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LA THÈSE A ÉTÉ
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THERMOCHEMICAL PARAMETERS FOR ORGANIC
RADICALS AND RADICAL CATIONS

by

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Submitted in partial fulfillment
of the requirements for the Degree of
Doctor of Philosophy
at Dalhousie University
November, 1984.

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" TO MY WIFE AND PARENTS "

" I know how to get along with humble means, and also I know how to live in prosperity; in any and every circumstance, I have learned the secret of being filled and going hungry, both of having abundance and suffering need. I can do all things through him who strengthens me.

Nevertheless, you have done well to share with me in my afflictions. "

Philippians 4 : 12-14.

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ABSTRACT

Methods of estimating the acidity of a radical cation, based on thermochemical cycles are developed. The pK_a of the radical cations of toluene and benzene are found to be -12 ± 1 and -2 ± 3 in acetonitrile solution. Difficulties of directly determining the pK_a of hydrocarbon radical cations in solution are discussed.

A thermochemical cycle is used to estimate the gas phase acidity of radical cations and the proton affinity (PA) of radicals. Also, *ab initio* molecular orbital (MO) calculations are used to estimate these PA values. The agreement between the two approaches is found to be satisfactory.

The existing methods of assessing radical stability are critically analysed and shown to be incorrect. Radical stability is defined in terms of the net stabilization (or destabilization) energy; the energy conferred on the open-shell species as a result of the interaction of the unpaired electron with the reference species.

Electron spin resonance (esr) hyperfine coupling constants (hfc's) of methylenic hydrogens of *pi*-radicals are shown to be linearly related to the *pi*-stabilization energy of these radicals. The σ_a^+ scale (introduced by Arnold, Dust and Wayner) and *ab initio* MO calculations are

used to rationalize substituent effects on spin delocalization in benzyl radicals.

The effects of alpha-methyl substituents on the relationship between esr hfc's of benzylic alpha- and beta-hydrogens in benzylic radicals is studied. A study of the phenethyl radical system provides strong evidence that both alpha- and beta-hfc's are linearly related to spin density. Charge effects on spin delocalization (merostabilization) are observed in the cumyl radicals relative to the benzyl system.

LIST OF ABBREVIATIONS

Thermochemical:

DG° - the standard bond dissociation free energy,
 DH° - the standard bond dissociation enthalpy,
 DS° - the standard bond dissociation entropy,
 $TrG^{\circ}(Y)_S$ - the standard free energy of transfer of
species Y from water to a solvent S.
 ΔG°_{sol} - the standard free energy of solvation.

Solvents : Ac - Acetonitrile.

$SE^{\circ}[R^{\cdot}, RX]$ - the net stabilization energy of a radical
R $^{\cdot}$ relative to the R component of RX.

$SE(R^{\cdot})$ - π -stabilization energy.

$R(RX)$ - R component of RX.

Esr:

G - gauss.

hfc - hyperfine coupling constant.

α -hfc = a-hfc = a_{α} .

β -hfc = b-hfc = a_{β} .

Infrared spectra:

s - strong; m - medium; w - weak.

NMR spectra:

s - singlet; d - doublet; t - triplet;

q - quartet; m - multiplet.

All other abbreviations and symbols used are standard notation.

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PREFACE

Organic radicals and radical cations are encountered usually as short-lived intermediates, rendering an accurate determination of their thermochemical parameters difficult. In this thesis, efforts at circumventing this problem and estimating several parameters of fundamental importance to the understanding of the behaviour of these species in the gas phase and in solution, are described. This thesis is divided into four chapters.

In chapter 1, the estimation of acid-base properties of open-shell species (radicals and radical cations) in the gas phase and in solution, is described. Here, the value of using thermochemical cycles to estimate parameters that are not directly determinable by experiment is illustrated. Furthermore, the feasibility of using *ab initio* calculations to determine gas phase acid-base properties of open-shell molecules is studied.

In chapter 2, a critical analysis of the existing methods of assessing radical stability, shows that present definitions of this concept are inaccurate. A new definition of radical stability, based on reference states that are isomeric with the corresponding radical, is proposed.

Hence, this approach uniquely defines the stability of the radical and is not biased by effects on reference molecules. The stability of representative alkyl radicals is determined by this method.

In chapter 3, methods of assessing the stability of pi-radicals are discussed. A common characteristic of all open-shell species is the presence of one or more unpaired electrons in the molecule. Thus, electron spin resonance (esr) spectroscopy has been used widely in identifying these species. It is shown that esr hyperfine coupling constants (hfc's) also can be used to assess the stability of benzyl and other related pi-radicals and that ab initio molecular orbital (MO) calculations provide valuable information regarding factors governing unpaired spin interactions in these systems. Furthermore, these studies show that esr hfc's of benzyl radicals at the benzylic position can be regarded as pseudo thermochemical parameters, because of their relationship to stability.

In chapter 4, substituent effects on esr hfc's of benzylic radicals in ring substituted phenethyl and cumyl radicals are studied, so as to, analyse factors that affect alpha- and beta-hfc's in these systems, substantiate the claim that benzylic alpha-hfc's are related to spin delocalization, and establish the relationship between benzylic beta-hfc's and spin density. In addition, these studies enable a comparison of the effects of merostabilization (charge effects on spin delocalization) on the spin distribution in these systems.

CHAPTER 1. THE ACIDITY OF RADICAL CATIONS

1.1. INTRODUCTION

1.1.1 The determination of the acidity of a radical cation in solution

A radical cation can be obtained by the removal of an electron from a neutral molecule (1,2). These oxidations:

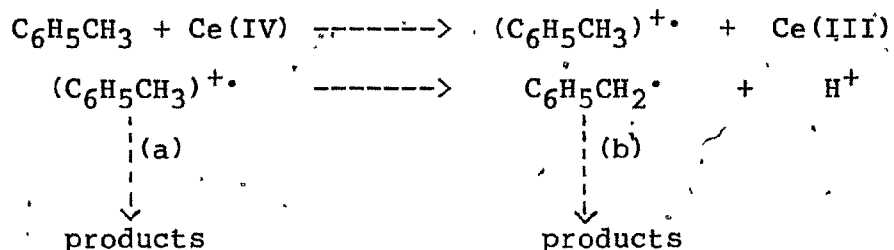


have been achieved by chemical oxidants (e.g., concentrated sulphuric acid (3), the sulphate radical anion (4), metal ion oxidants (5) and Lewis acids (6)), physical methods (e.g., photoionization, pulse radiolysis and electron impact) (7), anodic oxidation (2,8), and photosensitization (electron transfer) (9).

Reaction [1] shows that a radical cation is a positively charged open-shell species, and hence it will show properties expected of both ions and radicals. A characteristic reaction of positive ions is the elimination of a cationic moiety to yield a neutral species.

Deprotonation is the simplest example of such a process.

The deprotonation of radical cations has been found to be an important reactive pathway, for example, in the oxidation of alkyl aromatics (5,10 and 11). The cerium (IV) ion catalysed oxidation of methyl benzene (toluene) (5b) is believed to involve the sequence shown in scheme 1.



SCHEME 1.

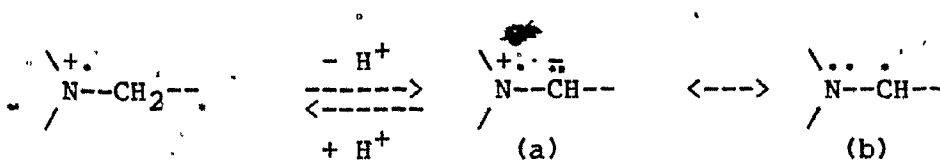
One of the factors that determine the ratio of products obtained from paths (a) and (b), in scheme 1, will be the acidity of the radical cation of toluene. Reactions of this type make the study of the acidity of these reactive radical ions of general interest, and it is surprising that so little is known.

The pK_a of neutral hydrocarbons has been expressed in terms of standard oxidation potentials and bond dissociation enthalpies (12). The pK_a of a radical cation likewise can be related to several important thermochemical parameters (13) via simple thermochemical cycles which will be discussed below. Conversely, such relationships enable the estimation of a related thermochemical parameter if the pK_a of the radical cation can be obtained by an independent method. For example, differences in solvation energies of ions cause deviations in the linear correlation observed between gas phase ionization potential data and standard oxidation potentials in solution (14,15). The relationship between the acidity of a radical cation in the gas phase

and in solution should enable the estimation of the solvation free energies of these ions.

Various types of radical cations have been recognised and described in the literature (1a). For the purpose of discussing the acidity of radical cations it is convenient to classify these species according to the nature of their respective conjugate base. The benzene radical cation is considered a sigma-acid since the deprotonation yields a phenyl sigma-radical. The toluene radical cation yielding a benzyl radical is a pi-acid. The radical cation of phenol is classed as a hetero-pi-acid, since the radical of the conjugate base (the phenoxyl radical) is delocalized. If the unpaired electron was localized on oxygen it would be a hetero-sigma-acid. The amine radical cations of the type RNH_2^+ (R = alkyl) are considered as hetero-sigma-acids if deprotonation occurs from nitrogen.

Recent studies (16) of the behaviour of the tertiary amine radical cations, R_3N^+ , suggests that these species can undergo fast proton exchange with other protic species in solution. This can be rationalized by the following resonance structures of their conjugate bases.



SCHEME 2.

These radical cations can be considered as p-acids, albeit, profoundly stabilized by the nitrogen substituent which allows three-electron bonding ((a) $\longleftrightarrow$ (b) in scheme (2)).

Very few studies of the pK_a of radical cations have been reported. In fact pK_a values have been determined only for the hetero-sigma- or/hetero-pi-acid type radical cations. The pK_a of the radical cation of durohydroquinone was estimated to be -1 by Bridge, Land and Porter (17a,b). They also estimated a pK_a of -5 for the radical cation of 2,4,6-triphenylphenol (7c and 17c). The phenoxyl radicals were generated by flash photolysis, chemical oxidation and photolysis of glasses. The pK_a values were estimated by observing the absorption spectrum of the phenoxyl radicals as a function of pH. Dixon and Murphy (13a, 18) generated phenoxyl radicals in aqueous solution using cerium (IV) oxidation in a flow system, and, followed the equilibrium :

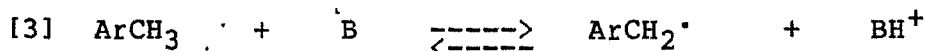


as a function of H^0 , by esr spectroscopy. The pK_a of a number of phenol radical cations was determined in this manner.

The acidities of a few hetero-sigma-acids have been determined (19). For example, a study of the intermediates produced in the one-electron oxidation and reduction of hydroxylamines enabled the determination of the pK_a of

three amine radical cations, $\text{RNH}_2^{+\cdot}$ (where $\text{R} = \text{H}, \text{OCH}_3, \text{OH}$) (19a), when pulse radiolysis was used to generate the radical cations and their conjugate bases. The pK_a of the radical cations was determined by observing the optical absorption spectra of the intermediates formed.

A direct determination of the pK_a of aromatic hydrocarbons in solution has not been reported. An equilibrium constant for the acid-base equilibrium of the radical cation of hexamethylbenzene (HMB) and the conjugate base of HMB, a benzylic radical, in the solvent system dichloromethane-trifluoroacetic acid was estimated from kinetic data obtained in an anodic oxidation of HMB (20).



However, a reliable pK_a for $(\text{HMB})^{+\cdot}$ cannot be obtained from the deduced K_3 value because the nature of the base (B) in reaction [3] is unknown. Furthermore, the equilibrium constant value they deduced is not reliable (21).

In a study by Sehested and Holcman, radical ions of polyalkylbenzenes were generated in solution by pulse radiolysis. They then attempted to correlate relative rates of deprotonation of the radical cations with the ionization potential of the corresponding neutral molecules (10d, 22). These kinetic indications of acidity are informative with regard to the reactivity of radical cations; however, it is

clearly desirable to know thermodynamic acidities of these species.

In general hydrocarbon radical cations are extremely reactive and, are therefore, short-lived under usual experimental conditions. In such situations, determining acidities of radical cations will be difficult. Also, attempts to set up an acid-base equilibrium by protonating the conjugate base (a radical) have thus far failed. For example, attempts to protonate the benzyl radical even in strongly acidic media did not produce any radical cation (10d).

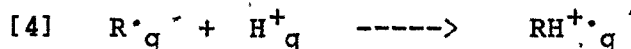
There are several reasons, other than short life times, why an equilibrium involving a radical cation of a aromatic hydrocarbon and the conjugate base cannot be followed as conveniently as for hetero-atom containing radical cations. This can be understood if we consider reactive paths other than deprotonation, that are available to the acid (radical cation) (1b). Often, reaction of a radical cation with nucleophiles occurs much more rapidly than deprotonation (2). Hence, these ions react with water in neutral aqueous solution, and with the hydroxide ion in alkaline media. Consequently, the acidity of radical cations, can be studied conveniently only in weakly nucleophilic solvents, free from nucleophilic impurities.

