can be derived from the thermochemistry of methyl-X compounds. The average bond energy of an H-C bond in a methane molecule is given by

$$\bar{D}(\text{H-C}) = \frac{1}{4} \Delta_{at}H^O(\text{CH}_4)$$

$$= \frac{1}{4} [4 \Delta_fH^O(\text{H}) + \Delta_fH^O(\text{C}) - \Delta_fH^O(\text{CH}_4)] \tag{4}$$

For a single, monatomic substituent, X, the average bond energies can be calculated as

$$\bar{D}(\text{X-C}) = \Delta_{at}H^O(\text{CH}_3\text{X}) - 3 \, D(\text{H-C})$$

$$= 0.25 \, \Delta_fH^O(\text{C}) + \Delta_fH^O(\text{X}) + 0.75 \, \Delta_fH^O(\text{CH}_4)$$

$$- \Delta_fH^O(\text{CH}_3\text{X}) \tag{5}$$

For a methyl substituent, $X = CH_3$, the average bond energy of C-C in ethane can be obtained from

$$\bar{D}(\text{C-C}) = \Delta_{at}H^O(\text{C}_2\text{H}_6) - 6 \, D(\text{H-C})$$

$$= 0.5\Delta_fH^O(\text{C}) - \Delta_fH^O(\text{C}_2\text{H}_6) - 1.5\Delta_fH^O(\text{CH}_4) \tag{6}$$

Note the method to determine the average bond energy in our work is different from the popular method.[114] Take $\bar{D}(\text{H-C})$ and $\bar{D}(\text{C-C})$ as examples. Our $\bar{D}(\text{H-C})$ and $\bar{D}(\text{C-C})$ are only based on the reference compounds, methane and ethane, respectively. Both of them are not the average value over several hydrocarbons.

The differences between the BDEs and the average bond energies may be described as

$$DH^O(\text{X-CH}_3) - \bar{D}(\text{X-C}) = \Delta_fH^O(\text{CH}_3) - 0.25 \, \Delta_fH^O(\text{C}) - 0.75 \, \Delta_fH^O(\text{CH}_4)$$

$$= 5.6 \text{ kcal/mol} \tag{7a}$$

when X represents the univalent atoms, such as halogen and hydrogen. Note that the left side in eq. (7a) seems to be a function of the nature of X, but the right side is independent of X. If X is methyl itself, then we have

$$DH^O(\text{CH}_3\text{-CH}_3) - \bar{D}(\text{C-C}) = 2[\Delta_fH^O(\text{CH}_3) - 0.25\Delta_fH^O(\text{C}) - 0.75\Delta_fH^O(\text{CH}_4)]$$

$$= 2\text{x}5.6 \text{ kcal/mol} \tag{7b}$$

It is just double the result in of eq.(7a). There are two carbon atoms in

the CH_3-CH_3 bond. We may guess, thus, that the value of 5.6 kcal/mol could be related to the bonding nature of the carbon atom. It will be proved that this guess is right.

The X-methyl compounds are the reference or prototypical compounds in our work. There are no second order or higher order interactions in these compounds. The bonding of C and X is the first order or direct interaction. How can we understand the constant difference of 5.6 kcal/mol from chemical bond theory? This interesting problem will be discussed in Section 6.3.

6.3 Thermochemical Cycles

Taking an H-C bond dissociation in methane as an example, a thermochemical cycle is designed, as shown in Fig. 7.

The cycle consists of three steps:

(1) Adiabatic cleavage of an H-CH_3 bond. Supply an energy, D^o(H-C), and cleave the H-CH_3 bond with retention of geometry and electron distribution in the CH_3 group. Make the bond length and the H-C-H bond angles the same as those in the methane molecule.

(2) Relaxation of the group CH_3. An energy, $V(CH_3)$, is released as the CH_3 group relaxes to its proper geometry and new electron distribution.

(3) Recombination of the CH_3 radical and H atom. This is the reverse process of the bond dissociation. It releases an enthalpy equal to DH^o(H-CH_3). Thus,

$$DH^o(H-CH_3) = D^o(H-C) - V(CH_3) \qquad (8)$$

To clarify the nature of the quantity D^o(H-C), a second thermochemical cycle is also designed, as shown in Fig. 8. Here C(gas, ^{3}P) represents the ground state of a gas-phase carbon atom; C(gas, sp^3) represents the hypothetical valence state of the carbon atom with sp^3 hybridization; and
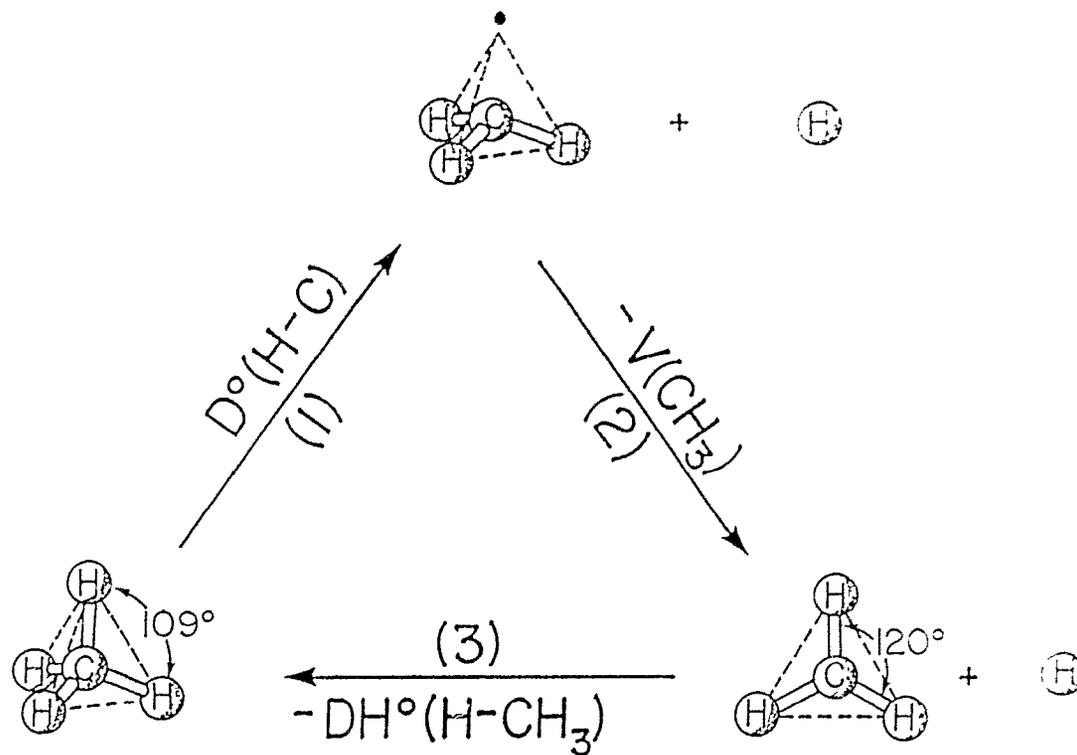
Fig. 7:

Dissociation of H-CH$_3$ Bond

$$C(gas, sp^3) \quad + \quad 4H(gas) \underline{\quad\quad -4D°(H-C) \quad\quad}$$

$$\uparrow E_V(c)$$

$$C(gas, {}^3p) \quad + \quad 4H(gas) \quad \underline{\quad -4\bar{D}(H-C) \quad}$$

$$\uparrow \triangle_{sub}H° \qquad\qquad 2DH°(H_2)\uparrow$$

$$C(graphite, solid) \quad + \quad 2H_2(gas) \xrightarrow{\quad -\triangle_f H° \quad} CH_4 \leftarrow$$
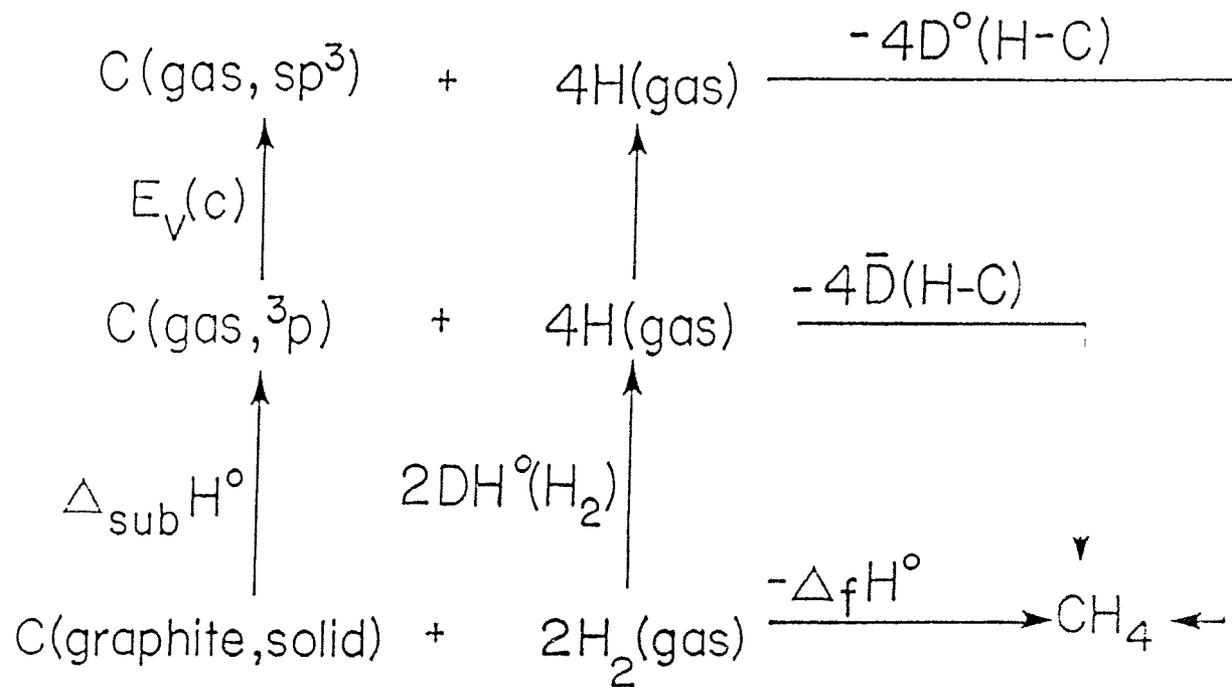
Fig. 8:

Relation of D°(C-H), D̄(H-C) and E_v(c)