In this thesis, the use of thermochemical cycles to estimate the acidity of radical cations will be described.

Such an approach is useful because it enables a better understanding of the behaviour of these species in solution. In section 1.3, three methods to estimate the pK_a of these ions will be discussed. These methods are then applied to the radical cations of benzene and toluene.

1.1.2. The protonation of hydrocarbon radicals in the gas phase

Radical cations can be formed by protonation of radicals in the gas phase. This reaction:



is usually a facile process and in the absence of solvent all protonation reactions are highly exergonic (23). This is the direct consequence of the relative instability of the unsolvated proton, which attaches to any radical with which it collides. This is in contrast to the behaviour in solution, where hydrocarbon radicals show little or no tendency to protonate even in strongly acidic conditions (10d).

A direct measure of the intrinsic basicity of a radical is obtained from the energy change for reaction [4]. The occurrence of the proton transfer reaction :

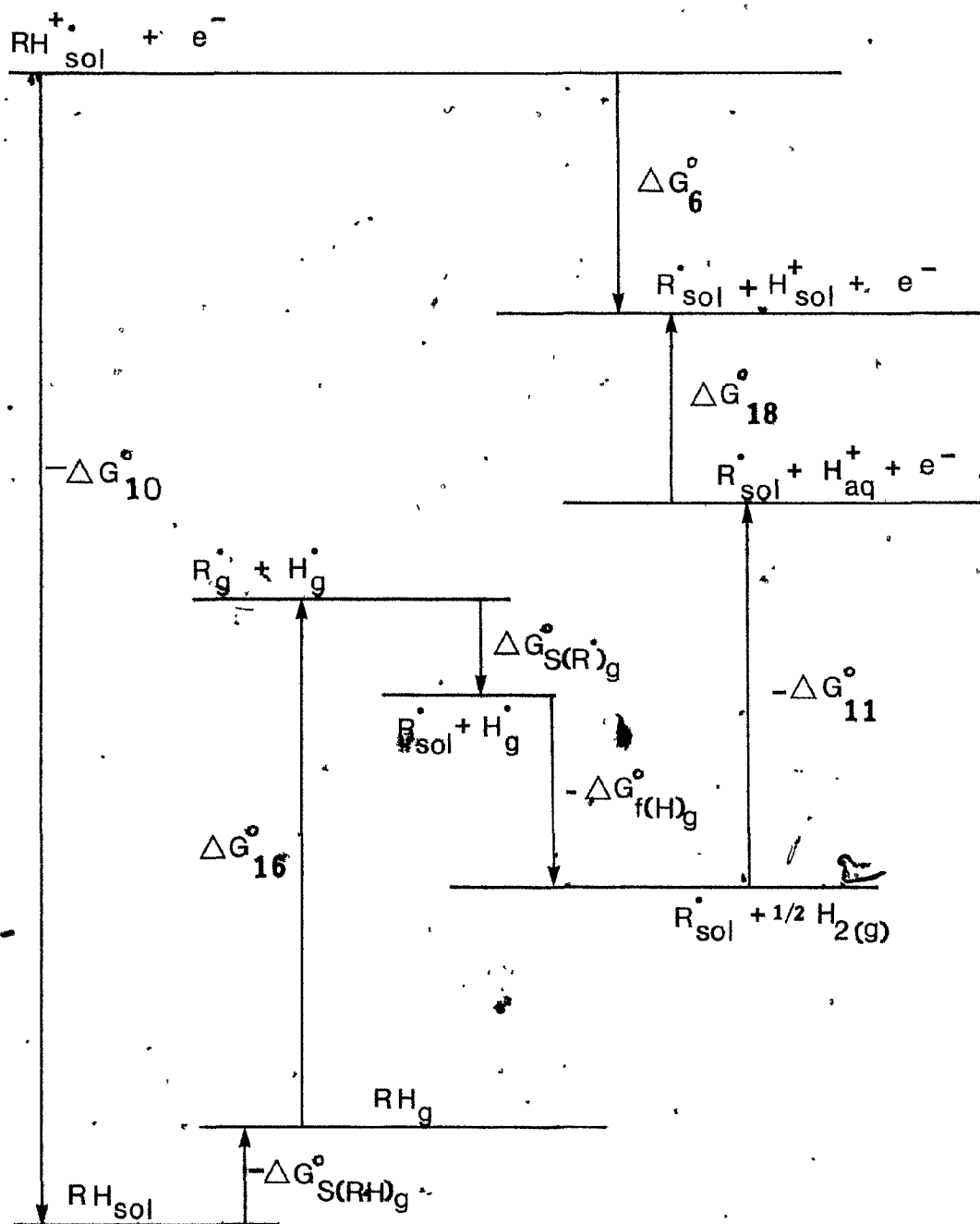


has been used to bracket the proton affinity of a radical relative to standard bases (24, 25).

In section 1.2 it will be shown how thermochemical cycles may be used to estimate the pK_a of a radical cation in the gas phase and in solution. Similarly such cycles can be used to establish an absolute scale of proton affinities (PA) for radicals. Also, the PA values obtained using ab initio calculations will be compared to the corresponding thermochemical values. Then, the gas phase acidity of several hydrocarbon radical cations are estimated because they will be useful in understanding the behaviour of these reactive species in solution.

The prediction of equilibrium geometries and relative energies of neutral molecules, radicals and radical ions is one of the promising areas for the application of MO theory (26, 27). Ab initio, single determinant, self-consistent field (SCF) theory can be used to determine the energy change for reaction [4], at 0 K. R and RH^+ have the same number of electrons and multiplicity, which minimizes the difference in their correlation energies (23). If this difference is neglected ΔE^0_4 can be obtained directly using Hartree-Fock (SCF) wave functions (vide infra).

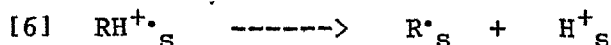
Figure 1. A schematic representation of the use of a thermochemical cycle to estimate the free energy change for the deprotonation of a radical cation ($RH^{+\bullet}$) in solution.



1.2. THE ESTIMATION OF THE pK_a OF A RADICAL CATION IN SOLUTION

1.2.1. METHOD I is based on the standard oxidation potential of RH ($E^\circ(RH)$) and the bond dissociation free energy of RH ($DG^\circ(RH)$).

The pK_a of the radical cation $RH^{+\bullet}$ in solution is related to the standard oxidation potential of RH (E°_{RH}) and the free energy associated with the homolytic cleavage of the R-H bond (DG°) in the gas phase. This relationship can be defined using the thermochemical cycle summarised in Figure 1, which shows that the pK_a of the radical cation is dependent upon the free energy change for the reaction:



and is given by:

$$[7] \quad pK_a(RH^{+\bullet}) = \Delta G^\circ_6 / \ln 10 RT.$$

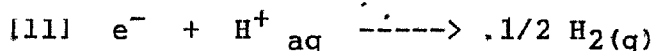
G the Gibbs free energy is a thermodynamic property:

$$[8] \quad \Delta G (\text{cyclic process}) = 0.$$

Application of eq. [8] to the thermochemical cycle in Figure 1 gives :

$$[9] \quad \Delta G^\circ_6 = -\Delta G^\circ_{10} + \Delta G^\circ_{14} + \Delta G^\circ_{16} + \Delta G^\circ_{13} - \Delta G^\circ_{17}.$$

The sum of the free energies for reactions [10] and [11]:



can be expressed in terms of the standard oxidation potential of RH referred to the standard hydrogen electrode (S. H. E.) and given by:

$$[12] \quad E^\circ (\text{RH})_s = (\Delta G^\circ_{10} + \Delta G^\circ_{11}) / n.F$$

where F is the Faraday constant, n is the number of electrons involved in the redox reaction and E° is expressed in volt (2).

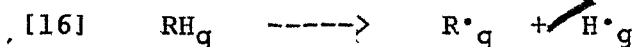
The free energies of solvation of gaseous neutral compounds and radicals are known to be small compared with solvation energies of ions (2). It has also been shown that the difference in the free energies of solvation of a neutral compound RH and the corresponding radical, $\text{R}^\bullet$, is likely to be very small (28). This energy difference has been neglected in previous studies (2). Thus, by considering the following reactions:



it is reasonable to assume that:

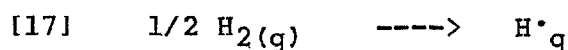
$$[15] \quad \Delta G^{\circ}_{13} + \Delta G^{\circ}_{14} = \Delta G^{\circ}_{\text{sol}}(\text{R}^{\bullet}) - \Delta G^{\circ}_{\text{sol}}(\text{RH}) = 0.$$

The standard free energy change for reaction [16]:



is that associated with the homolytic cleavage of the R-H bond in the gas phase ($\Delta G^{\circ}(\text{R-H})_g$), where the H-atom indicated is the acidic proton of the radical cation, $\text{RH}^{+\bullet}$. In reaction [16] all species are in their standard state of 1 atm pressure.

The other free energy terms required to complete the cycle in Figure 1 are for the following reactions:



where the free energy change for reaction [17] is equal to the standard free energy of formation of the hydrogen atom, because by convention the standard free energy of formation of the hydrogen molecule is zero (29). The free energy change for reaction [18] is that associated with the transfer of a proton from water to the solution of interest (denoted by $\text{TrG}^{\circ}(\text{H}^+)_s$ in this thesis) (30). Substitution of eqs. [7], [12] and [15] in [9], and rearranging terms gives:

$$[19] \quad pK_a(RH^{\bullet})_S = \{ -nFE^{\circ}(RH)_S + TrG^{\circ}(H^+)_S + DG^{\circ}(R-H)_g - \Delta_f G^{\circ}(H)_g \} / \ln 10 \cdot RT.$$

The standard free energy of formation of the hydrogen atom can be calculated (29). The free energy of transfer of a proton from water to other solvents has been estimated (31). Consequently, if $E^{\circ}(RH)_S$ and $DG^{\circ}(R-H)_g$ are known, the pK_a of the radical cation $RH^{\bullet}$ can be estimated.

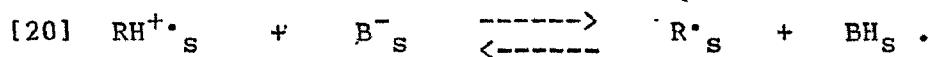
The most precise method of obtaining $DG^{\circ}(R-H)_g$ is by direct measurement of the equilibrium constant, K_{16} , for reaction [16]. However, this is not usually feasible. The alternative method of obtaining DG° from DH° and DS° (the entropy change associated with bond dissociation), is subject to a greater error, because the uncertainty in DH° and DS° is rarely better than $\pm 6 \text{ kJ mol}^{-1}$ and $\pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively (32, 33).

Standard oxidation potentials of several aromatic hydrocarbons have been measured (2, 34). Methods of determining or estimating these quantities have been described in the literature (8, 34-36).

1.2.2. METHOD II (based upon the standard oxidation potential and bond dissociation free energy of R-H in comparison with the standard oxidation potential of B⁻ and the bond dissociation free energy of B-H).

Protolytic or proton transfer reactions can be used to determine the pK_a of an acid relative to a standard.

Similarly, the pK_a of a radical cation can be obtained by considering the proton transfer reaction from the radical cation to the conjugate base of an acid, BH , with a known pK_a :



It is assumed that the only interaction between the radical cation and base is proton transfer. Thus, effects of counter ions on the stability of ions in solution are ignored. Also, it is assumed that all ions are solvated but remain as discrete species in solution. The above assumptions are reasonable since Method II is not based on the results of a single experiment involving equilibrium [20], but on data related by a thermochemical cycle.

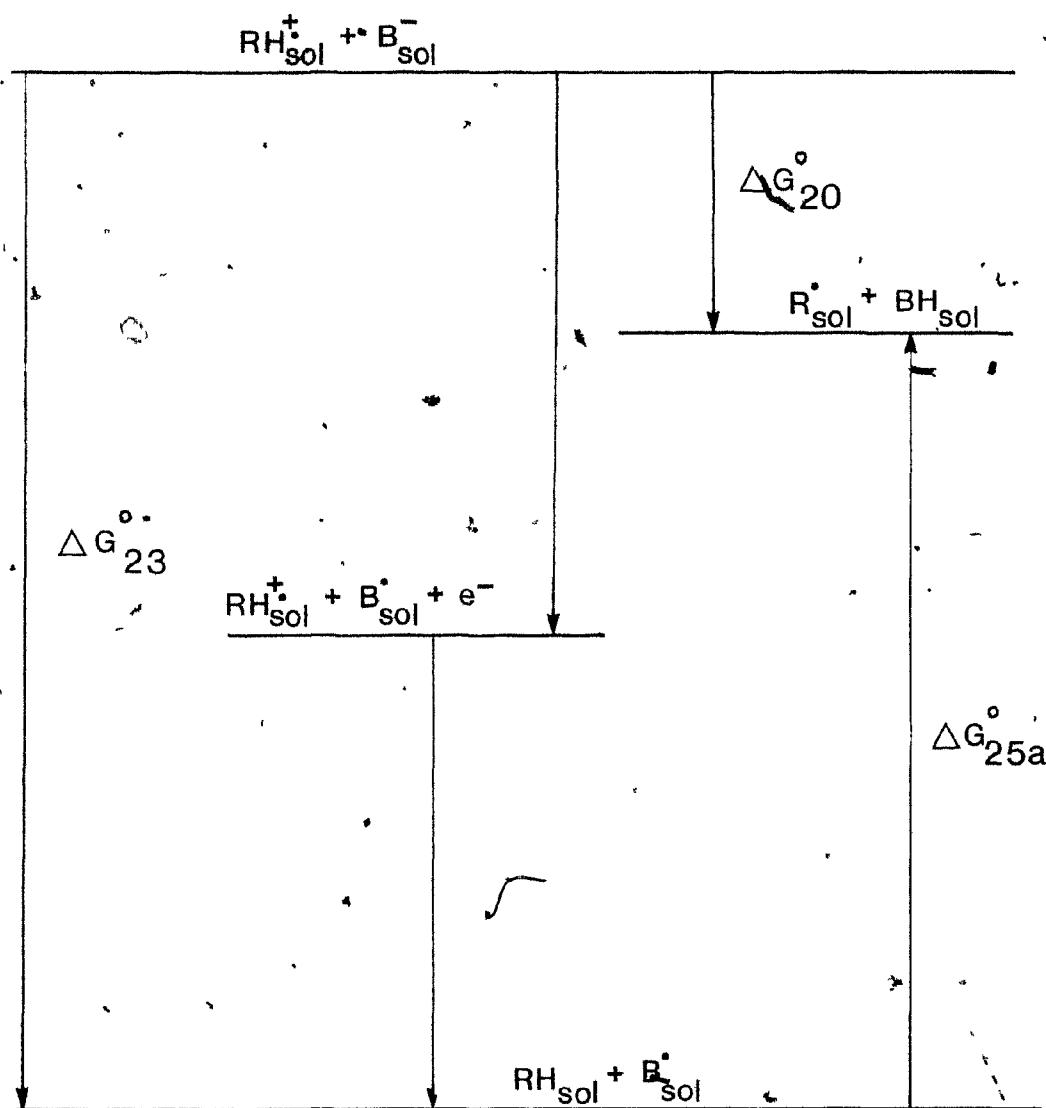
The free energy change for reaction [20] is related to the acidity of the radical cation by:

$$[21] \quad pK_a(RH^{\bullet+})_s = pK_a(BH)_s + \Delta G^{\circ}_{20} / \ln 10 \cdot RT.$$

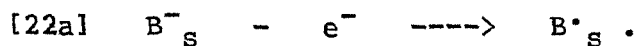
It is useful to define the relationship in eq. [21] in terms of the thermochemical cycle in Figure 2.

The free energy change for reaction [20] is related to the oxidation potentials of RH and B^- and the free energy associated with the homolytic cleavage of the $R-H$ and $B-H$ bonds.

Figure 2. A schematic representation of the use of a thermochemical cycle to estimate the free energy change for the deprotonation of a radical cation ($RH^{+\bullet}$) in solution, relative to that of a standard acid (BH).



The oxidation of anion B^- will result in the formation of $B^{\bullet}_S$:



Combining reaction [22a] with the reduction of H^+ ions to hydrogen gas, (reaction [11]), gives:

$$[22b] \quad \Delta G^{\circ}_{22a} + \Delta G^{\circ}_{11} = nFE^{\circ}(B^-)_S$$

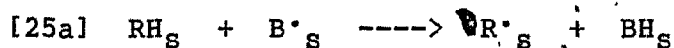
where $E^{\circ}(B^-)_S$ is the standard oxidation potential of the anion B^- . Combining eq. [12] and [22b] we obtain an expression for the free energy associated with the indirect electron transfer from anion B^-_S to radical cation $RH^{\bullet+}_S$:



in terms of the standard oxidation potentials of B^- and RH :

$$[24] \quad \Delta G^{\circ}_{23} = nF [E^{\circ}(B^-)_S - E^{\circ}(RH)_S]$$

If the free energy change for reaction [23] can be determined by independent measurements of $E^{\circ}(B^-)_S$ and $E^{\circ}(RH)_S$, the only term required for obtaining $pK_a(RH^{\bullet+})_S$ is the free energy associated with the formation of $R^{\bullet}_S$ (the conjugate base of the radical cation $RH^{\bullet+}$) and BH_S by an indirect hydrogen atom transfer between RH_S and $B^{\bullet}_S$:



which can be expressed in terms of $DG^{\circ}(R-H)_S$, where the H

atom indicated is the acidic proton of the radical cation $RH^{+\bullet}$, and $DG^{\circ}(B-R)_s$:

$$[25b] \quad \Delta G^{\circ}_{25a} = DG^{\circ}(R-H)_s - DG^{\circ}(B-H)_s.$$

As before, by assuming that the difference in free energy of solvation of between RH and $R^{\bullet}$ (or BH and $B^{\bullet}$) is negligible, from Figure 2 the relationship:

$$[26] \quad \Delta G^{\circ}_{20} = nF \{ E^{\circ}(B^{\bullet})_s - E^{\circ}(RH)_s \} + DG^{\circ}(R-H)_g - DG^{\circ}(B-H)_g$$

is obtained. By substitution of eq.[26] in eq.[21], an expression for the pK_a is obtained:

$$[27] \quad pK_a(RH^{+\bullet})_s = pK_a(BH)_s + [nF \{ E^{\circ}(B^{\bullet})_s - E^{\circ}(RH)_s \} + DG^{\circ}(R-H)_g - DG^{\circ}(B-H)_g] / \ln 10.RT.$$

If all the terms of the right hand side of eq. [27] are estimable, the pK_a value can be obtained. However, if $pK_a(BH)_s$ is unknown, BH can be chosen as a standard and the acidity of a radical cation expressed relative to this species.

In the absence of the required free energy data, an approximate pK_a value may be derived (eq. [29]) from the corresponding enthalpy data, if we assume that:

$$[28] \quad S^{\circ}(RH)_g - S^{\circ}(R^{\bullet})_g = S^{\circ}(BH)_g - S^{\circ}(B^{\bullet})_g$$

$$[29] \quad pK_a(RH^{\cdot+})_s = pK_a(BH)_s + [nF \{E^{\circ}(B^-)_s - E^{\circ}(RH)_s\} + DH^{\circ}(R-H)_g - DH^{\circ}(B-H)_g] / \ln 10 \cdot RT.$$

Using eq. [27] two other useful relationships can be derived as shown below.

case (i):

If BH is identical to RH and the acidic hydrogen of RH and the radical cation are the same, from eqs. [15 and 25b]:

$$[30] \quad \Delta G^{\circ}_{25a} = 0.$$

Substitution of eq. [30] in eq. [27] yields:

$$[31] \quad pK_a(RH^{\cdot+})_s = pK_a(RH)_s + nF \{E^{\circ}(R^-)_s - E^{\circ}(RH)_s\} / \ln 10 \cdot RT.$$

case (ii):

If BH and B $\cdot$ correspond to, respectively, RH $_2^+$ and RH $^{\cdot+}$, then, B $^-$ and RH are identical. Hence:

$$[32] \quad \{E^{\circ}(B^-)_s - E^{\circ}(RH)_s\} = 0.$$

Substitution of eq. [32] in eq. [27] gives:

$$[33] \quad pK_a(RH^{\cdot+})_s = pK_a(RH_2^+)_s + DG^{\circ}(R-H)_g - DG^{\circ}(RH_2^+)_g.$$

The free energy of bond dissociation considered in RH $_2^+$ is associated with the bond that when cleaved gives the same

radical cation as obtained on oxidizing RH in solution.

From eq. [31] it is evident that a knowledge of the standard oxidation potentials of an organic molecule RH and the anion R^- along with the pK_a of RH in the solvent of interest provides a direct estimate of the pK_a of $RH^{\bullet+}$, the radical cation. Similarly, eq. [33] shows that if the bond dissociation free energy of RH and RH_2^+ and the pK_a of RH_2^+ are known, the pK_a of the radical cation is calculable.

1.2.3. METHOD III (based on the relationship between the acidity in the gas phase and in solution).

Solvation has a profound influence on the acid-base properties of any species in solution. Recently, considerable effort has been applied to the determination of gas phase acidities of organic molecules (36, 37), where intrinsic molecular properties free of solvation effects will be reflected. The determination of gas phase acidities are, however, of additional interest because they constitute a further means of estimating pK_a values in solution.

The pK_a of a radical cation, $RH^{\bullet+}$, in solution is related to the corresponding gas phase acidity and the free energy of solvation of the species, $RH^{\bullet+}$, $R^{\bullet}$ and H^+ . It is useful to define this relationship in terms of Figures 3 and 4.

Figure 3. The pK_a of a radical cation ($RH^{+\bullet}$) in solution in relation to the gas phase acidity of $RH^{+\bullet}$ and the standard free energy of solvation of the species $RH^{+\bullet}_g$, $R^{\bullet}_g$, and H^+_g .