$E_v(C)$ is its valence state energy [20,44,114,285] relative to the ground state. According to the cycle in Fig 8, we obtain an interesting relation:

$$D^o(H-C) = \bar{D}(H-C) + \bar{E}_v(C) \tag{9}$$

where $\bar{D}(H-C)$ is the thermochemical average bond energy of the H-C bonds in methane; and $\bar{E}_v(C) = E_v(C)/4$ is called the specific valence state energy. Assume that the contributions to relaxation energy from the 3 H-C bonds in the cleaved group CH_3 are additive, then $V(CH_3) = 3\ V_{C-H}$, where V_{C-H} is the contribution per C-H bond. Thus we have

$$DH^o(H-CH_3) = \bar{E}_v(C) + \bar{D}(H-C) - 3\ V_{C-H} \tag{10}$$

or

$$DH^o(H-CH_3) - \bar{D}(H-C) = \bar{E}_v(C) - 3\ V_{C-H} \tag{11}$$

In general, we have

$$DH^o(X-CH_3) = D^o(X-C) - 3\ V_{C-H}$$
$$= \bar{E}_v(C) + \bar{D}(X-C) - 3\ V_{C-H} \tag{12}$$

and

$$DH^o(X-CH_3) - \bar{D}(X-C) = \bar{E}_v(C) - 3\ V_{C-H} \tag{13}$$

when X represents univalent atoms. When X is a methyl group, the BDE of the C-C bond can be written

$$DH^o(CH_3-CH_3) = D^o(C-C) - 6\ V_{C-H}$$
$$= 2\ \bar{E}_v(C) + \bar{D}(C-C) - 6\ V_{C-H} \tag{14}$$

and

$$DH^o(CH_3-CH_3) - \bar{D}(C-C) = 2\ (\ \bar{E}_v(C) - 3\ V_{C-H}\ ) \tag{15}$$

The right sides in eqs. (13) and (15) are independent of the nature of X and are only determined by the bonding nature of the carbon atom. Comparing with the empirical eq. (7), we obtain

$$\bar{E}_v(C) - 3\ V_{C-H} = 5.6\ kcal/mol \tag{16}$$

Then the parameter V_{C-H} we used in Chapter 3 of this thesis can be calculated:

$$V_{C-H} = (E_v(C) / 4 - 5.6) / 3 \qquad (17)$$

Using the recent theoretical value of the valence state energy of a carbon atom with sp^3 hybridization of 8.263 ev,[20] we obtain V_{C-H} = 14.0 kcal mol.

6.4 A Generalized Model of C-C Bond Cleaving

Considering the homolysis of a general covalent C-C bond, R_1-R_2, we have a similar cycle, as shown in Fig. 9.

There are also three steps in this cycle. The first step is the cleavage of the bond, which requires an energy $D^o(C-C)$ and gives two cleaved groups. In the cleaved groups, R_1 and R_2, the bond length, the bond angle and the distribution of electron density are exactly the same as those in the molecule R_1R_2. The second step of the cycle is the structural "relaxation" of the cleaved groups, R_i. The free valence electron of each cleaved group is attracted or repelled by the chemical structural units in the interior of the cleaved group, R_i. This can lead to the delocalization of the free valence electron, and the system changes to the proper shape and electron distribution for the free radical in its ground state. This releases an energy V(R),

$$V(R) = V(R_1) + V(R_2) \qquad (18)$$

The third step is the recombination of two free radicals. Then we obtain

$$DH^o(R_1-R_2) = D^o(C-C) - V(R) \qquad (19)$$

where $D^o(C-C)$ is the adiabatic cleavage energy, and V(R), the relaxation energy. Similarly, we have an equation which relates the cleavage energy to the average bond energy of a C-C bond from the reference compound C_2H_6.

$$D^o(C-C) = \overline{D}(C-C) + 2\,\overline{E}_v(C) \qquad (20)$$

where $\overline{E}_v(C)$ is the specific valence state energy of the carbon atom with the free valence electron in the cleaved alkyl groups, R_1 and R_2. The cleavage energy should be a constant for homologous bond cleaving within
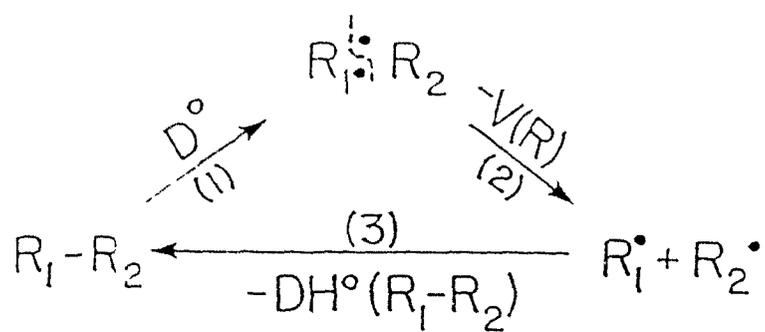
Fig. 9:

Dissociation of R_1 - R_2 Bonds

the limitation of the concept of additivity.

The model is called "the cleaving-relaxation model". The BDEs between any alkyls are described as the difference between a constant and a variable, that is:

$$DH^o(R_1 - R_2) = [\ \bar{D}(C-C) + 2\ \bar{E}_v(C)\ ] - [\ V(R_1) + V(R_2)\ ] \qquad (21)$$

Two important theoretical problems, thus, remain. How can determine the constant and the variable? Scientists have tried to address these problems since the 1950's. Their opinions will be reviewed in the last section of this Chapter.

The calculation of the first term or the constant term in eq.(21) is difficult for any chemical bond theory. The valence state is a pure theoretical idea. We may imagine and describe it by a lot of words and mathematical language, but we cannot observe or measure it by means of any experiment. In general, the valence state of an atom is described as a statistical average of a few stationary spectroscopic states.[20] For example, the spectroscopic terms contributing to valence state energy for a carbon atom with sp^3 hybridization consist of $^5S_2$, $^3D_1$, $^3D_3$, $^3S_1$ and $^1D_2$, in which the weight ratios are 5:2:4:3:2. The latest value, 8.263 ev, for a carbon atom with sp^3 hybridization has been calculated from the energy of these states.

It is known very well that the propagator of the inductive effect in physical organic chemistry, the valence state energy in quantum chemistry, and the average bond energy and heats of formation of species in thermochemistry all seem independent or unrelated. But now, all of the interesting concepts converge together into the cleaving-relaxation model for estimating chemical bond dissociation energies.

From concrete practice, it is rewarding to find that the absolute value of the constant in eq. (21) is not very important or necessary for

estimating BDEs in polyatomic hydrocarbon molecules. The reason is that the constant term can be canceled out if we take difference methods. For example,

$$DH^O(R_1-R_2) = DH^O(CH_3-CH_3) +$$
$$+ [V(CH_3) - V(R_1)] + [V(CH_3) - V(R_2)] \qquad (22)$$

where the BDE of the C-C bond in ethane, the reference compound, is equal to 90.2 ± 0.2 kcal/mol. It has a very small uncertainty. The estimation of the relaxation energy, thus, becomes a key problem for theoretical chemists. It will be addressed in Section 6.5.

6.5 Relaxation Energy and Inductive and Steric Effects on Bond Cleavage

As pointed out, the relaxation energy, $V(R)$, is a delocalization energy, when a parent molecule R_1R_2 is dissociated and delocalized to form stable free alkyls R_1 and R_2. According to eq. (22), we must determine the differences between two pairs of relaxation energies, $V(CH_3)$ vs. $V(R_1)$ and $V(CH_3)$ vs. $V(R_2)$, for estimating the BDE of a C-C bond. The differences, in fact, may be described as the differences between the BDEs of CH_3-CH_3, CH_3-R_1 and CH_3-R_2 bonds. That is

$$V(CH_3) - V(R_1) = DH^O(CH_3-R_1/CH_3-CH_3) \qquad (23a)$$
$$V(CH_3) - V(R_2) = DH^O(CH_3-R_2/CH_3-CH_3) \qquad (23b)$$

The right sides in eq. (23) have already been discussed well and described quantitatively in ref. 209. Every methyl group or carbon atom at the β-position in the radicals R_1 and R_2 can decrease the BDE by 1.7 kcal/mol relative to the BDE of the C-C bond in ethane. Consequently, we have a very simple result:

$$DH^O(R_1-R_2) \approx 90.2 - 1.7 \beta \quad kcal/mol \qquad (24)$$

where β is the number of carbon atoms at the β-positions in both radicals. Eq. (24) is valid for linear hydrocarbons, as shown in Table 39. For the

available six C-C bonds, the average deviation is only 0.2 kcal/mol.

TABLE 39: The BDEs of Typical C-C Bonds, in kcal/mol

	R_1	R_2	ΔV_{nb}	$DH^o(R_1-R_2)$ est.[a]	obs.[b]	Δ^c
I	CH_3	CH_3		90.2	90.2±0.2	0
	CH_3	C_2H_5		88.5	88.5±0.5	0
	C_2H_5	C_2H_5		86.8	86.8±0.7	0
	CH_3	$i-C_3H_7$		86.8	87.2±0.6	0.4
	C_2H_5	$i-C_3H_7$	-0.8	84.3	85.1±0.8	0.8
	$i-C_3H_7$	$i-C_3H_7$	-1.6	81.8	82.6±0.9	0.8
	CH_3	$t-C_4H_9$		85.1	85.2±0.7	0.1
	C_2H_5	$t-C_4H_9$	-1.6	81.8	82.8±1.0	1.0
	$i-C_3H_7$	$t-C_4H_9$	-3.2	78.5	78.8±1.0	0.3
	$t-C_4H_9$	$t-C_4H_9$	-4.8	75.2	73.7±1.0	-1.5
II	CH_3	$n-C_3H_7$		88.5	88.6±1.1	0.1
	C_2H_5	$n-C_3H_7$		86.8	87.0±1.2	0.2
	$n-C_3H_7$	$n-C_3H_7$		86.8	86.9±1.5	0.1
	$i-C_3H_7$	$n-C_3H_7$	-0.8	84.3	85.3±1.2	1.0
	$s-C_4H_9$	$n-C_3H_7$	-1.6	83.5	83.8±1.5	0.3
	$t-C_4H_9$	$n-C_3H_7$	-1.6	81.8	82.6±1.3	0.8
III	CH_3	$s-C_4H_9$	-0.8	86.0	86.4±1.2	0.4
	C_2H_5	$s-C_4H_9$	-1.6	83.5	84.1±1.2	0.6
	$i-C_3H_7$	$s-C_4H_9$	-2.4	81.0	82.1±1.2	1.1
	$s-C_4H_9$	$s-C_4H_9$	-3.2	80.2	80.1±1.5	-0.1
	$t-C_4H_9$	$s-C_4H_9$	-4.0	77.7	77.1±1.3	-0.6

	R	R'	ΔBDE[c]	BDE
	CH_3	$i\text{-}C_4H_9$	−0.8	87.7
	C_2H_5	$i\text{-}C_4H_9$	−0.8	86.0
	$n\text{-}C_3H_7$	$i\text{-}C_4H_9$	−0.8	86.0
IV	$i\text{-}C_3H_7$	$i\text{-}C_4H_9$	−1.6	83.5
	$i\text{-}C_4H_9$	$i\text{-}C_4H_9$	−1.6	85.2
	$s\text{-}C_4H_9$	$i\text{-}C_4H_9$	−2.4	82.7
	$t\text{-}C_4H_9$	$i\text{-}C_4H_9$	−2.4	81.0
	CH_3	$n\text{-}C_4H_9$		88.5
	C_2H_5	$n\text{-}C_4H_9$		86.8
	$n\text{-}C_3H_7$	$n\text{-}C_4H_9$		86.8
V	$i\text{-}C_3H_7$	$n\text{-}C_4H_9$	−0.8	84.3
	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$		86.8
	$i\text{-}C_4H_9$	$n\text{-}C_4H_9$	−0.8	86.8
	$s\text{-}C_4H_9$	$n\text{-}C_4H_9$	−1.6	83.5
	$t\text{-}C_4H_9$	$n\text{-}C_4H_9$	−1.6	81.8

[a] Based on eq. (27). [b] The values based on experimental heats of formation of free alkyls and hydrocarbons are labeled observed. The data on free radicals are from Table 8 and those on hydrocarbons are from ref. 102. [c] These are the differences between the observed BDEs and the estimated ones.