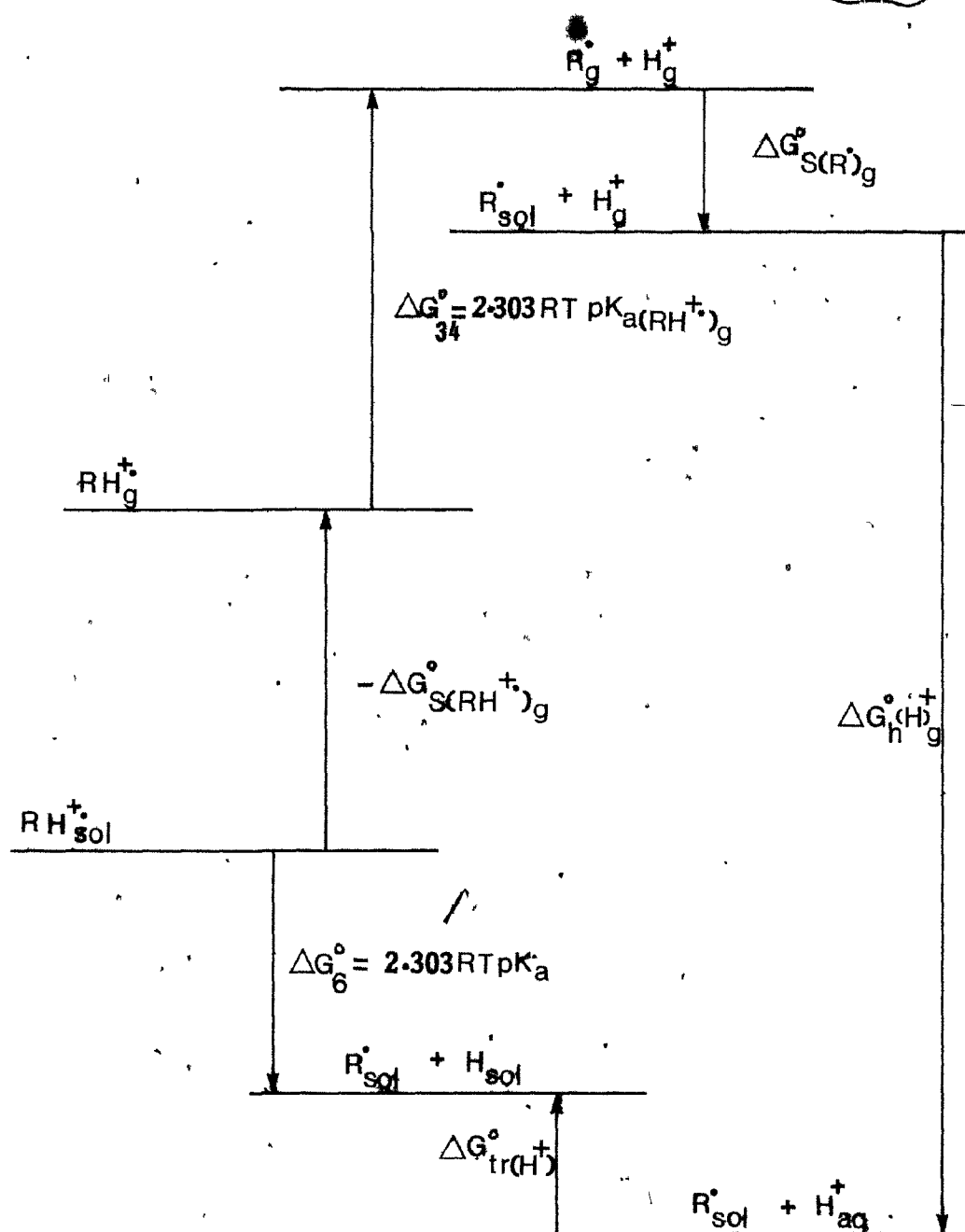
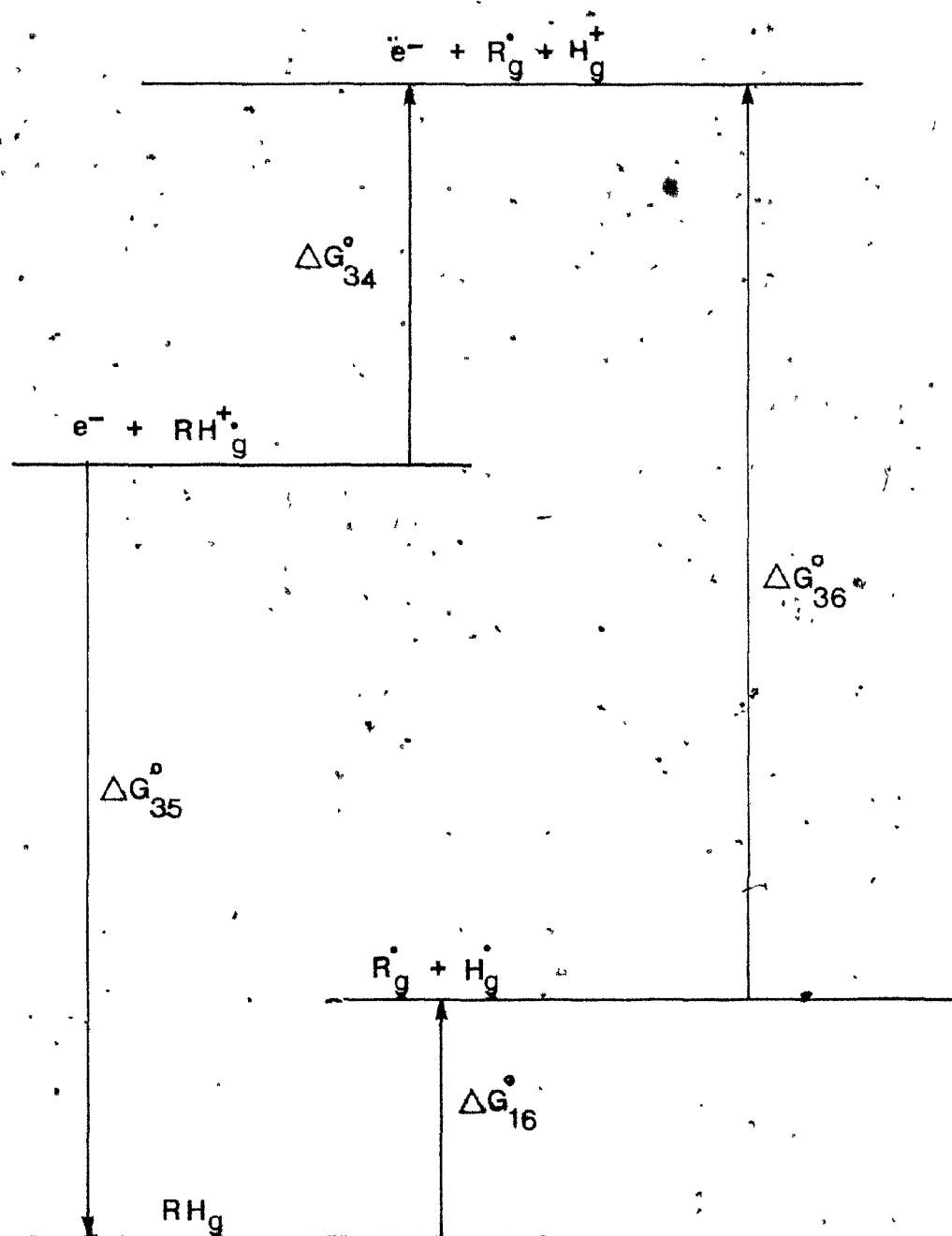
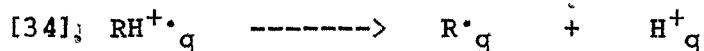


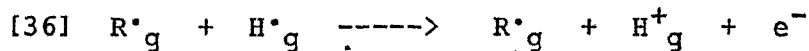
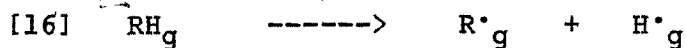
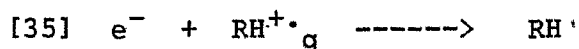
Figure 4. The relationship between the pK_a of a radical cation ($RH^{+\bullet}$) in the gas phase, the adiabatic ionization potential of RH ($IP(adiabatic)_{RH}$), and the standard gas phase bond dissociation free energy of $R-H$ ($DG^0(R-H)_g$).



The gas phase acidity of a radical cation can be expressed in terms of the free energy change for the deprotonation reaction:



and be calculated from existing data, using the relationship summarised in Figure 4 and expressed by reactions [34]-[36] and [16]:



where the pK_a of the radical cation in the gas phase is given by:

$$\begin{aligned} [37] \quad \text{pK}_a(\text{RH}^{\bullet+})_g &= -\Delta G^{\circ}_{34} / \ln 10 \cdot RT \\ &= (\Delta G^{\circ}_{35} + \Delta G^{\circ}_{16} + \Delta G^{\circ}_{36}) / \ln 10 \cdot RT. \end{aligned}$$

The free energy change and enthalpy change for reaction [35] are assumed to be equal, because the entropy change has been shown to be negligible (38, 39). The enthalpy change is given by:

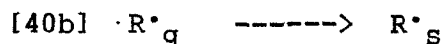
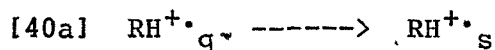
$$[38] \quad \Delta H^{\circ}_{35} = -\text{IP (adiabatic)}_{\text{RH}} - \Delta \int C_p dT$$

where IP (adiabatic) is the adiabatic ionization potential, the energy difference between the ground vibrational and

rotational level of the lowest electronic state of the radical cation and the ground vibrational and rotational level of the lowest electronic state of the molecule. This is equal to the difference in the enthalpies of formation of $\text{RH}^{\bullet+}$ and RH at 0 K. For most organic compounds the heat capacities of the molecule and the corresponding radical cation are effectively the same, so that the enthalpy change for eq. [35] can be approximated by the IP value. Hence, it is assumed that:

$$[39] \quad \Delta G^{\circ}_{35} = -\text{IP (adiabatic)}_{\text{RH}}.$$

The solvation of the species in reaction [34] can be expressed by the following reactions [35-37] and [18].



From Figure 3 we get:

$$[42] \quad \Delta G^{\circ}_6 = -\Delta G^{\circ}_{40a} + \Delta G^{\circ}_{34} + \Delta G^{\circ}_{40b} + \Delta G^{\circ}_{41} + \Delta G^{\circ}_{18}.$$

Substitution of the result of eq. [42] in eq. [7] gives :

$$[43] \text{pK}_a (\text{RH}^{+\bullet})_s = \text{pK}_a (\text{RH}^{+\bullet})_g + \{ \sum \Delta G^{\circ}_{\text{sol}} \}_{34} / \ln 10 RT$$

where $\{ \sum \Delta G^{\circ}_{\text{sol}} \}_{34}$ is the difference in the free energy of solvation of the products and reactants of reaction

[34].

Application of eq. [43] to estimate the pK_a is limited because the free energies of solvation of many radical cations have not been determined. However, the free energy of solvation of the radical cations of a series of alternant aromatic hydrocarbons have been reported (15a) permitting the estimation of pK_a values for these radical ions (eq. [43]) (40-41).

In addition, since an experimental pK_a value has been determined for the phenol radical cation, it is possible to estimate acidities of radical cations relative to this ion (eq. [45])

The acidity of the phenol radical cation has been determined in aqueous solution (13a). A measure of the acidity of a radical cation relative to the phenol radical cation enables an estimate of the pK_a to be made.

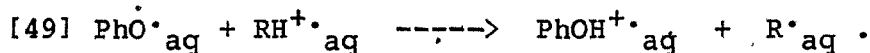
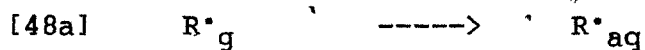
Using eq. [43], the pK_a of the phenol radical cation in aqueous solution is expressed by:

$$[44] \text{pK}_a (\text{PhOH})_s^{+\bullet} = \text{pK}_a (\text{PhOH})_g + \{ \sum \Delta G^{\circ}_{\text{sol}} \}_{34} \quad (\text{R=OPh})$$

Subtraction of eq. [44] from eq. [43] gives, on rearrangement:

$$[45] \quad pK_a(RH^{\bullet+})_{aq} = pK_a(RH^{\bullet+})_g - pK_a(PhOH^{\bullet+})_g + pK_a(PhOH)_s^{\bullet+} + \Delta G^{\circ}_{sol} / \ln 10 \cdot RT$$

It is convenient to summarise the relationship in eq. [45] in terms of Figure 5 using the following eqs. [46]-[49]:



The difference in the acidities of the radical cations of phenol and RH in the gas phase is given by:

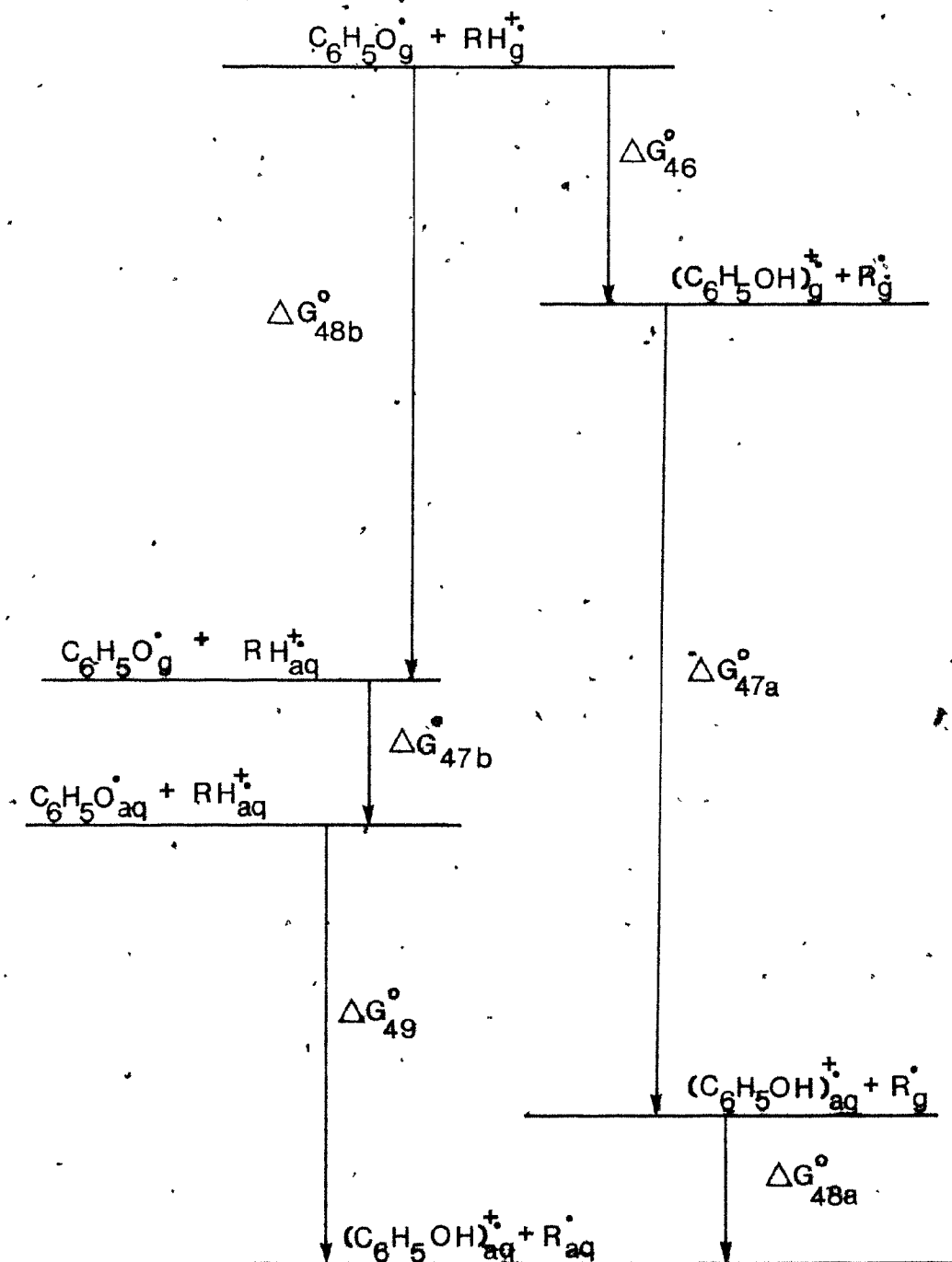
$$[50] \quad pK_a(RH^{\bullet+})_g - pK_a(PhOH^{\bullet+})_g = \Delta G^{\circ}_{46} / \ln 10 \cdot RT.$$

and the other term of interest can be expressed by:

$$[51] \quad \Delta G^{\circ}_{sol} = \Delta G^{\circ}_{47a} + \Delta G^{\circ}_{48a} - \Delta G^{\circ}_{47b} - \Delta G^{\circ}_{48b}$$

The free energy of solvation of neutral radicals is known to be small (2, 28) and the eq. [52] may be assumed.

Figure 5. The relationship between the pK_a of a radical cation ($RH^{+\bullet}$), relative to the pK_a of the phenol radical cation, in the gas phase and solution.



$$[52] \quad \Delta G^{\circ}_{47b} = \Delta G^{\circ}_{48a}$$

If the radical cation $RH^{\bullet+}$ does not contain a hetero-atom it will be less extensively hydrated in solution as compared to the phenol radical cation (14b). This may be expressed by:

$$[53] \quad -\Delta G^{\circ}_{47a} > -\Delta G^{\circ}_{48b}$$

Substitution of eq. [52] and inequality [53] into eq. [45] gives:

$$[54] \quad pK_a(RH^{\bullet+})_{aq} < pK_a(RH^{\bullet+})_g - pK_a(PhOH)_g + pK_a(PhOH)_{aq}$$

Thus, the inequality [49] can be used to estimate an upper limit for the pK_a of an aromatic hydrocarbon radical cation in aqueous solution. However, if the difference in solvation free energies are estimable, the pK_a can be derived from eq. [45].

1.3. THE ESTIMATION OF THE PROTON AFFINITY OF RADICALS

The purpose of this section is to study the thermodynamics of the protonation of hydrocarbon radicals and to ascertain the feasibility of using ab initio, single determinant, MO calculations to determine the proton affinity of a radical. As mentioned previously, radicals can be classified according to the type of orbital an

unpaired electron occupies and in this work the protonation of representative p, sigma, and pi radicals are described.

1.3.1 Thermochemical calculations

The proton affinity of a radical $R^\bullet$ in the gas phase, $PA(R^\bullet)$, is related to the enthalpy change for reaction [4] and is given by:

$$[55] \quad PA(R^\bullet) = -\Delta H^\circ_4 = -IP(\text{adiabatic})_{RH} + DH^\circ(R-H)_g + \Delta_f H^\circ(H^+)_g - \Delta_f H^\circ(H)_g.$$

The difference in the heat of formation of a proton and a hydrogen atom is approximately equal to the ionization potential of H. This simplifies eq. [55] to:

$$[56] \quad PA(R^\bullet) = -IP(\text{adiabatic})_{RH} + IP_H + DH^\circ(R-H)_g.$$

Thus, if the $IP(\text{adiabatic})_{RH}$ and $DH^\circ(R-H)_g$ are known $PA(R^\bullet)$ can be obtained from eqs. [55] or [56].

1.3.2 Ab initio calculations

The energy difference between $R^\bullet$ and RH^+ at 0 K has been related to the gas phase proton affinity of $R^\bullet$, $PA(R^\bullet)$ by (42):

$$[57] \quad PA(R^\bullet) = \Delta E^\circ_4 - \Delta ZPE + (5/2)RT.$$

The term ΔZPE is the difference in the zero point energies of $R^\bullet$ and RH^+ , and $(5/2)RT$ is a thermodynamic temperature correction term. The term ΔE°_4 includes the

dominant Hartree-Fock energy difference and any correlation energy corrections. In this thesis, the Hartree-Fock energy contribution to the proton affinity of a radical, is defined as the Hartree-Fock proton affinity and denoted by PA_{HF} , where it can be expressed under standard conditions at any temperature (T), by:

$$[58] \quad PA_{HF}(R^\bullet) = E_{HF}(R^\bullet) - E_{HF}(RH^{+\bullet}) + (5/2)RT.$$

Basis sets of limited size have been used in this work, because of the large computational (CPU) time required in using near Hartree-Fock basis sets. However, a fair estimate of the energy difference between two species, at the Hartree-Fock level, can be obtained using basis sets of limited size (26). Thus, eq. [59] has been assumed, where the Hartree-Fock energy E_{HF} has been replaced by E_{SCF} , the energy computed using an ab initio, single determinant, self-consistent field procedure.

$$[59] \quad PA_{HF}(R^\bullet) = E_{SCF}(R^\bullet) - E_{SCF}(RH^{+\bullet}) + (5/2)RT$$

The difference (δ) between the PA_{HF} and the true PA value is given by:

$$[60] \quad \delta PA = \Delta ZPE + \Delta CE + BSE$$

where Δ denotes the difference in the values (for the indicated parameter) between the radical cation and the conjugate base the radical. ZPE and CE represent the zero-

point and correlation energies. BSE denotes the error arising from the choice of basis sets of limited size.

Details of calculations:

Standard single determinant MO theory was used. The ab initio MO calculations described were obtained by the use of the GAUSSIAN 76 program (43). The open-shell, spin-unrestricted (UHF) procedure was employed (44) to compute the energies of all the radicals and radical cations. The basis sets used in this work have been extensively used and are described in the literature (26, 27, 45). The minimal STO-3G (46), and extended basis sets of two types were used. These were the split-valence basis sets, without (3-21G (47), 4-31G (48), and 6-31G (49)) and with (4-31G* and 6-31G* (50)) polarization functions on carbon. The variation of PA_{HF} (eq. [59]), with basis sets, was studied while constraining the radical cations and the conjugate bases to the STO-3G geometry. The 3-21G PA_{HF} values for the methyl, ethyl, vinyl and ethynyl radicals were also computed using 3-21G optimized geometries. In addition, the effects of complete optimization on the $PA_{HF}(\text{methyl})$ was studied at the 4-31G, 6-31G*, 6-31G** and 6-311G** levels (51).

Also the effect of electron correlation on the proton affinity of the methyl radical was studied by incorporating valence electron correlation using Møller-Plesset(MP) perturbation theory (52) terminated at the second- and

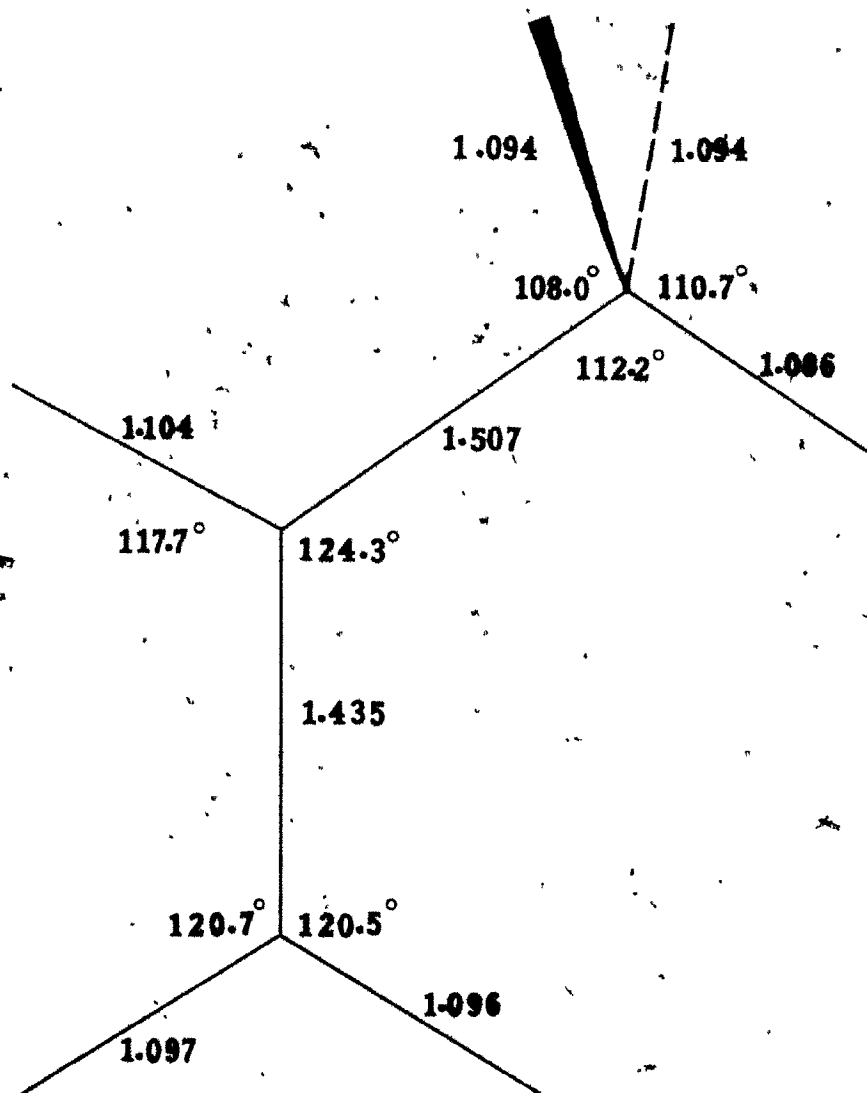
third-order in the 6-31G** basis sets. Calculations using these second and third order MP basis sets (denoted by MP2/6-31G** and MP3/6-31G** respectively), were carried out with the GAUSSIAN 80 system of programs (53, 54) on a Perkin-Elmer 3230 minicomputer.

Geometries:

Geometry optimization, subject only to the imposed symmetry constraints, were carried out at the STO-3G level. Complete optimizations were performed; at the STO-3G level for the radical cations of propene (C_s symmetry) and benzene (D_{6h} symmetry); at the 3-21G level, for the radical cations of ethane, acetylene and ethylene. The STO-3G geometry of the cyclopropane radical cation was computed in our laboratory as part of another program (55). All other optimized geometries at the STO-3G and 3-21G levels used in this work were obtained from the work of Pople and his co-workers (26, 56). Only partial optimization of the geometries of the phenyl and benzyl radicals and the toluene radical cation were performed because of the large CPU time required for a complete optimization.

Propene radical cation: Rotation around the C-C single bond indicated that the lowest energy (with C_s symmetry) was obtained, when the molecule was oriented as shown in Figure 6 (57, 58).

Figure 6. The completely optimized STO-3G structure for the propene radical cation ($C_3H_6^{+\cdot}$), with C_s symmetry. All bond lengths indicated in the figure are in Angstroms.



Benzene radical cation: $C_6H_6^+$ is obtained by the removal of a π -electron from a $(1a_{2u})^2(1e_{1g})^2$ electronic configuration. The Jahn-Teller theorem states that in such a situation the molecule distorts from a D_{6h} symmetry such that the degeneracy of the e_{1g} orbitals is removed. However, a D_{6h} symmetry was assumed in this work. (59).

Phenyl radical: A C_{2v} symmetry was assumed, together with a further constraint that the carbon skeleton $C_2-C_3-C_4$ and the hydrogens H_2 , H_3 and H_4 were fixed in the same positions as in the the STO-3G optimized structure of benzene(2.19). Optimization of the remaining parameters, assuming $r(C_1-H_1) = 1.083$ Å, $r(C_5-H_5) = 1.083$ Å, and

$\angle H_1C_1C_2 = 120^\circ$, $\angle H_5C_5C_4 = 120^\circ$, lead to the structure given in Figure 7a.