Let us consider the steric effect for C-C bond cleavage. An example for a branched alkane follows. In the 2,2,3-trimethylbutane molecule, the steric strain energy is large. The steric repulsion energy can be released after cleaving of the central C-C bond in the molecule. But there is no steric strain in the isopropyl and tertbutyl radicals. In order to estimate the BDEs better we have to deduct the steric release. In general, we have

$$DH^{o}(R_1-R_2) = DH^{o}(CH_3-CH_3) + [V(CH_3) - V(R_1)] +$$

$$+ [V(CH_3) - V(R_2)] + \Delta V_{nb} \qquad (25)$$

where ΔV_{nb} is the steric compression relief due to bond dissociation and is equal to the net change in non-bonded interactions before and after bond cleavage:

$$\Delta V_{nb} = V_{nb}(R_1) + V_{nb}(R_2) - V_{nb}(R_1R_2) \qquad (26)$$

where V_{nb} represents non-bonded interactions or steric repulsions in the parent molecule and radicals. For non-cyclic saturated hydrocarbon compounds, there are only two kinds of steric repulsive interactions: 1,4-gauche and 1,5-H repulsion. They have been studied well quantitatively; 0.5 -1.0 kcal/mol is allowed for each gauche repulsion (See Section 1.3); 1.5 kcal/mol is allowed per 1,5-H repulsion. But, 1,5-H repulsion does not occur for any of the compounds in Table 39. The equation, thus, for estimating these BDEs reduces to a very simple form, that is

$$DH^{o}(R_1-R_2) \approx 90.2 - 1.7 \beta - 0.8 \Delta g \quad kcal/mol \qquad (27)$$

where $\Delta V_{nb} = - 0.8\Delta g$ kcal/mol and Δg is the change in the number of gauche conformations between the radicals and parent molecules. It is acceptable that we only count the numbers of carbon atoms at the β-positions and the gauche interactions in the species if we want to know the BDEs of C-C bonds between any kind of alkyls. Eq.(27) is also dependable. As seen in Table 39, the average deviation is 0.5 kcal/mol with one maximum deviation of 1.5 kcal/mol for the 21 available C-C bonds between alkyls. The big deviation in heavily branched compounds may be expected because no simple scheme can ever account for such a distant interaction.[125] That means the uncertainty of our method for estimating BDEs has become the same as that of currently available methods [114,116-7,119,125] for estimating the thermochemistry of organic and organometallic compounds. Most deviations in

Table 39 are positive. This originates from the fact that 0.8 kcal/mol was chosen for each gauche correction, as in Benson's work.[116] These deviations would decrease if 0.5 or 0.6 kcal/mol were chosen for each gauche correction.

Two examples of estimations of BDEs of C-C bonds are given below:

(1) $DH^o(\;C\text{-}C\text{-}\overset{C}{\underset{C}{\overset{|}{\text{C}}}}\text{-}C\text{-}C\;)_{est}$ = 90.2 - 1.7 × 5 - 0.8 × 4 =

$$= 78.5 \text{ kcal/mol}$$

$$\text{obs.} = 78.8 \pm 1.0 \text{ kcal/mol}$$

(2) the estimated BDEs of four C-C bonds in iso-octane.

$$C_1 -\!\!-\!\!\overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{C_2}}-\!\!-C_3 -\!\!-\overset{\overset{\displaystyle C}{|}}{C_4}-\!\!-C_5$$
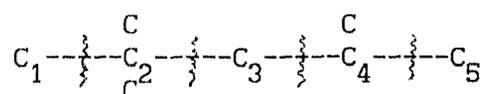
$DH^o(C_1\text{-}C_2)_{est}$ = 90.2 - 1.7 × 3 - 0.8 = 84.3 kcal/mol

$DH^o(C_2\text{-}C_3)_{est}$ = 90.2 - 1.7 × 4 - 0.8 × 3 = 81.0 kcal/mol

$DH^o(C_3\text{-}C_4)_{est}$ = 90.2 - 1.7 × 3 - 0.8 × 3 = 82.7 kcal/mol

$DH^o(C_4\text{-}C_5)_{est}$ = 90.2 - 1.7 × 2 - 0.8 = 86.0 kcal/mol

There are no observed values for comparison.

An example for which one must consider 1,5 H-repulsion energy is the BDE of a central C-C bond in 2,2,4,4,-tetramethyl pentane. There are 4 carbon atoms at the β-positions in the radicals, and 4 gauche conformations and two pairs of 1,5-H repulsions in the parent molecule. The BDE of the C-C bond is

$$DH^o(\;C\text{-}C\text{-}\overset{C}{\underset{C}{\overset{|}{\text{C}}}}\text{-}C\text{-}\overset{C}{\underset{C}{\overset{|}{\text{C}}}}\text{-}C\;)_{est} = 90.2 - 1.7 \times 4 - 0.8 \times 4 - 1.5 \times 2 =$$

$$\approx 77.2 \text{ kcal/mol}$$

There is no observed value. All observed values of the BDEs in this work are calculated based on the observed heats of formation of free radicals in Table 12 and of compounds in ref. 102.

6.6 Discussion

In general, the BDE of one atom or group, R_1, and another group, R_2, can be described as

$$DH^O(R_1-R_2) = D^O(1,2) - V(R) \qquad (28)$$

or further

$$= \{\bar{E}_v(1) + \bar{E}_v(2) + \bar{D}(1,2)\} - \{V(R_1) + V(R_2)\} \qquad (29)$$

if the steric interaction may be neglected. Here $D^O(1,2)$ is the cleavage energy, $\bar{E}_v$ is the specific valence state energy, $\bar{D}(1,2)$ is the average bond energy between the central atoms 1 and 2 from a reference compound and $V(R)$, is the relaxation energy of the groups, R_i. The difference between the valence state energy and the relaxation energy for univalent atoms may be assigned to be zero. Eq.(29) reduces to

$$DH^O(X-R) = [\bar{E}_v(Y) + \bar{D}(X-Y)] - V(R) \qquad (30)$$

when X represents univalent atoms, such as halogen and H, and Y is the central atom in the free radical. When Y is a polyvalent atom, we may obtain the following relation from eq. (29)

$$DH^O(R_1-R_2) = \frac{1}{2} \{DH^O(R_1-R_1) + DH^O(R_2-R_2)\} \qquad (31)$$

For example, we have

$$DH^O(CH_3-C_2H_5) = \frac{1}{2} \{ DH^O(CH_3-CH_3) + DH^O(C_2H_5-C_2H_5)\} \qquad (32)$$

and

$$DH^O(RO-OH) = \frac{1}{2} \{ DH^O(HO-OH) + DH^O(RO-OR)\} \qquad (33)$$

The relations, like eqs. (32) and (33), may also be inferred from group additivity rules.[114,116-7,119,125] The relations have all been supported by a lot of experiments. Conversely, such a relation is a method to check if steric hindrance or another effect exists in the species. Two examples are

offered below. First, $DH^O(CH_3-t-Bu)$ is not equal to half of the sum of $DH^O(CH_3-CH_3)$ and $DH^O(t-Bu-t-Bu)$ because the steric effect in 2,2,3,3,-tetramethylbutane is very big. Next, $DH^O(CH_3-CN)$ is equal to 121.5 $\pm$ 2.1 kcal/mol and much greater than half of the BDE value sum of CH_3-CH_3 and NC-CN bonds. The central C-C bond in the latter dimer weakens due to the repulsions of four pairs of pi electrons at the two sides of the C-C bond. $DH^O(NC-CN)$ is only 128 $\pm$ 1 kcal/mol. BDEs in unsaturated compounds will be discussed in the near future.

A more general cleaving-relaxation model with a steric correction can be obtained. Then the BDEs are expressed as

$$DH^O(R_1-R_2) = D^O(1,2) - V(R) + \Delta V_{nb} \qquad (34)$$

or further

$$= \{\bar{E}_v(1) + \bar{E}_v(2) + \bar{D}(1,2)\} - \{V(R_1) + V(R_2)\} + \Delta V_{nb} \qquad (35)$$

where every term is the same as that in eqs. (26), (28) and (29).

More than 30 years ago, Semenov and coworkers [156] found eq. (28). Later, Szabo [158] used it for estimating the BDEs and gave V_{C-H} = 13 kcal/mol, which was a purely empirical assumption. But they did not reveal the secret of the constant, $D^O(1,2)$, and did not find eqs. (29) and (30). And they suggested that V(R) was a constant. The steric correction was not considered. The opinion that V(R) is a constant does not agree with a lot of facts. It is unfortunate that these pioneer works have been almost forgotten in modern chemistry.

Sanderson [36,39,40] offered an equation for estimating the BDEs. It was presented as

$$DH^O(R_1-R_2) = CBE + E_R(1) + E_R(2) \qquad (36)$$

where CBE is the contributing bond energy, which is only dependent on the two bonding atoms, and $E_R(i)$ is the reorganizational energy of the radical i, where i = 1 or 2. The reorganizational energies are explained as the

energies required when the free radicals rearrange to a stable form. The reorganizational energy of a given radical is assigned as a constant. For example, the reorganizational energies of methyl, ethyl, isopropyl and tertbutyl radicals are assigned to be 3.9, 2.0, 0.9 and -1.7 kcal/mol, respectively. The concept of constant reorganizational nergies, actually, is equivalent to that in Semenov-Szabo's theory. As emphasized previously, (See Section 1.4 and Chapter 3) such theories fail to explain the three orders of the BDEs of X-alkyl bonds. It is impossible that the electron distribution for an ethyl group is the same in fluoroethane, chloroethane, bromoethane, iodoethane, ethanol or ethane. The electron distribution of an ethyl group in these compounds depends on the electronegativity of the substituent X. The energy required for rearrangement of the free ethyl radical to form the given molecules should also be different.