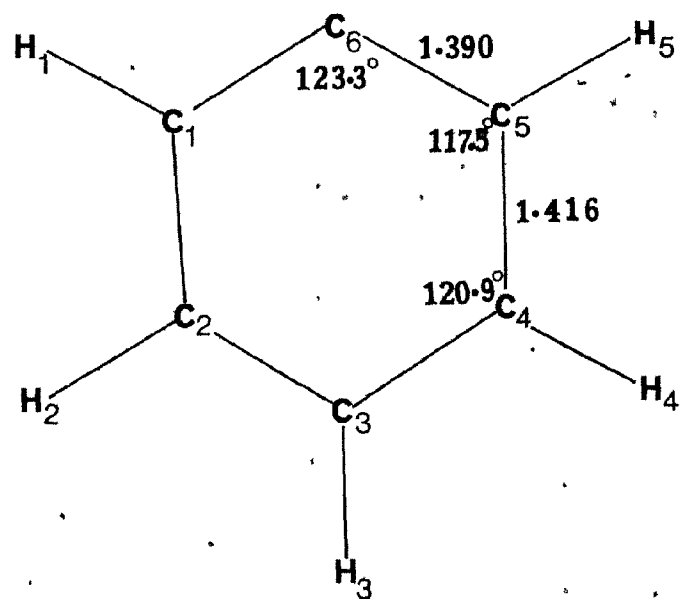
Benzyl radical: The geometrical parameters of the CH_2 group attached to a standard phenyl ring were optimized.(Fig 7b) (60, 61).

Toluene radical cation: A hydrogen of $C_6H_6^+$ (D_{6h}) was replaced by a model CH_3 group ($r_{CH} = 1.09$ Å and $\angle HCH = 109.47^\circ$) at an optimized C-C bond distance (C_s symmetry, $r_{CC} = 1.525$ Å).

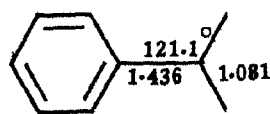
Figure 7. Partially optimized STO-3G structures of:

(a) The phenyl radical ($\text{C}_6\text{H}_5^\bullet$) with C_{2v} symmetry.

(b) The benzyl radical ($\text{C}_7\text{H}_7^\bullet$) with C_{2v} symmetry.



(a)



(b)

1.4 RESULTS AND DISCUSSION

1.4.1. The pK_a of a radical cation in solution

The pK_a of the radical cations of benzene and toluene, estimated using methods I, II and III, are tabulated in Table 1. The data required to estimate the pK_a values are given in Tables 2 to 4. In addition, the following data was used.

$$\Delta_f G^\circ(H_2)_g = 0 \quad (29).$$

$$\Delta_f G^\circ(H)_g = 203.2 \text{ kJ mol}^{-1} \quad (29).$$

$$\Delta_f G^\circ(H^+)_g = 1517 \text{ kJ mol}^{-1} \quad (62,63).$$

$$\text{Tr}G^\circ(H^+)_{ac} = 46.4 \text{ kJ mol}^{-1} \quad (31).$$

$$\text{Tr}G^\circ(Cl^-)_{ac} = 42.1 \text{ kJ mol}^{-1} \quad (31).$$

$$\text{Tr}G^\circ(Br^-)_{ac} = 31.3 \text{ kJ mol}^{-1} \quad (31).$$

$$\Delta G^\circ_{\text{hydration}}(H^+)_g = -1098 \pm 2 \text{ kJ mol}^{-1} \quad (64).$$

$$\Delta G^\circ_{\text{sol}}(C_6H_6^{+\bullet})_g = -186 \pm 15 \text{ kJ mol}^{-1} \text{ (solvent=ac) (15b).}$$

$$\Delta G^\circ_{\text{sol}}(H^+)_g = -1098 \pm 2 \text{ kJ mol}^{-1} \text{ (solvent=ac) (65).}$$

The free energy of solvation of the phenyl and benzyl radicals in acetonitrile were assumed to be zero (2).

$$pK_a(HCl)_{ac} = 8.9 \quad (66).$$

$$pK_a(HBr)_{ac} = 5.5 \quad (66).$$

Table 1. The pK_a of the radical cations of benzene and toluene at 300 K in acetonitrile solution^a

Parent molecule	Method I eq. [19]	Method II eq. [27]	Method III eq. [43]
		BH = HCl BH = HBr	
Benzene	-2.1±2	-1.7±2, -0.8±2	-3.7±3
Toluene	-12.9±1	-12.1±1, -11.1±1	-11.8±3 ^{b,c}

^a E^0 values of 2.9 ± 0.1 and 2.61 ± 0.05 were used for benzene and toluene, as recommended in reference 34, to obtain the pK_a values by methods I and II.

^b Estimated assuming the free energy of solvation of the radical cations of toluene and benzene are equal.

^c A value of -12 has been reported in reference 67 using method III and assuming entropy effects on the radical cation and the conjugate base are equal.

Table 2. Standard oxidation potentials in acetonitrile and aqueous solution at 300 K.

Species	E^0 / V (vs. S. H. E)	
	Acetonitrile(ac)	Water(aq)
Benzene	3.03 ± 0.05^a , 2.9 ± 0.1^b , 2.9 ± 0.2^c	2.4 ± 0.2^c
Toluene	2.61 ± 0.05^a , 2.5 ± 0.2^c	-
Br^-	1.66 ± 0.05	1.98 ± 0.05^d
Cl^-	2.07 ± 0.05	2.51 ± 0.05^d

^a Reference 8a.

^b Reference 34.

^c Reference 36 (based on thermochemical cycle).

^d Reference 68.

Table 3. Gas phase bond dissociation data^a at 300 K.

Species	DH ⁰ /kJ mol ⁻¹	DS ⁰ /J mol ⁻¹ K ⁻¹	DG ⁰ /kJ mol ⁻¹
Benzene	464 ± 8	136 ± 4	423 ± 8
Toluene	368 ± 6	109 ± 4	335 ± 6
HCl	431.6 ^b	92.9	403.7
HBr	366.2 ^b	90.9	338.9
Phenol	362 ± 8	108 ± 4	330 ± 8
Methane	439 ± 4	123 ± 4	402 ± 4
Ethane	410 ± 8	128 ± 4	372 ± 8
Ethylene	460 ± 8	131 ± 4	421 ± 8
Acetylene	552 ± 20	121 ± 4	516 ± 20
Propene	361 ± 6	108 ± 4	329 ± 6
Cyclo- propane(i)	445 ± 6	130 ± 4	406 ± 6
Cyclo- propane(ii)	329 ± 6 ^c	137 ± 4 ^c	288 ± 6 ^c

^a Unless specified otherwise, DH⁰ values are from reference 32, and DS⁰ values are calculated from data in reference 33a. DG⁰ values have been calculated from the corresponding DH⁰ and DS⁰ values.

^b Reference 29.

^c Energetics involving the formation of the allyl radical has been considered.

Table 4. Gas phase acidities of radical cations

Species	IP/kJ mol ⁻¹ ^a	pK _a ^b (eq. ^a [371])
Benzene	892	147
Toluene	851	139
Phenol	820	143
Methane	≤ 1217	≥ 87
Ethane	1110	100
Ethylene	1014 ^c	126
Acetylene	1101	127
Propene	940	122
Cyclopropane(i)	946	135
Cyclopropane(ii) ^d	946	114

^a Reference 62. Uncertainty less than 1 kJ mol⁻¹, except where noted.

^b Uncertainty ± 1.

^c Uncertainty ± 3 kJ mol⁻¹.

^d Data calculated for the (c-C₃H₆⁺/ allyl radical) acid-base system. However, note that the kinetically controlled product, for the deprotonation of the cyclopropane radical cation in the gas phase, is the cyclopropyl radical (25).

From Table 1. we see that there is general agreement in the estimated pK_a values by the three methods, within the limits of experimental error.

These estimates indicate that the deprotonation of the radical cations of benzene and toluene is thermochemically favourable in acetonitrile solution. Whether acetonitrile would be appreciably protonated by these radical cations cannot be predicted because the pK_a of protonated acetonitrile is not known. However, rough estimates indicate this value to be between -4 and 0 (69, 70), so that protonation of acetonitrile by the toluene radical cation should be thermochemically feasible.

Application of methods I-III indicate that the radical cation of benzene is a moderately strong acid in acetonitrile solution with a pK_a between -1 and -4. This is indeed a surprising result because unambiguous evidence for the deprotonation of the benzene radical cations in solution has not been reported (71).

The cobalt (III) ion oxidation of benzene in trifluoroacetic acid (TFA) is believed to occur via the radical cation. Proton incorporation was not observed during the cobalt (III) ion oxidation of perdeutero-benzene (C_6D_6) in TFA, where the only trifluoroacetate ester formed was $C_6D_5O_2CCF_3$; conversely, C_6H_6 in TFA-d1 produced only $C_6H_5O_2CCF_3$ (5c). Under these conditions, there was no evidence for an acid-base equilibrium between the benzene

radical cation and the phenyl radical. Even evidence for the formation of the phenyl radical by deprotonation of the radical cation was absent. When stoichiometric amounts of the reagents were used biphenyl and other oxidative condensation products, which would have resulted from phenyl radicals, were not detected. However, the deprotonation of the benzene radical cation and subsequent biphenyl formation in acetonitrile have been suggested (71a).

Studies on the oxidation of benzene by the sulphate radical anion demonstrate the reactivity of the benzene radical cation in aqueous solution. Product analysis shows the formation of phenol in greater yield than biphenyl. This indicates that the formation of the hydroxycyclohexadienyl radical is probably preferred to that of the phenyl radical. However, the formation of biphenyl does not prove that deprotonation of the radical cation has occurred, because it can arise, for example, from the attack of the benzene radical cation on benzene. In fact, such a reaction of benzene with the radical cation, has been proposed to explain the increase in yield of biphenyl with an increasing initial benzene concentration (5c).

From methods I and II, it is evident that the low pK_a value of the benzene radical cation is primarily due to the high oxidation potential of benzene. The apparent

reluctance of the benzene radical cation to deprotonate may be because of more rapid competing reactions, reaction with nucleophile, for example. However, there may be an appreciable activation barrier to forming the sigma-radical from a pi-delocalized radical cation. Also, rapid deprotonation requires a pre-formed hydrogen bond.

The toluene radical cation is an extremely strong acid in acetonitrile solution with a pK_a of -12 ± 1 . When we compare this value to the reported pK_a value of toluene in acetonitrile (12a), a difference of over 60 pK_a units is indicated. Although this may appear surprising at first, it can be easily understood in terms of eq. [31]. The standard oxidation potential of the benzyl anion is between -1.1 V and -1.6 V versus S. H. E. ; ($E_{1/2} = -1.1$ V (12b) and $E^0 > -1.6$ V (12)); this difference, of about 3.5 to 4 V in the standard oxidation potentials of toluene and the benzyl anion, corresponds to a difference of 60-70 units in the acidities of toluene and the radical cation.

In the case of phenol the corresponding difference is 12 pK_a units (13a) since the difference between the standard oxidation potentials of phenol and the phenoxide anion will not be as great as it is for toluene. Phenol will be expected to have a considerably lower oxidation potential than toluene and the phenoxide anion should have a considerably higher oxidation potential than that of the benzyl anion.

From methods I and II it is evident that the extremely low pK_a value estimated for the toluene radical cation is a result of both the relatively low bond dissociation free energy and the high oxidation potential of toluene. A comparison of standard oxidation potentials shows that the toluene radical cation is more stable than the benzene radical cation relative to the respective parent molecules. However, the conjugate base of the toluene radical cation, the benzyl radical, a π -radical, is resonance stabilized. This is shown by the large difference (88 kJ mol⁻¹) in the bond dissociation free energy of toluene and benzene. This difference far outweighs the lower oxidation potential of toluene as compared to that of benzene (ΔE° ca. 40 kJ mol⁻¹).

In general, for compounds with very similar standard oxidation potentials a difference in the respective bond dissociation free energies of ca. 10 kJ mol⁻¹ corresponds to a difference of ca. 2 pK_a units in the acidity of the respective radical cations. Conversely, for compounds with very similar bond dissociation free energies a difference in the respective oxidation potentials of 0.1 V corresponds to a difference of ca. 2 pK_a units in the acidities of the radical cations.

Attempts to obtain equilibrium constants for the acid-base equilibrium between radical cations of methylated benzenes and their conjugate bases from kinetic methods

have met with little or no success. Primarily this is because benzylic radicals show no tendency to protonate even in strongly acidic media (10d). If protonation is energetically favourable an activation barrier may preclude it.

So far equilibrium acidities have been emphasized. It has been mentioned that an acid-base equilibrium between the radical cation and conjugate base is not easily established in solution, and that kinetic considerations become important in understanding radical cation reactivity. Estimation of equilibrium acidities may be used, however, to understand the kinetic reactivity by predicting the type of transition state involved in the deprotonation.

The estimated pK_a value for the toluene radical cation strongly suggests that deprotonation will be highly exergonic in dilute acid solutions. From the Hammond postulate (69), a reactant-like transition state is indicated, for the deprotonation of this ion; the energy of the reactant (radical cation) will govern the rate of deprotonation. For example, the rate constant for the deprotonation of the radical cations of a series of methylated benzenes in 0.5 M $HClO_4$ acid was found to correlate with the adiabatic ionization potentials of the parent compounds, where IP is primarily governed by the energy of the highest occupied MO. This in turn is related

to the stability of the radical cation (27c). When the strength of the acid solution is gradually increased deprotonation becomes increasingly more difficult. This causes the transition state to gradually acquire more product-like (benzylic radical) character. In fact, the rate of deprotonation of the radical cations of toluene, ethylbenzene and cumene in 8M HClO_4 acid does not correlate with the corresponding ionization potentials (22). Under these conditions deprotonation appears to be endergonic; the rate depending on the stability of the radicals formed. Thus, a knowledge of the stability of a radical is important and will be the topic of the next chapter.

1.4.2. Acidity of radical cations in the gas phase:

The comparison between the acidity of radical cations in the gas phase and in solution provides a means of obtaining free energies of solvation of radical cations. We have also shown how upper estimates of the pK_a value in solution can be obtained from the corresponding gas phase values. Hence, a study of the gas phase acidity of a radical cation is useful.

Tables 3 and 4 show that the gas phase acidity of a radical cation ($\text{RH}^{+\bullet}$) is not directly correlated to either the ionization potential or the bond dissociation free energy of RH. Similarly, the variation of PA ($\text{R}^\bullet$) for the series of radicals studied in this work must be discussed in terms of both IP (RH) and DH° (RH). Table 4 shows that

the radical cation of methane is the strongest acid ($pK_a = 87$) and the benzene radical cation the weakest ($pK_a = 147$) of those studied.

Compared to benzene, saturated hydrocarbons have higher IP values and lower DH° and DG° values which make their radical cations stronger acids than the benzene radical cation. Molecules containing π -electrons and/ or heteroatoms with nonbonding electron pairs, usually have IP values lower than that of saturated compounds. Among these molecules the aromatics usually have lower IP values relative to the aliphatics. In general, aliphatic hydrocarbon radical cations are stronger acids than their aromatic counterparts. The aliphatic radical cations should be very strong acids in solution, and it is not surprising that deprotonation of these species has been suggested in a sulphur hexafluoride matrix (72).

The acidity of the radical cations also depends on the nature of the conjugate base. For example, the IP values of propene and toluene are lower than those of ethylene and benzene respectively; but the radical cations of propene and toluene are stronger acids than those of ethylene and benzene respectively. This is because the radical cations of propene and toluene are π -acids and on deprotonation yield resonance stabilized radicals, while the radical cations of ethylene and benzene are σ -acids.

Table 5. The computed UHF total energies (E) of open-shell species at the STO-3G level

Species	Symmetry	- E / au
CH ₃ [•]	C _{3v}	39.07701 ^a
CH ₄ ⁺	D _{2d}	39.29386 ^a
C ₂ H ₅ [•]	C _s	77.66300 ^a
C ₂ H ₆ ⁺	D _{3d}	77.94048 ^a
C ₂ H ₃ [•]	C _s (planar)	76.43573 ^a
C ₂ H ₄ ⁺	D _{2h}	76.79755 ^a
C ₂ H [•]	C _{∞v}	75.19609 ^a
C ₂ H ₂ ⁺	D _{∞h}	75.53549 ^a
C ₃ H ₅ [•]	C _{2v}	115.05429 ^b
C ₃ H ₆ ⁺	C _s	115.40747
c-C ₃ H ₅ [•]	C _s	115.01383 ^b
c-C ₃ H ₆ ⁺	C _{2v}	115.38241 ^c
C ₆ H ₅ [•]	C _{2v}	227.23946
C ₆ H ₆ ⁺	D _{6h}	227.65759
C ₆ H ₅ CH ₂ [•]	C _{2v}	265.87734
C ₆ H ₅ CH ₃ ⁺	C _s	266.25329

^a Reference 26.

^b Reference 56.

^c Reference 55.

Table 6. The effect of the basis set on the total UHF energy of open shell species at the STO-3G geometry.^{a,b}

Species	$E_{\text{STO-3G}} - E_{\text{X//STO-3G}}$				
	X				
	3-21G	4-31G	6-31G	4-31G*	6-31G*
1. $\text{CH}_3^\cdot$	0.26473	0.42692	0.46861	0.44176	0.48138
2. CH_4^+	0.23402	0.39971	0.44069	0.41651	0.45516
3. $\text{C}_2\text{H}_5^\cdot$	0.50009	0.82229	0.90486	0.85577	0.93368
4. C_2H_6^+	0.47139	0.79308	0.87428	0.82907	0.90647
5. $\text{C}_2\text{H}_3^\cdot$	0.52595	0.84644	0.92941	0.87493	0.95350
6. C_2H_4^+	0.47123	0.79834	0.88102	0.83460	0.91213
7. $\text{C}_2\text{H}^\cdot$	0.53581	0.85099	0.93238	0.87605	0.95386
8. C_2H_2^+	0.48995	0.81230	0.89336	0.84853	0.92546
9. $\text{C}_3\text{H}_5^\cdot$	0.76802	1.25051	1.37467	1.29623	1.41327
10. C_3H_6^+	0.70691	1.19357	1.31722	1.24757	1.36345
11. $\text{c-C}_3\text{H}_5^\cdot$	0.74212	1.22487	1.34975	1.28466	1.40124
12. $\text{c-C}_3\text{H}_6^+$	0.70308	1.18689	1.31094	1.24756	1.36383
13. $\text{C}_6\text{H}_5^\cdot$	1.54261	2.48241	2.74763	--	--
14. C_6H_6^+	1.46186	2.42691	2.67063	--	--

^a All values in atomic units.

^b The 4-31G//STO-3G energy of the species (1) to (8) were obtained from reference 26.

Proton affinity of hydrocarbon radicals

Ab initio calculations show that the $PA(R^\bullet)_{HF}$ values at the STO-3G level are generally higher compared to the extended basis sets (Tables 5 to 8). The difference between the true Hartree-Fock and thermochemical proton affinities of radicals will not be expected to be greater than 40 kJ mol^{-1} (23). The best agreement with the thermochemical and HF values are for the 3-21G results at the STO-3G geometry.

The energies of $RH^{+\bullet}$ and $R^\bullet$ are lowered to a greater extent by increasing the number of primitives that describe the core rather than adding polarization functions on carbon (Table 6). The addition of polarization functions on carbon to the 4-31G and 6-31G split-valence basis sets had a greater effect on the energy of $RH^{+\bullet}$; while, increasing the number of Gaussian functions describing the core in the 4-31G and 4-31G* basis sets lowered the energy of $R^\bullet$ by a greater amount. Consequently, the PA_{HF} value was increased by the addition of polarization functions, and decreased by increasing the number of primitives describing the core.

Complete optimization at the 3-21G level did not change the PA_{HF} values significantly (Table 9). Thus single point calculations using larger basis-sets at the STO-3G geometry may yield useful information about the effects of basis set size on PA_{HF} .

Table 7. A comparison of the thermochemical and Hartree-Fock proton affinities of hydrocarbon radicals at 300 K.

PA / kJ mol ⁻¹			
Radical	Thermochemical (eq. [55])	HF(STO-3G) (eq. [59])	Experimental ^a
Methyl	≥534±4	576	-
Ethyl	615±8	735	-
Vinyl	758±8	956	746±8
Ethynyl	763±20	897	-
Allyl(i)	733±6	933	754±8
Allyl(ii)	695±6	868	-
Cyclopropyl	808±6	974	785±8
Phenyl	883±8	1104	-
Benzyl	828±6	993	830±8

^a All values are from reference 25.

Table 8. The effect of basis set on the Hartree-Fock
proton affinity (PA_{HF}) of radicals.^a

$PA_{HF}(X//STO-3G) /kJ mol^{-1}$						
X						
Radical	STO-3G	3-21G	4-31G	6-31G	4-31G*	6-31G*
Methyl	576	495	504	502	509	507
Ethyl	735	659	658	654	665	663
Vinyl	956	813	830	829	850	848
Ethynyl	897	777	796	795	825	823
Allyl(i)	933	773	784	783	806	803
Allyl(ii)	868	697	701	700	740	738
c-propyl	974	872	874	872	877	876
Phenyl	1104	892	959	902	-	-
Benzyl	993	-	-	-	-	-

^a Calculated using UHF energies from Table 6.

Table 9. The effect of complete optimization at the 3-21G level on total energies and proton affinities.^{a,b}

RH	$\Delta E(R^\bullet)^c$	$\Delta E(RH^{+\bullet})$	$\Delta PA_{HF}(R^\bullet)$	$PA_{HF}(R^\bullet)^d$
Methane ^e	-2.5	-3.0	0	495
Ethane	-2.0	-14.0	14	673
Ethylene	-2.5	-6.5	4	817
Acetylene ^f	-0.1	-0.1	0	777

^a All values in kJ mol^{-1}

^b Δ indicates the difference between the (3-21G//3-21G) and (3-21G//STO-3G) basis sets.

^c E(3-21G//3-21G) values were obtained from reference 19.

^d Value for the (3-21G//3-21G) basis set.

^e The computed PA_{HF} values after complete optimization at the 4-31G and 6-31G* levels are not significantly different from the corresponding value for these basis sets at the STO-3G geometry (Table 8).

$$PA_{HF}(4-31G//4-31G) = 506 \text{ kJ mol}^{-1}.$$

$$PA_{HF}(6-31G*//6-31G*) = 509 \text{ kJ mol}^{-1}.$$

^f Complete optimization at the 6-31G* level does not significantly change the PA_{HF} value.

$$PA_{HF}(6-31G*//6-31G*) = 828 \text{ kJ mol}^{-1}.$$

Table 10. The proton affinity of the methyl radical^a

Basis set	PA _{HF} ^b /kJmol ⁻¹		ΔPA ^{b,c} /kJmol ⁻¹	
	(C _{2v})	(D _{2d})	(C _{2v})	(D _{2d})
6-31G [*] //6-31G [*]	520	509	-14	-25
6-31G ^{**} //6-31G ^{**}	543	520	9	-14
6-311G ^{**} //6-311G ^{**}	547	522	13	-12
MP2/6-31G ^{**} //MP2/6-31G ^{**}	558 ^d	544 ^d	24 ^e	10 ^e
MP3/6-31G ^{**} //MP2/6-31G ^{**}	561 ^d	546 ^d	27 ^e	12 ^e

^a The energies of the radical cation for the 6-31G^{*} and 6-31G^{**} basis sets are from reference 75. The energy of the methyl radical at the 6-31G^{*} level is from reference 56.

All other UHF energies were calculated in this work;

CH₃⁺ (C_{3v}/2A₁): E(6-31G^{**}//6-31G^{**}) = -39.56446 au.

E(6-311G^{**}//6-311G^{**}) = -39.57291 au.

E(MP2/6-31G^{**}//MP2/6-31G^{**}) = -39.69270 au.

E(MP3/6-31G^{**}//MP2/6-31G^{**}) = -39.71018 au.

CH₄⁺ (C_{2v}/2B₁): E(6-311G^{**}) = -39.77891 au

(D_{2d}/2B₂): E(6-311G^{**}) = -39.76922 au

^b The symmetry of the radical cation is indicated in parentheses.

^c Thermochemical PA value is from Table 7.

^d Also includes a contribution from valence electron correlation (see text).

^e Excluding the contribution from valence electron correlation computed by MP perturbation theory.

1.4.4. Comparison of the thermochemical and Hartree-Fock proton affinities

In this section the thermochemical and Hartree-Fock proton affinities of representative radicals are compared. The uncertainty in the results obtained is also discussed. Comparisons with experimental determinations of $PA(R^\bullet)$ are made in the few cases where data is available.

Methyl:

The thermochemical method gives only a lower limit of $PA(R^\bullet)$ because the IP adiabatic has been reported as an upper limit of the true value. The DH° value used here is based on recent experimental results and a critical review of earlier data and is the value recommended currently (32).

PA_{HF} values (for protonation to the radical cation with a $D_{2d}(^2B_2)$ state) were found to be lower than the thermochemical value for all the extended basis sets. This is surprising, because ΔZPE in eq. [57] is found to be positive (73, 74) and the correlation energy is usually small (23). (*vide infra*).