The chemical behavior of any group or ion in a species depends not only on its chemical composition and structure, but also on its chemical environment. The ethyl group in ethyl derivatives, C_2H_5X, is in different chemical environments although the ethyl group has the same chemical composition and almost the same geometric structure. That is why the ideas of the traditional, fixed substituent constants and group electronegativities are not accepted. The method of atomic electronegativity plus the electronic and steric effects is preferred.

Now let us look back on the path followed in studying the BDEs of C-C bonds. This is a winding path. It includes 6 steps at the least. First is to describe quantitatively the relation [97] between the covalent potential of X, V_x, and the heats of formation of $XC(CH_3)_mH_{3-m}$ using accurate thermochemical data.[102] Second is to determine a purely empirical equation [209] for describing the BDEs of $CH_3-C(CH_3)_mH_{3-m}$ bonds and find the decrement of the successive replacement for H by CH_3 at the β-position is about 1.7

kcal/mol per CH_3. Third is to infer the propagator of the inductive effect
from the above-mentioned empirical relations. Fourth is to understand
whether the third and higher order interactions may be neglected (See
Chapter 3), using the concept of the inductive effect. We have found the
third order inductive interaction is a small quantity relative to chemical
accuracy and is about 0.6 kcal/mol per alkyl group at the γ-position. Fifth
is to study the BDEs between any alkyl groups using the cleaving-relaxation
model in this Chapter in order to extend our previous results. The sixth or
the last step is to introduce steric compression relief. Our study
resembles climbing a few hills. In all processes, from the particular rules
to the more general ones, the presently available experimental data are our
food and drink, the popular GA rules and the concept of the inductive
effect are our inseparable friends.

Certainly, we have big trouble in determining the absolute value of
the valence state energy for various polyvalent atoms. The cleavage energy
or the valence energy and the average bond energy from a simple reference
compound belong intrinsically to the first or direct interaction energy.
For this reason, we have to take the difference method to cancel them out
and try hard to attack the problems of the second, third and higher order
interactions when cleaving chemical bonds. We have started from methyl
derivatives where all data on $\Delta_f H^o(CH_3X)$ and $DH^o(CH_3-X)$ have high
precision. The concept of the inductive effect helps us to extend from
methyl derivatives to any alkyl ones. In this way, the trouble with the
calculations of the absolute values of the valence state energy or the
direct interaction in C-X bonds have been avoided or hidden. Anyway, our
final results are simple, clear and useful, like eqs. (2) and (27). The
deviations for most estimated values are within 1 kcal/mol or less. These
have been verified by many very concrete examples in this thesis.

We may also take the routine method to get the BDFs. First, determine the heats of formation using GA with the third order correction (See Chapter 3). Then find heats of formation of parent compounds and calculate the BDEs. Both the routine method and eq.(27) offer the same values. Clearly, the estimate based on eq.(27) is simpler and faster.

The method with the steric correction can be extended to H-Si bonds. An example follows. In the two molecules, $HSiEt_3$ and $HSi(Me)_2Si(Me)_3$, the 1,4-H and 1,5-H distances are larger, at 2.6 A. That means there is no steric repulsion in the two molecules. But in the staggered structure of $HSi(SiMe_3)_3$, the 1,5-H distance is about 1.8 A. It is about equal to the 1,4-H distances in the staggered structure of the 2,2,3,3-tetramethylbutane molecule. Therefore we suggest that the steric repulsion contribution from each 1,5-H pair in $HSi(SiMe_3)_3$ is about 0.8 kcal/mol. The total steric compression release due to cleaving the H-Si bond is about 4.8 kcal/mol for six pairs of 1,5-H repulsions. From this idea and the discussion in Chapter 5 in this thesis, it is very easy to explain the values of the BDEs of H-Si bonds measured by Dr. Griller's group.[193,299] We obtain

$$DH^O(H\text{-}SiEt_3)_{est} \approx DH^O(H\text{-}SiH_3) = 90.3 \pm 1.2 \text{ kcal/mol}$$

$$DH^O(H\text{-}Si(Me)_2SiMe_3)_{est} \approx DH^O(H\text{-}Si_2H_5) = 86.3 \pm 2 \text{ kcal/mol}$$

$$DH^O(H\text{-}Si(SiMe_3)_3)_{est} \approx DH^O(H\text{-}Si_2H_5) - 4 \ 8 = 81.5 \pm 2 \text{ kcal/mol}$$

The observed values[193,299] are 90.1±2.0, 85.3±2.0 and 79.0±2.0 kcal/mol, respectively. The fact that BDEs of H-Si bonds are not sensitive to methyl substitution, unlike H-C bonds in hydrocarbons, has been explained, in Chapter 5. The values of BDEs of H-Si bonds in SiH_4 and Si_2H_6 are taken from refs. 103 and 167.

According to the cleaving-relaxation model, empirical relations previously proposed for estimating the BDEs may be reproduced easily. The problem of estimating the BDEs of X-alkyl bonds, where X = halogen, H, CH_3, SiH_3, OH, SH, NH_2 and alkyls, is resolved within the range of the experimental uncertainty. Of course, it is to extend or generalize these methods from X = OH, SH, NH_2 and SiH_3 to O-, S-, N- and Si-centered groups. Theses methods are also suitable for X = GeH_3, SnH_3, PH_2, SeH, Ge-, Sn-, P- and Se-centered groups. Thermochemical data for these compounds are absolutely necessary for advanced technology and chemistry but are scarce now.

Chapter VII Effects of Alkyl Substitution on Ionization Potentials

of Molecules

7.1 Introduction

As pointed out in Section 1.7, the equation of Bachiri et al.[309] for estimating adiabatic IPs is not valid for hydrocarbons and halogenated hydrocarbons. Holmes and Lossing's equation with four parameters[269,270]

$$\Delta_f H^o (RX^+)_{est} = A + BN + C/N + Dn_b \tag{1}$$

has only indirectly given IPs of organic compounds.

In this Chapter, the method we used in Chapters 2 to 6 will be extended to describe the IPs of neutral molecules and heats of formation of odd-electron molecular cations. Simple methyl derivatives will be discussed first. Secondly, the cations of hydrocarbons and chloro-, bromo- and iodoalkanes with longer linear and branched chains will be reported.

7.2 A Simple Relation for $\Delta IP(CH_3X/C(CH_3)_m H_{3-m} X)$

The recommended values of the adiabatic IPs of neutral molecules are from ref. 189. The data on IPs of methyl derivatives, $C(CH_3)_m H_{3-m} X$, are listed in Table 40. Here X represents the univalent atoms, H, F, Cl, Br and I; and m is the degree of methyl substitution. The group $C(CH_3)_m H_{3-m}$ or R represents the prototypical alkyls, ethyl, iso-propyl and tert-butyl when m equals 1, 2 and 3, respectively.

In Table 41 are listed values for the following differences in IPs:

$$\Delta IP(MeX/EtX) = IP(MeX) - IP(EtX) \tag{2}$$

$$\Delta IP(MeX/i\text{-}PrX) = IP(MeX) - IP(i\text{-}PrX) \tag{3}$$

$$\Delta IP(MeX/t\text{-}BuX) = IP(MeX) - IP(t\text{-}BuX) \tag{4}$$

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TABLE 40: Ionization Potentials of Methyl Derivatives, in eV [a]

X	Me	Et	i-Pr	t-Bu
H	12.51	11.52±0.01	10.95±0.05	10.57
		(11.51)	(10.96)	(10.57)
F [b]		11.6	11.08	
	(11.83±0.2)	(11.45±0.2)	(11.19±0.2)	(10.98±0.2)
Cl	11.22±0.01	10.97±0.02	10.78±0.02	10.61±0.03
		(10.95)	(10.75)	(10.58)
Br	10.541	10.28	10.07±0.01	9.92±0.03
		(10.31)	(10.13)	(9.97)
I	9.538	9.346	9.175	9.02±0.02
		(9.33)	(9.16)	(9.00)

[a] The values in parentheses are estimates based on eq. (8), see text.

[b] See the discussion after eq. (8) in the text.

TABLE 41: Differences between Ionization Potentials, in eV

X	ΔIP [a]		
	MeX/EtX	MeX/i-PrX	MeX/t-BuX
H	0.99	1.56±0.05	1.94
F	(0.38)	(0.64)	(0.85)
Cl	0.25±0.03	0.44±0.03	0.61±0.04
Br	0.26±0.01	0.47±0.02	0.62±0.03
I	0.192	0.363	0.518±0.02

[a] The values in parentheses are estimates based on eq. (5), see text.

We have found three linear relations between ΔIP and $1/n^2$ as shown in Figure 10. Here n is the principal quantum number of the valence electrons of the univalent atom X. The fluorides are not shown. They will be discussed later. The values of the intercepts, I(m), the slopes, S(m), and the correlation coefficient, r, for the straight lines in Figure 10 are listed in Table 42:

$$\Delta IP(MeX/RX) = I(m) + S(m)/n^2 \tag{5}$$

TABLE 42: Slopes, Intercepts and Correlation Coefficients in Figure 10

	S(m)/ev		I(m)/eV		r
	obs.	est.[a]	obs.	est.[b]	
m = 1	0.81±0.03	0.81	0.18±0.02	0.18	0.998
m = 2	1.22±0.04	1.22	0.34±0.02	0.33	0.998
m = 3	1.46±0.04	1.46	0.48±0.02	0.48	0.999

[a] Based on eq. 7. [b] Based on eq. 6

The slopes and intercepts of these three straight lines may be further described as:

$$I(m) = 0.03 + 0.15m \tag{6}$$

$$S(m) = 0.084 (8.21 - m)(m + 0.34) \tag{7}$$

As shown in Table 42, values of the intercepts and slopes derived from eqs. (6) and (7) are in excellent agreement with the observed values.

In general, an empirical expression for estimating $IP(C(CH_3)_m H_{3-m} X)$ can be described as:

$$IP(C(CH_3)_m H_{3-m} X) = IP(CH_3 X) - (0.03 + 0.15m) -$$
$$- 0.084(8.21 - m)(m + 0.34)/n^2 \tag{8}$$

Estimated values based on eq. (8) are listed in parentheses in Table 40. The average deviation between the estimated and observed values is less
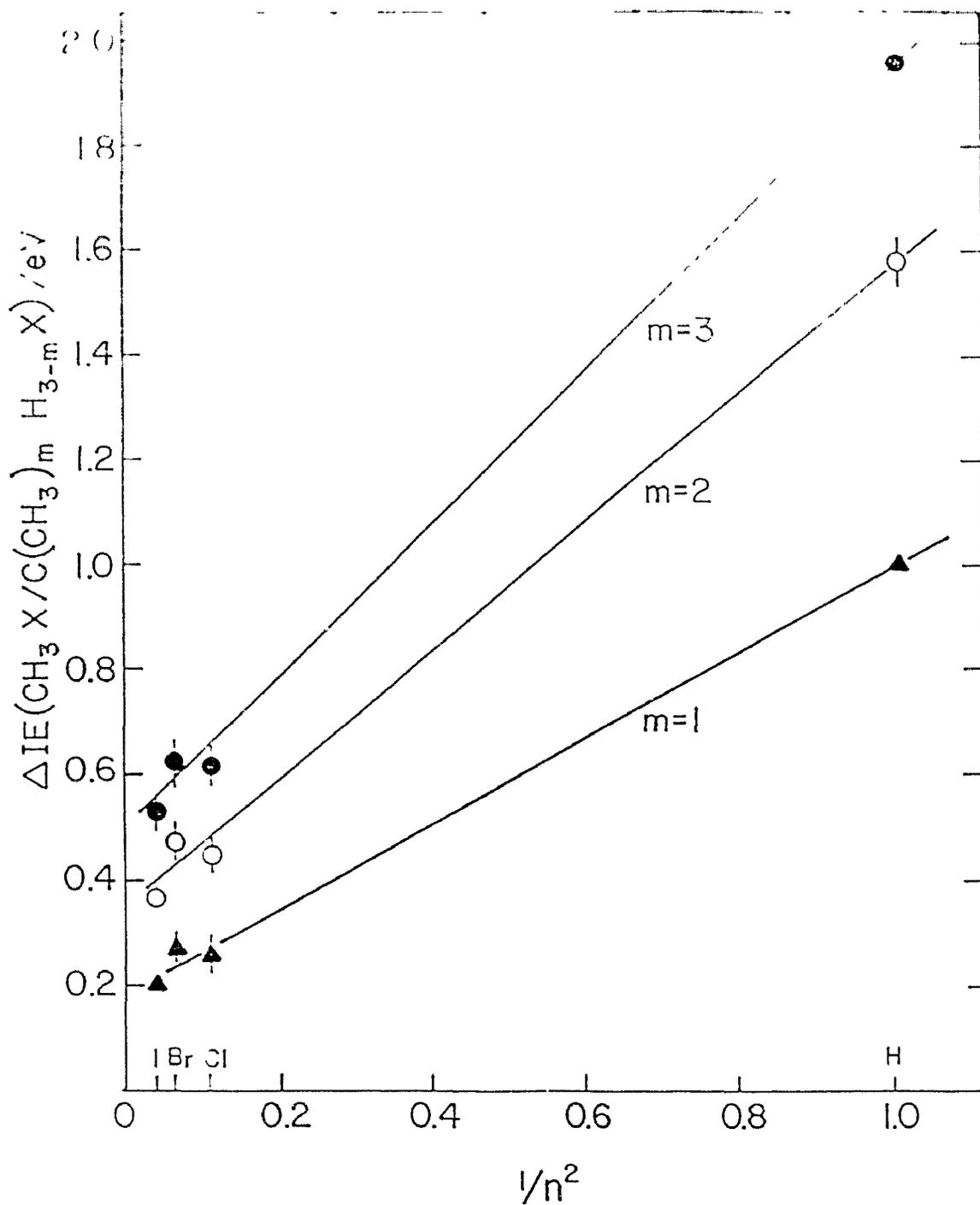
Fig. 10

Linear Relations betweem $\Delta IP(CH_3X/C(CH_3)_m H_3-mX)$ and $1/n^2$

than 0.025 eV, with a maximum deviation of 0.06 eV for i-PrBr.

It is necessary to have a reference point for the IPs of fluorides. If the IPs of CH_3F were known, eq. (8) could be used to estimate the values of IPs of EtF, i-PrF, and t-BuF. There are two ionized isomers for methyl fluoride as follows:[189,370] CH_3F^+ (I), the conventional ionized fluoromethane cation, and CH_2F^+H (II), the ylidion or methylenefluoronium radical cation. Both mass spectral experiments[370] and ab initio MO calculation[371,373] have shown that structure (II) is favored, unlike the situation for chloro-, bromo- and iodomethane. For chloromethane, both experiments[189,372] and ab initio MO calculations,[373] at the MP4/6-311G(df,p) level, pointed out that the conventional isomer, CH_3Cl^+, is more stable than the ylidion, CH_2Cl^+H. Therefore the value of the IP forming the CH_2F^+H cation could be selected as a reference point for alkyl fluorides. The heat of formation of this cation was measured by Holmes' group to be 217 ± 4 kcal/mol.[370] Using the heat of formation of CH_3F,[97] we may estimate the value of the IP forming structure (II) to be 11.83 ± 0.2 eV. This value will be considered as the reference point. Further the values estimated based on eq. (8) for other alkyl fluorides are shown in parentheses in Table 40. The crude values in ref. 189 were 11.8 and 11.08 eV for EtF and i-PrF, respectively. Clearly, this approach is capable of correlating the IPs for fluoroalkanes as well.

7.3 Heats of Formation of Methyl Derivatives

According to thermochemistry, heats of formation of molecular cations are the sum of the ionization potentials, IP(RX), and heats of formation, $\Delta_f H^o(RX)$, of molecules, i.e.

$$\Delta_f H^o(RX^+) = IP(RX) + \Delta_f H^o(RX) \qquad (9)$$

In ref. 97, a relation was reported for heats of formation of

substituted alkanes

$$\Delta_f H^o(RX) = \Delta_f H^o(MeX) + [0.9 - 1.5m(m-1)] - \cfrac{m}{0.67 + 0.21m} V_x \qquad (10)$$

(See page 31.)

Substituting eqs. (8) and (10) into eq. (9), we obtain

$$\Delta_f H^o(C(CH_3)_m H_{3-m} X^+) = \Delta_f H^o(CH_3 X^+) - 1.5m(m + 1.4)$$

$$- 1.93 \cfrac{(8.21 - m)(m + 0.34)}{n2} - \cfrac{m}{0.67 + 0.21m} V_x \qquad (11)$$

Here, the energies are in kcal/mol.

The first term on the right in eq. (11) has been recalculated in this work. That is

$$\Delta_f H^o(CH_3 X^+) = IP(CH_3 X)_{obs} + \Delta_f H^o(CH_3 X)_{obs} \qquad (12)$$

Here, the values of IPs and heats of formation were taken from refs. 189 and 102, respectively. Note that the values recalculated based on eq. (12) are little different from the values reported in ref. 189. The values recalculated in this work are listed in the second line for each substituent X in Table 43.

Values for the simple methyl derivative cations have also been calculated based on eq. (11) and are listed in the second line for each substituent X in Table 43. The average deviation between the observed values and the estimated cnes, excluding the fluorides, was 0.6 kcal/mol. The maximum deviation was 3.4 kcal/mol for i-PrBr. Three compounds, i-PrBr, t-BuBr and i-PrI, have large deviations. As pointed out in ref. 97, the observed heats of formation of these three compounds have not yet been determined with better than $\pm$ 1 kcal/mol accuracy.

TABLE 43: Heats of Formation of Methyl Derivative Cations, in kcal/mol

$$\Delta_f H^{\circ}(RX^{+})\ ^{a}$$

	Me	Et	i-Pr	t-Bu
H	271	245.6	227.5	212
	(270.7)	(245.4)	(227.5)	(211.1)
	[272.6]	[243.7]	[226.9]	[211.5]
	{271.6}	{244.8}	{226.7}	{213.0}
F^{a}	217±4	205	185	
	(217.0)	(197.5)	(181.6)	(165.9)
Cl	239	226	214	201
	(239.1)	(225.4)	(212.9)	(199.3)
	[237.5]	[227.3]	[214.4]	[202.4]
	{240.7}	{223.7}	{212.2}	{203.5}
Br	234	222.2	209	197
	(234.6)	(223.9)	(212.4)	(198.7)
	[235.0]	[222.2]	[209.1]	[197.6]
	{235.9}	{219.2}	{207.9}	{199.3}
I	223.6	213.3	202	191
	(223.4)	(213.1)	(202.5)	(190.1)
	[222.4]	[214.0]	[202.4]	[191.5]
	{225.3}	{210.7}	{200.7}	{193.2}

a Values in parentheses, ( ), square brackets, [ ], and braces, { }, are estimated using eq. (11) from this work, eqs. (1) and (13) from refs. 269 and 270, respectively, see the discussion in the text.

The deviations for fluoride cations are greater than for the other halogens, as shown in Table 43. The reason is that the values of the heats of formation of fluoride compounds in ref. 189 are questionable. The

problem was discussed in ref. 97. The values of heats of formation of fluorides in this work are taken from ref. 97. Consequently, there are bigger discrepancies between the estimated values and those reported in ref. 189 for fluoride cations.

7.4 Ionization Potentials of Haloalkanes

IPs of molecules have been considered as a function of molecular size and structure.[189,269,270,311] IPs for a homologous series, however, do not have a linear dependence on the molecular size and cannot be reproduced satisfactorily by simple additivity schemes, like those for prediction of thermochemical data for neutral molecules and radicals. The IPs of molecules fall at a decreasing rate with increasing molecular size.

We have suggested that the γ effect for IPs of haloalkanes could be expressed in a form similar to the equation for IPs of alkyl radicals (See Chapter 4), i.e.

$$IP(alkyl) = IP(C(CH_3)_m H_{3-m}) - 0.06 \, \gamma^+ \qquad (13)$$

Using observed values of the IPs, we have found the following equations for chloro-, bromo- and iodoalkanes, respectively:

$$IP(RCl) = IP(ClC(CH_3)_m H_{3-m}) - 0.16 \, \gamma^+ \qquad (14)$$

$$IP(RBr) = IP(BrC(CH_3)_m H_{3-m}) - 0.10 \, \gamma^+ \qquad (15)$$

$$IP(RI) = IP(IC(CH_3)_m H_{3-m}) - 0.05 \, \gamma^+ \qquad (16)$$

The values estimated based on eqs. (14) to (16) have been listed in Table 44, where they may be compared with observed values. The average deviation between observed values and values estimated using the three equations is 0.04 eV for 35 compounds.

TABLE 44: Ionization Potentials, in eV, of Chlorides, Bromides and Iodides and Heats of Formation, in kcal/mol, of their Cations

RX	$\gamma+$	IP/eV obs.[a]	est.	$\Delta_f H^o(RX)$[b]	$\Delta_f H^o(RX^+)$ obs.[c]	est. Holmes[d]	this work
Chlorides							
CH_3Cl		11.22±0.01	11.22[e]	-19.6	239	237.5	239.1
C_2H_5Cl	0	10.97±0.02	10.95	-26.8	226	227.3	225.7
		[11.04]					
C_3H_7Cl							
Cl C-C-C	0	10.78±0.02	10.75	-34.9	214	214.4	213.0
C-C-C-Cl	1	10.82±0.03	10.79	-31.5	218	219.4	217.3
		[10.70]					
C_4H_9Cl							
C-C-C-C-Cl	2	10.67±0.03	10.63	-37.0	209	212.4	208.1
		[10.46]					
Cl C-C-C-C	1	10.53	10.59	-38.5	204	207.4	205.7
C C-C-C-Cl	2	10.66±0.03	10.63	-38.1	208	209.4	207.0
C C-C-Cl C	0	10.61±0.03	10.58	-43.6	201	202.4	200.4
$C_5H_{11}Cl$							
C-(C)$_3$-C-Cl	3		10.47	-41.8		205.7	199.6
$C_6H_{13}Cl$							
C-(C)$_4$-C-Cl	4	[10.28]	10.31	(-46.6)	[190.5]	199.3	191.1
$C_7H_{15}Cl$							
C-(C)$_5$-C-Cl	5		10.15	(-51.6)		192.9	182.5

$C_8H_{17}Cl$

Compound	n						
C-(C)$_6$-C-Cl	6	[10.10]	9.99	-57.1	[175.8]	186.7	173.3

Bromides

Compound	n						
CH$_3$Br		10.541	10.541[e]	-8.5	234	235.0	234.6
C$_2$H$_5$Br	0	10.28	10.31	-14.8	222.2	?22.2	222.9

C_3H_7Br

Compound	n						
Br C-C-C	0	10.07±0.01	10.12	-23.8	209	209.1	209.6
C-C-C-Br	1	10.18±0.01	10.21	-20.8	214	214.1	214.6

C_4H_9Br

Compound	n						
C-C-C-C-Br	2	10.13	10.11	-22.6	208	207 6	210.5
Br C-C-C-C	1	9.98±0.01	10.02	-28.8	201	202.6	202.3
C C-C-C-Br	2	10.09±0.02	10.11	(-27.5)	(205)	204.6	205.6
C-C-Br C	0	9.92±0.03	9.95	-31.6	197	197.6	197.8

$C_5H_{11}Br$

Compound	n						
C-C-C-C-C-Br	3	10.09±0.02	10.01	-30.8	202	202.0	200.0
C C-C-C-Br C	3	10.04	10.01	(-35.1)	196	196.0	195.7

$C_6H_{13}Br$

Compound	n						
C-(C)$_4$-C-Br	4	[10.06]	9.91	(-35.5)	[196.5]	196.8	193.0

$C_7H_{15}Br$

Compound	n						
C-(C)$_5$-C-Br	5		9.81	-40.1		191.8	186.1

$C_8H_{17}Br$

Compound	n						
C-(C)$_6$-C-Br	6	[10.04]	9.71	-45.3	[186.2]	187.0	178.6

Iodides

CH_3I		9.538	9.538[e]	3.5	233.6	222.4	223.4
C_2H_5I	0	9.346	9.33	−1.8	213.3	214.0	213.3
C_3H_7I							
$\begin{matrix} I \\ C\text{-}C\text{-}C \end{matrix}$	0	9.175	9.15	−9.6	202	202.4	201.4
C-C-C-I	1	9.269	9.28	−7.2	206	207.4	206.8
C_4H_9I							
C-C-C-C-I	2	9.229	9.23	(−12.1)	(200)	201.5	200.7
$\begin{matrix} I \\ C\text{-}C\text{-}C\text{-}C \end{matrix}$	1	9.09±0.02	9.10	(−14.7)	(195)	196.5	195.1
$\begin{matrix} C \\ C\text{-}C\text{-}C\text{-}I \end{matrix}$	2	9.202	9.23	(−14.1)	(197)	[198.5][f]	198.7
$\begin{matrix} C \\ C\text{-}C\text{-}I \\ C \end{matrix}$	0	9.02±0.02	9.00	−17.2	191	191.5	190.3
$C_5H_{11}I$							
C-C-C-C-C-I	3	9.021	9.18	(−17.1)	(195)	195.9	194.6
$\begin{matrix} I \\ C\text{-}C\text{-}C\text{-}C \\ C \end{matrix}$	1	(8.93)	8.95	(−21.4)	(184)	185.9	185.0
$\begin{matrix} C \\ C\text{-}C\text{-}C\text{-}C\text{-}I \end{matrix}$	3	9.192	9.18	(−18.3)	(193)	[192.9][f]	193.4
$C_6H_{13}I$							
$C\text{-}(C)_4\text{-}C\text{-}I$	4	9.179	9.13	(−22.1)	(190)	190.4	188.4

[a] The observed values of IPs are from ref. 189, except the values in square brackets. The values in the parentheses have not been established or evaluated, see original reference. The values in square brackets are from ref. 311. [b] Ref. 102, unless noted. The values in the parentheses are estimated by Benson's additivity rules.[116, 131] [c] The observed values are from ref. 189, except the values in square brackets. The values in square brackets are calculated using the observed IPs of Dr. Holmes' group[311]

and the heats of formation of the compounds, in this Table. [d] Using the parameters in ref. 189. [e] The reference points in this work. [f] The values in the parentheses in this column are estimated using the method of Holmes' group and the assigned correction parameter, -3 kcal/mol, in this work. See the text.

7.5 Heats of Formation of Haloalkane Cations

Using eq. (9), heats of formation of haloalkane cations can be determined. Here IP(RX) may be estimated from eqs. (14) to (16). Heats of formation of the neutral compounds are known with high accuracy [102] and are listed in the fifth column of Table 44. Benson's group additivity rules (See Section 1.3.3), reproduce these data very well. The estimation of heats of formation of haloalkane cations in this way is simple. The values are listed in the last column in Table 44. The observed values in the sixth column are taken from ref. 189. The estimated and observed values are in agreement within current experimental uncertainty.

7.6 Ionization Potentials of Alkanes

The non-linear relation between the IPs of n-alkanes and the number of carbon atoms, n_c, was first described by Widing and Levitt. [276] The non-linear relation between IPs and the total number, N, of atoms in n-alkane molecules was described by Holmes et al. [269,270] Both non-linear relationships are smooth trends for 7 linear alkanes, $n-C_nH_{2n+2}$, where n equals 1 to 7. The curve becomes a little better if we study the relation between the IPs and the number of carbon atoms in alkanes, which will be discussed later. It has been found that

$$\Delta IP(CH_4/C_2H_6) \gg \Delta IP(C_2H_6/C_3H_8) > \Delta IP(C_3H_8/C_4H_{10})$$
$$> \Delta IP(C_4H_{10}/C_5H_{12}) \approx \Delta IP(C_5H_{12}/C_6H_{14}) \text{ and so on.}$$

This interesting order inspires us to try a linear function of γ^+ to fit the smooth curve:

$$IP(RH) = IP(HC(CH_3)_m H_{3-m}) - (a + b\,\gamma^+) \tag{17}$$

Using linear least squares for the IPs of 19 hydrocarbons with m = 2 and 3 in ref. 189, we obtain

$$IP(RH) = IP(HC(CH_3)_m H_{3-m}) - (0.14\,\gamma^+ + 0.25) \tag{18}$$

The multiple correlation coefficient is 0.926. The average deviation between the estimated and observed values [189] is 0.08 eV with a maximum deviation of 0.34 eV for the 2-methyldecane molecule, as shown in Table 45. We feel that the observed value for 2-methyldecane is not reliable. This will be discussed later. In general, the empirical equation (18) is dependable within the current experimental uncertainty.[189] In applying eq. (18) it is important to note that the correction term is zero (not 0.25) when γ^+ is zero.

TABLE 45: Ionization Potentials, in eV, of Hydrocarbons and Heats

of Formation, in kcal/mol, of the Cations

RH	$\gamma+$	IP/eV obs.[a]	est.	$\Delta_f H^o(RH)$[b]	$\Delta_f H^o(RH^+)$ obs.[a]	est. Holmes[c]	this work
CH_4		12.51	12.51^d	-17.8	271	272.6	270.7
C_2H_6		11.52±0.01	11.52	-20.0	245.6	243.7	245.7
C_3H_8		10.95±0.05 [10.90]	10.96	-25.0	227.5	226.9	227.7
C_4H_{10}							
C-C-C-C	1	10.53±0.10	10.57	-30.0	213	214.5	213.7
C-C-C C		10.57	10.57	-32.1	(212)	211.5	211.6
C_5H_{12}							
C-C-(C)$_2$-C	2	10.35±0.01 [10.22]	10.43	-35.1	204	204.1	205.4
C C-C-C-C	1	<10.22	10.18	-36.7	<199	201.1	198.1
C C-C-C C		<10.21	$(10.21)^d$	-40.2	<195	198.1	195.2
C_6H_{14}							
C-C-(C)$_3$-C	3	10.13	10.29	-39.9	194	194.9	197.4
C C-C-C-C-C	2	10.12	10.04	-41.8	(191)	191.9	189.7
C C-C-C-C-C	2	10.18	10.04	-41.1	(191)	191.9	190.4
C C C-C-C-C	2	10.02	10.04	-42.6	(189)	188.9	188.9
C C-C-C-C C	1	10.06	10.07	-44.5	(188)	188.9	187.7

C_7H_{16}

C-C-(C)$_4$-C   4   9.92±0.09   10.15   -44.9   184   186.4   189.2

C_8H_{18}

C-C-(C)$_5$-C   5   (9.82)   10.01   -49.9   (177)   178.3   180.9

C
C-C-C-(C)$_3$-C   4   9.84   9.76   -51.5   176   175.3   173.6

C C
C-C-C-C   3   9.8   9.79   -53.9   172   166.3   172.6
C C

C   C
C-C-(C)$_2$-C-C   4   9.86   9.76   -53.2   171   172.3   171.9

C_9H_{20}

C-C-(C)$_6$-C   6   (9.72)   9.87   -54.5   (170)   170.r   173.1

$C_{10}H_{22}$

C-C-(C)$_7$-C   7   (9.65)   9.73   -59.6   163   162.9   164.8

$C_{11}H_{24}$

C-C-(C)$_8$-C   8   (9.50)   9.59   -64.7   (156)   155.5   156.4

C
C-C-(C)$_7$-C   7   (9.68)   9.34   -64.4[e]   (157)   152.5   151.0

[a] Ref. 189 unless noted. The values in the parentheses have not been established or evaluated. See original reference. The values in square brackets are from ref. 311. [b] Ref. 102, unless indicated. [c] Using the parameters ref. 189. [d] The reference point in this work. [e] Based on Benson's group additivity rules [116,131] and including one gauche correction. Therefore the value in this work is 1.6 kcal/mol higher than that estimated in ref.189.

In equation (18), the first term on the right side is known very well. The method of calculating γ^+ is very important. The determination of the value of γ^+ depends on the probability of forming hydrocarbon cations, as

follows:

tertiary > secondary > primary

We have shown how to determine m and γ^+ in hydrocarbon cations in Table 46. According to this scheme, for straight chain hydrocarbons, γ^+ is always equal to the total number of carbon atoms minus three (the formal charge center and its two nearest neighbors). For branched hydrocarbons containing a tertiary carbon atom, γ^+ is always equal to the total number of carbon atoms minus four (the formal charge center and its three nearest neighbors).

Table 46: Determination of γ^+ in Hydrocarbons [a]

Chains	the Position of Formal Charge	γ^+	Reference molecules
Straight	primary	$n_C - 2$	C-C
	secondary	$n_C - 3$	C-C-C
Branched	tertiary	$n_C - 4$	C C-C-C
	quaternary	$n_C - 5$	C C-C-C C

[a] n_C represents the total number of carbon atoms in the cations.

Branched hydrocarbons containing a quaternary carbon may also be considered using a similar approach. There is a good straight line for the IPs for C_2H_6, C_3H_8, $i-C_4H_{10}$ and $neo-C_5H_{12}$. It is given by:

$$\Delta IP(CH_3CH_3/C(CH_3)_{m+1}H_{3-m}) = C.37\ m + 0.203 \qquad (19)$$

The correlation coefficient is 0.9999. Therefore, the experimental IP of $neo-C_5H_{12}$, 10.21 eV, is selected as a reference point for systems containing a quaternary carbon atom. In this group, γ^+ is always equal to the total number of carbon atoms minus five. The values of γ^+ for 2,2-

dimethyl-butane and 2,2,3,3-tetramethylbutane are 1 and 3, respectively. Then we have

$$IP(\text{quaternary hydrocarbons}) = IF(\text{neo-pentane}) - 0.14\gamma^{+} \qquad (20)$$

The values estimated by eq. (20) are also listed in Table 45.

In general, calculations of the IPs of hydrocarbon molecules are very simple using eqs. (18) and (20) and the reference points in Table 40.

7.7 Heats of Formation of Alkane Cations

Values of heats of formation of alkane cations estimated using eqs. (18) and (20) have been listed in the last column in Table 45 and are compared with observed values.[189] The average deviation for 22 alkane cations is about 1.5 kcal/mol, with a maximum deviation of -6.0 kcal/mol for 2-methyldecane.

Two examples of estimation of IPs of alkanes and heats of formation of cations are as follows:

(1) $n\text{-}C_{11}H_{24}$
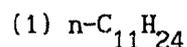
Here $\gamma^{+} = 8$,

$$IP(RH)_{est} = IP(C_3H_8)_{est} - 0.14 \times 8 - 0.25 = 9.59 \text{ eV}.$$

$$\text{obs.} = 9.50 \text{ eV}$$

$$\Delta_f H^{o}(RH^{+})_{est} = 9.59 \times 23.06 - \Delta_f H^{o}(RH) = 156.4 \text{ kcal/mol}.$$

$$\text{obs.} = 156 \text{ kcal/mol}$$

(2) 2,2,3,3-tetramethylbutane
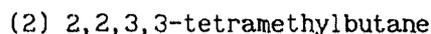
Here $\gamma^{+} = 3$,

$$IP(RH)_{est} = IP(\text{neo-pentane}) - 0.14 \times 3 = 9.79 \text{ eV}.$$

$$\text{obs.} = 9.8 \text{ eV}$$

$$\Delta_f H^{o}(RH^{+})_{est} = 9.79 \times 23.06 - \Delta_f H^{o}(RH) = 172.6 \text{ kcal/mol}.$$

$$\text{obs.} = 172 \text{ kcal/mol}$$

7.8 Discussion

Nine years ago, Holmes and Lossing [270] reported a simple equation for correlating heats of formation of molecular cations with the total number, N, of atoms in a molecule. For example, the heats of formation of cations of methyl derivatives were reported to be a linear function of the logarithm of N:

$$\Delta_f H^o(M^+) = constant + \alpha\ logN \qquad (21)$$

Here α is another constant.

In Table 43, we have compared the estimated values based on eqs. (11), (1) and (21) with the observed ones. For eq. (1), the average deviation for 16 points is 0.9 kcal/mol with a maximum deviation of 1.9 kcal/mol for C_2H_6. For eq. (21), the average deviation for 16 points is 1.7 kcal/mol with a maximum deviation of -3.0 kcal/mol for EtBr. Clearly, the values estimated in our work are, with an average deviation of 0.6 kcal/mol, closer to the observed data.

Equation (5) is purely empirical. Its simplicity rem nds us of the expression for the ionization potential of the hydrogen atom. In Bohr's model and quantum mechanics, ionization potentials for the hydrogen atom are inversely proportional to the second power of the principal quantum number, n.

$$IP(H) = constant/n^2 \qquad (22)$$

It is interesting to speculate about the similarity between equations (5) and (22). However, we have not found a satisfactory theoretical explanation at present.

For haloalkanes, we have calculated values and have listed them in the second last column in Table 44, using Holmes and Lossing's eq. (1) and the assigned parameters. Their method does not work for the cations of i-BuI and 1-iodo-3-methyl-butane because the empirical parameter for such

structures is not available at present. We may assign a correction term of 3 kcal/mol for each branch that is not adjacent to the iodine atom in the molecular framework. This correction is the same as that in chloro- and bromoalkanes. Then the values estimated by Holmes's approach for i-BuI and 1-iodo-3-methyl-butane would be 198.5 and 192.5 kcal/mol, respectively, as in the square brackets in this column.

For alkanes, Holmes' equation is

$$\Delta_f H^O(RH^+) = 224 - 2.2N + 298/N - 3\imath_b \qquad (23)$$

The values estimated based on eq. (23) have been listed in Table 45. The average deviation between the values estimated from eq. (23) and the observed values is 1.4 kcal/mol, almost the same as that for eqs (18) and (20). The maximum deviation of -5.7 kcal/mol occurs for 2,2,3,3-tetra-methylbutane, which is a highly branched compound subject to a steric effect. Based on eq. (23), we obtain $\Delta_f H^O(RH^+)_{est}$ = 166.3 kcal/mol. There are six gauche interactions. Using Benson's [116] assigned correction value, the total gauche correction is 4.8 kcal/mol. In this way the value estimated by eq. (23) would be adjusted to 171.1 kcal/mol. The adjusted value is closer to the observed one. That means that Holmes's equation with four parameters could be improved by including a steric correction.

For 2-methyl..ine, the values estimated using eqs. (18) and (23) have bigger deviations from the experimental value. Here γ^+ = 7 and IP(RH)$_{est}$ = 9.34 eV, but the value observed is 9.68 eV. Compared to the IPs of other 2-methyl-hydrocarbon molecules, the observed value for the 2-methyldecane molecule is irregular and too high. It is also higher than the value for its isomer, normal undecane. We would suggest the observed value is uncertain. From Table 45, Holmes' value and our value for the heat of formation are 4.5 or 6.0 kcal/mol less than observed. One gauche correction was not considered in estimating the heat of formation of the neutral

compounds in ref. 189.

Levitt and Widing [48,376] showed that the IPs of n-alkanes and haloalkanes were linear functions of Taft's inductive substituent constant or a revised scheme, calculated from the structure of the alkyl group according to delocalization, inductive and field effects. We have tested these functions. The average deviations are always bigger than those of our work. Secondly, these functions are limited to a given set of alkyl groups, unlike our work.

A linear relation between the IPs of n-alkanes and the reciprocal of the total number, N, of atoms in the molecules was reported by Holmes et al. [269,270] In their original work, only 6 alkanes were described. Very recently, Holmes and Lossing [311] have re-examined the relation for ten n-alkanes, C_nH_{2n+2} with n = 2 to 11. We have calculated that the average deviation between experimental values and those estimated using this linear relation is about 0.07 eV. The relation of ref. 311 has not yet been applied to branched structures.

The IPs of 11 linear hydrocarbons, from CH_4 to $n-C_{11}H_{24}$, in Table 45 have also been fitted by means of other functions. For example, we have tested the polynomials

$$IP(n-RH) = a_1 + a_2Z + a_3Z^2 \tag{24}$$

$$IP(n-RH) = a_1 + a_2Z + a_3Z^2 + a_4Z^3 + a_5Z^4 \tag{24a}$$

the logarithmic functions

$$IP(n-RH) = a_1 + a_2\log Z \tag{25}$$

$$IP(n-RH) = a_1 + a_2Z + a_3\log Z \tag{25a}$$

and the reciprocal functions

$$IP(n-RH) = a_1 + a_2/Z \tag{26}$$

$$IP(n-RH) = a_1 + a_2Z + a_3/Z \tag{26a}$$

Where Z represents n_C, the number of carbon atoms in RH, or N, the total

number of atoms in RH. We have found that the correlation quality for carbon atoms only is often a little better than that for all atoms, as shown in Table 47. Eqs. (24) to (26), however, do not work as well for the IPs of the branched hydrocarbors as for linear alkanes and most are more complicated than eq. (18). That is why we prefer to replace N by n_C or, further, γ^+ for empirical correlation of the IPs of organic compounds. Because the degree of methyl substitution, m, is considered in (18), this equation can offer better correlations for both linear and branched structures of organic compounds.

Table 47: Analysis of the Correlation Quality for Some Equations

IP(n-RH) =	Z			
	N		n_C	
	r	S.D/eV	r	S.D/eV
A + BZ + CZ^2	.9856	.17	.9856	.17
(1) A + B logZ	.9890	.14	.9803	.09 [a]
A + B/Z	.9904	.13	.9652	.25
A + BZ + CZ^2 + DZ^3 + EZ^4	.9992	.05	.9992	.05
(2) A + BZ + C logZ	.9988	.05	.9995	.03 [a]
A + BZ + C/Z	.9990	.05	.9966	.08
(3) eq. (9) (for 11 linear chains)			.9980	.06
(for all compounds)			.9850	.12

[a] The best correlation coefficient.

Jossing and Holmes[272] point.d out that the ionic charge of cations is not localized at the formal charge site but that the charge must be distributed over the whole ion. This idea inspired us to establish eq. (13).

Thus, eq. (17) was suggested by analogy and the empirical eq. (18) proved to be acceptable. Eq. (18) is really very similar to eq. (13). This similarity implies that the mechanism of delocalization of the ionic charge from the primary state to a given state is sim'lar for the cations o" hydrocarbon molecules and those of alkyl radicals. The delocalization arises from atomic interactions in cations, particularly from the interactions between the formal charge center and the other carbon atoms. We would imagine that the interactions between the formal charge center and the neighboring atoms are very strong. Interactions with the next nearest-neighboring atoms are strong, too. The distant interactions between the center and other atoms should decrease rather smoothly because the Coulomb force is a long-range force.

Comparing eqs (13) to (20), the γ effect shows a different pattern in the different families. This means that the delocalization of the ionic charge in the different families is not the same. The addition of a CH_2 group or a carbon atom in both linear and branched chain hydrocarbons causes almost the same lowering of the IPs, i.e. 0.14 eV per carbon atom. In alkyl radicals the decrement rate of the IPs is about 0.06 eV per carbon atom, much smaller than that in alkanes. For the three halogens, the coefficient of the γ effect appears to be linearly correlated with the covalent potential of the halogen atoms, which bear the formal charge. The result is not certain because of the lack of values for the fluorides. For ethyl fluoride ($\gamma^+ = 0$) and n-propyl fluoride ($\gamma^+ = 1$) the difference between the observed IPs [189] is 0.3 eV. This is near the value, 0.34 eV, extrapolated from the decrement for Cl, Br and I atoms. This proposal should be tested further experimentally.

It has been emphasized by the author that the γ effect is one of four factors which moderate the energetics of the species. A summary of the γ

effect is listed in Table 48. From the Table, the γ effect is very important for ion thermochemistry, but it is small for molecules and alkyl radicals. We find the following order of the γ effect:

in ions $\gg$ in radicals $\approx$ in molecules

The reason is that the Coulomb force in ions is strongly different from the covalent force in radicals and molecules.

TABLE 48: A Summary of the γ Effect in Some Species [a]

No.	Species	γ Effect		Chapters
		eV	kcal/mol	(in Thesis)
1	Molecules	0	0	
2	Alkyl Radicals	< 0.03	< 0.6	3rd
3	Cations			
	R^+	$0.06\ \gamma^+$	$1.4\ \gamma^+$	4th
	RH^+	$0.25 + 0.14\ \gamma^+$	$5.8 + 3.2\ \gamma^+$	7th
	(primary, secondary and tertiary hydrocarbons)			
	R^+H	$0.14\ \gamma^+$	$3.2\ \gamma^+$	7th
	(quaternary hydrocarbons)			
	RCl^+	$0.16\ \gamma^+$	$3.7\ \gamma^+$	7th
	RBr^+	$0.10\ \gamma^+$	$2.3\ \gamma^+$	7th
	RI^+	$0.05\ \gamma^+$	$1.2\ \gamma^+$	7th
	$RF^{+\ [b]}$	$(0.34\ \gamma^+)$	$(7.8\ \gamma^+)$	7th

[a] R represents alkyl groups. [b] Suggested in this thesis.

A knowledge of heats of formation of molecules, radicals and cations has always been regarded as fundamental to chemistry. This knowledge is a necessary first step in the deduction of reaction mechanisms and in understanding reactivities.[116] For gas-phase ion chemistry, it is also essential for the full interpretation of mass spectrometric data.[271] Now both simple and dependable methods have been found in Chapter 4 for estimating the heats of formation of alkyl radicals and cations, and for hydrocarbon cations in this Chapter. Therefore it is possible to quantitatively describe the thermochemistry of all processes in the gas phase containing hydrocarbons, monohalogenates, alkyl radicals and their cations by means of a computer system. A computer system, which could be called "computer aided organic ion-chemistry", could provide the cracking patterns of the cations, the mass distribution of the fragments, the relative abundances of mass spectra, the equilibrium constants of organic ion reactions, the bond dissociation energies in the cations and others.

Chapter VIII Summary

There are two novel contributions in this thesis:

(1) **Application of a new scale of electronegativity** Luo and Benson had found that a new electronegativity scale, the covalent potential, V_x, correlates well with heats of formation of alkyl and alkylsilane derivatives,[96-7,144-7] group parameters,[131] the ionization potential for main group atoms,[280] and Lewis acid strengths.[305] The covalent potential was also used by Walsh [312] to correlate the divalent state stabilization energies of SiX_2. In this thesis, it is shown that the covalent potential also correlates well with the propagator of the inductive effect, and with homolytic and heterolytic dissociation energies of alkyl-X and alkylsilyl-X bonds, where X represents halogen, hydrogen, CH_3, SiH_3, GeH_3, NH_2, PH_2, OH, SH, and C- and Si-centerd groups. A summary of the development and application of the covalent potential will be published soon.[378]

Very recently, the author has found [105] there are good linear relations between the covalent potential, V_x, and Parr's electronic chemical potential, μ or $V(r_\mu)$, and total electronic potential, V_Q. The covalent potential is a measure of valence-state electronegativity. The two parameters in the covalent potential, the number of valence electrons in the bonding atom in X and the covalent radius, are well known. Thus, there is a great possibility (a) of using the new scale to correlate the energetics for polyatomic systems and chemical reactions and (b) of introducing and teaching the new scale in introductory classes.

(2) **A new approach to estimation of thermochemical quantities** Four factors which influence dissociation energies of alkyl-X and alkylsilyl-X bonds have been considered and correlated quantitatively. These factors are

(a) the covalent potential, V_x;

(b) the degree of methyl substitution at the radical center or the formal charge center, m;

(c) the interactions between the radical or charge centers and distant atoms, the γ effect. These are summarized in Table 48; and

(d) the steric compression relief due to bond cleavage, ΔV_{nb}.

New empirical approaches have emerged for estimating homolytic and heterolytic dissociation energies of alkyl-X bonds. A new model, "the cleaving-relaxation model", for estimating bond dissociation energies (BDEs) has been established. The uncertainties for most estimated values are within chemical accuracy ($\pm$ 1 kcal/mol). Simple algorithms have been established for estimating ionization potentials (IPs) of alkyl radicals, alkanes and haloalkanes and heats of formation of alkyl radicals and molecular cations. The working time to estimate each term is only one or two minutes, at most, not requiring a computer. The simple expressions for estimating the heats of formation of alkyl radicals and cations, the homolytic and heterolytic BDEs and the IPs of radicals and neutral molecules are summarized in Table 49.

This approach is new, different from the traditional approaches. The concept of atomic electronegativity has been accepted here, but the traditional ideas of "fixed" substituent constants and group electronegativities have been discarded. The chemical behavior of a group in a species not only depends on its chemical composition and structure, but also on its chemical environment. Thus, the concept and theories of traditional substituent or group constants have many limitations [375,397] and cannot explain, interpret and predict homolytic and heterolytic BDEs, or the IPs of radicals and neutral molecules.

The basic method used in this thesis should be applicable to alkenes, alkynes, other unsaturated hydrocarbon derivatives and organo-metallic

compounds in the near future.

TABLE 49: Summary of Methods for Estimating Thermochemical Properties

of Alkyl Radicals, Molecules and Cations [a]

Term	Estimation Method	References
1. Heats of Formation of Organic and Organo-Metallic Compounds, $\Delta_f H^o(RX)$	Benson's Group Additivity (GA) Rules in kcal/mol	102, 116, 125, 131
2. Heats of Formation of Free Alkyl Radicals, $\Delta_f H^o(R)$	$\Delta_f H^o_{GA} + V_{nb}$ in kcal/mol	116, 385 Chapter 3
3. Ionization Potentials of Alkyl Radicals, IP(R)	$= IP(C(CH_3)_m H_{3-m})$ $- 0.06\ \gamma^+$ in eV.	384 Chapter 4
4. Heats of Formation of Alkyl Cations, $\Delta_f H^o(R^+)$	$= IP(R) + \Delta_f H^o(R)$ in kcal/mol	384 Chapter 4
5. Homolytic BDEs, $DH^o(X-R)$	$= DH^o(X-C(CH_3)_m H_{3-m})$ $+ \Delta V_{nb}$ in kcal/mol	385 Chapter 3
6. Homolytic BDEs of C-C Bonds in Hydrocarbons $DH^o(C-C)$	$= DH^o(CH_3-CH_3) - 1.7\ \beta -$ $- 0.8\Delta g$ in kcal/mol	386 Chapter 6

7. Homolytic BDEs of H-, C- or Si-Si Bonds   381

$$DH^{o}(\text{X-alkylsilyl}) = DH^{o}(\text{X-SiH}_3) + \Delta V_{nb}$$ Chapters 5 and 6

for X = H, C- or Si-centerd groups

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8. Heterolytic BDEs, $= DH^{o}(\text{X}^{-}\text{-C}^{+}(\text{CH}_3)_m\text{H}_{3-m})$ 384

$$DH^{o}(\text{X}^{-}\text{-R}^{+})\qquad - 1.4\,\gamma^{+} + \Delta V_{nb}$$ Chapter 4

in kcal/mol

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9. Ionization Potentials of Molecules   382, 383

    Chapter 7

$$IP(HR) = IP(\text{HC}(\text{CH}_3)_m\text{H}_{3-m}) - 0.25 - 0.14\,\gamma^{+}$$

for primary, secondary and tertiary RH

$$= IP(\text{neo-C}_5\text{H}_{12}) - 0.14\,\gamma^{+}$$

for quaternary RH

$$IP(ClR) = IP(\text{ClC}(\text{CH}_3)_m\text{H}_{3-m}) - 0.16\,\gamma^{+}$$

$$IP(BrR) = IP(\text{BrC}(\text{CH}_3)_m\text{H}_{3-m}) - 0.10\,\gamma^{+}$$

$$IP(IR) = IP(\text{IC}(\text{CH}_3)_m\text{H}_{3-m}) - 0.05\,\gamma^{+}$$

in eV

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10. Heats of Formation of Molecular Cations

$$\Delta_f H^{o}(\text{RX}^{+}) = IP(RX) + \Delta_f H^{o}(RX)$$ 382, 383

    Chapter 7

[a] Here X = F, Cl, Br, I, H, CH_3, SiH_3, GeH_3, OH, SH, SeH, NH_2 and PH_2.

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