Recent theoretical (75, 76) and esr (76) studies indicate a $C_{2v}(^2B_1)$ ground-state for the methane radical cation. Extensive theoretical studies have shown that a basis set of double-zeta quality augmented by polarization

adequate description of the bonding in CH_4^+ and relative energies of the $\text{C}_{2v}(^2\text{B}_1)$ and $\text{D}_{2d}(^2\text{B}_2)$ states (75). Thus, a systematic study of the proton affinity of the methyl radical using such basis sets (i. e., 6-31G** and 6-311G**) and the effects of electron correlation on the theoretical PA value were undertaken. The results are given in Table 10.

Tables 8, 9 and 10 show that the agreement with the Hartree-Fock and thermochemical PA values are poor, unless the basis sets include polarization functions on hydrogen. For the basis sets without such functions (2p) a PA_{HF} value less than the thermochemical value is obtained, because of the inadequate description of the bonding in the radical cation. Furthermore, the PA values are affected to a greater extent by the addition of 2p functions on hydrogen, than incorporating valence electron correlation in the basis sets.

Ethyl:

As expected, all computed PA_{HF} values are larger than the thermochemical PA value. The error in the thermochemical proton affinity depends largely on the uncertainty in DH° because the error in IP (adiabatic) is small. The proton affinity of the ethyl radical is ca. 78 kJ mol^{-1} greater than the methyl radical. This indicates that replacing an H in methyl radical by a methyl group

results in a greater stabilization of RH^+ relative to R^+ .

Vinyl:

There is a fair agreement between the experimental and thermochemical PA values. The difference between the thermochemical and computed Hartee-Fock proton affinities is larger than that expected from ZPE and correlation energy contributions. The proton affinity of the vinyl radical is 146 kJ mol^{-1} greater than that of the ethyl radical. This results from the ease of ionization and the greater DH^0 value of ethylene relative to ethane.

Ethynyl:

There is a large variation between the DH^0 values of acetylene that have been reported (32, 33a, 33b). The value recommended currently, by Mcmillen and Golden (32), has been used to estimate the thermochemical PA value. No experimental determination is available to assess the accuracy of the thermochemical value. There is a large difference between the computed Hartee-Fock and thermochemical proton affinities; the uncertainty in the DH^0 value precludes a discussion of the reasons for this observation.

Allyl:

The allyl radical can, in principle, be formed by the deprotonation of the radical cations of both propene and cyclopropane. The proton affinity of the allyl radical to

form both these radical cations has been estimated. The thermochemical PA value for the formation of the propene radical cation is smaller than the experimental value. The error on the thermochemical value is largely dependent on the accuracy of DH^0 . The accuracy of the experimental determination is also limited to $\pm 8 \text{ kJ mol}^{-1}$ by the bracketing technique used (25). As expected, the PA_{HF} values are greater than the thermochemical proton affinity.

Cyclopropyl:

There is a large variation between DH^0 values of cyclopropane reported in the literature (32, 33a, 33b). The value recommended by Mcmillen and Golden (32) has been used to estimate PA. The experimental value is smaller, than the lower limit of $PA(R^{\bullet})$ obtained by the thermochemical method. This may indicate an error in the DH^0 value.

The difference in the PA_{HF} and the thermochemical PA is greater than in the propene system. As in the ethynyl system this difference cannot be explained by the absence of reliable thermochemical data. The cyclopropyl radical has a proton affinity larger than that of the vinyl and allyl radicals. This results from the relatively low $IP(\text{adiabatic})$ of cyclopropane.

Phenyl:

Attempts to experimentally determine PA have thus far failed. One of the reasons has been the absence of a suitable base with a proton affinity greater than 880 kJ mol^{-1} . The thermochemical approach provides a method of obtaining the PA value. The IP(adiabatic) of benzene has been accurately determined. Consequently, the uncertainty in the PA value estimated in this work depends on the error in the DH° value. Only a partial optimization was carried out to obtain the STO-3G equilibrium geometries for the phenyl radical and the benzene radical cation. Thus, the excellent agreement between the Hartree-Fock and thermochemical PA values may be due to a fortuitous cancellation of errors.

Benzyl:

The thermochemical PA value agrees well with the experimental determinations. The errors in the IP(adiabatic) and DH° values are small; it has been suggested that the thermochemical proton affinity of the benzyl radical is suitable to be used as a standard for a absolute scale of proton affinities(24).

1.5 CONCLUSIONS

The use of thermochemical cycles in assessing thermodynamically significant parameters not directly determinable by experiment has been demonstrated.

This work shows that in general hydrocarbon radical cations are strong acids in solution and that deprotonation can be slow because of the absence of a pre-formed hydrogen bond in these acids.

There is general agreement between the different methods used to estimate radical cation acidities. The establishment of reliable pK_a values for the radical cations of toluene and benzene is important, because it enables the estimation of these parameters for other ions using kinetic methods (35).

It has been demonstrated that a thermochemical approach can be used to obtain reliable proton affinities of free radicals, and to establish an absolute scale of such values. In general the trend in the ab initio and thermochemical proton affinities agree. Thus, the ab initio self-consistent field MO method can be used to estimate relative values of proton affinities in the absence of reliable thermochemical data.

CHAPTER 2. THE STABILITY OF ALKYL RADICALS

2.1. INTRODUCTION

Organic radicals are open-shell species which form an important class of reactive species. These moieties are formed as intermediates in processes that range from industrially useful polymerizations and petroleum cracking to intricate physiological reactions. Although some free radicals are persistent enough to be maintained in solution at fairly high concentrations, most are encountered only as short-lived intermediates. This fact has made the determination of accurate thermochemical parameters for radicals quite difficult. Most often, measured values have large uncertainties (32).

The energy of a chemical system cannot be measured absolutely; consequently, only relative stabilities can be defined in terms of energy. The relative thermochemical stability of a chemical species can be measured by the total energy (reference state: separated electrons and nuclei) or by the heat of atomization (reference state: separated atoms) (77).

The stability of two chemical systems can be compared only if they contain the same number of particles (electrons and nuclei, or atoms) (77). For example, the free energy change :



is a measure of the relative stability of the products (C+D) with respect to the reactants (A+B). However, the stability of, say D relative to B cannot be extracted from ΔG_{61} , (or ΔH_{61}) alone, unless D and B contain the identical number of particles and the total energies of A and C, are given. Moreover, even if the latter were known, individual bond contributions to the total energies of the participating species would be required before the relative importance of various factors governing the stability of one of the products (for example, a radical) can be defined in terms of one of the reactants.

In this thesis, it will be shown how the stability of a radical can be defined with respect to a reference state containing an identical number of particles, and how the energy of such reference states may be estimated. The stability measured relative to such reference states will be termed the net stabilization energy of a radical.

Radical stability is defined as the the stabilization (or destabilization) energy conferred on the open-shell species as a result of the interaction of the unpaired electron with the bonds in the molecule. Consequently, an ideal reference state, with respect to which radical stability may be assessed, should contain an identical number of particles as the radical and an

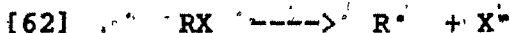
unpaired electron that is non-interacting.

In section 2.2, the suitability of the reference states, adopted in other approaches used to assess radical stability of alkyl radicals, will be analysed critically. A thermochemical cycle is used to assess the suitability of using isodesmic reactions (78) to obtain interaction energies between substituents attached to a common group. These concepts are then used to illustrate the limitations of using the DH° method to define radical stability.

In section 2.3 linear charge-energy relationships that have been established (79) are used to assess substituent effects on the intrinsic C-H and C-C bond strengths of hydrocarbons. By intrinsic is meant the contribution of that bond to the energy of atomization of the molecule. Such effects on molecules of the type RH, RCH_3 and RR are used in conjunction with the bond dissociation enthalpies ($DH^\circ(R-X)_g$, $X=H, CH_3$ and R) to define the net relative stabilization energy of the open-shell species $R^\bullet$ ($SE^\circ[R^\bullet, RX]$).

2.2. MERITS AND AMBIGUITIES IN CURRENT APPROACHES TO ASSESS RADICAL STABILITY

The enthalpy change for the homolytic cleavage:

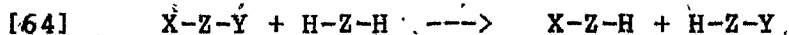


of the R-X bond in an organic molecule (RX) in the gaseous state, under standard conditions is :

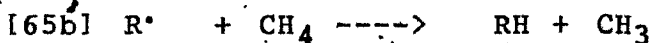
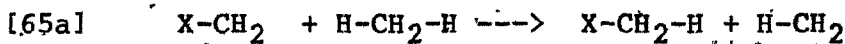
$$\begin{aligned} [63] \quad \Delta H_{62}^{\circ} &= \Delta_f H^{\circ}(R\cdot) + \Delta_f H^{\circ}(X) - \Delta_f H^{\circ}(RX) \\ &= DH^{\circ}(R-X) \end{aligned}$$

In this section, all species are considered in the gaseous state. However to simplify the notations used the symbol 'g' has been omitted.

Equation [63] has been the basis for most definitions of the "stabilization energy" of radicals (32, 33a). This stabilization energy is conveniently derived from reactions conserving the number and nature of all chemical bonds ("isodesmic reactions" (78)). The standard energy (or enthalpy) change, ΔE_{64}° (or ΔH_{64}°) has been defined as a measure of the interaction between X and Y (vide infra).



When Y = electron and Z = CH₂ reaction [64] yields:



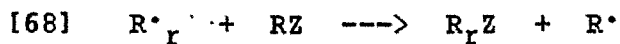
Szwarc identified ΔH_{65b}° as the (de)stabilization energy (RE) of a chosen radical R $\cdot$ (eq. [66]) (80).

$$[66] \quad RE(R^\bullet) = \Delta H_{65b}^\circ = DH^\circ(CH_3-H) - DH^\circ(R-H)$$

For π -resonance delocalized radicals, Benson's definition of stabilization energy (SE), eq.[67], has been used, where R_SCH_3 is the fully saturated compound analogous to $R_\pi CH_3$ (33a).

$$[67] \quad SE(R_\pi CH_2^\bullet) = DH^\circ(R_SCH_2-H) - DH^\circ(R_\pi CH_2-H)$$

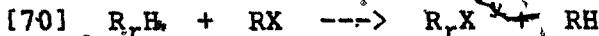
The DH° methods described above (eqs.[66] and [67]) assume that the relevant relative DH° values, depend only on the stability of the radicals formed (33). This suggests that the standard enthalpy change:



ΔH_{68}° , given by eq.[69] should not vary with Z, where R_Z is the molecule with respect to which relative DH° values $\{\delta(DH^\circ(R-Z))\}$ are measured.

$$[69] \quad \begin{cases} \Delta H_{68}^\circ = DH^\circ(R-Z) - DH^\circ(R_Z-Z) \\ = \delta(DH^\circ(R-Z)) \end{cases}$$

However, it can be shown that the variation in relative DH° values ($\delta(\Delta H_{68}^\circ)$) is given by the enthalpy change for the reaction:



by considering equation [71].

$$\begin{aligned}
 [71] \quad \delta(\Delta H^\circ_{68}) &= \Delta H^\circ_{68}(Z=X) - \Delta H^\circ_{68}(Z=H) \\
 &= \delta(DH^\circ(R-X)) - \delta(DH^\circ(R-H)) \\
 &= \Delta_f H^\circ(R_X) - \Delta_f H^\circ(RX) - \Delta_f H^\circ(R_H) \\
 &\quad + \Delta_f H^\circ(RH) \\
 &= \Delta H^\circ_{70}
 \end{aligned}$$

The use of the DH° method to estimate radical stability presupposes the absence of substituent effects on the stabilities of the parent undissociated molecules. This method actually assumes that ΔH°_{70} is zero. In Table 13 we critically assess the validity of this assumption.

The fact that $\delta(\Delta H^\circ_{68})$ is not zero does not indicate the absence (or presence) of radical stabilizing effects, because this term is independent of the heat of formation of the radicals (81). Indeed, the limitations of the DH° method are illustrated in Tables 11, 12 and 13.

Table 11. A correlation of gas phase bond dissociation enthalpies of R-X ($\text{DHO}(\text{R-X})$) with R-H ($\text{DHO}(\text{R-H})$) at 300 K. a, b, c.

X ^d	R ^d								rf
	(147) Me	(108) Et	(88) n-Pr	(76) i-Pr	(36) t-Bu	(329) Ph	(200) Bze	(164) Ale	
H	439	410	410	399	389	464	368	361	1.00
Cl	350	342	342	342	340	399	303	-	0.91
Br	296	283	284	286	281	337	248	230	0.94
I	238	224	227	225	215	274	207	179	0.95
OH	388	382	382	388	388	464	340	327	0.89
Me	378	360	361	358	351	426	318	311	0.97
Et	360	343	343	338	331	408	300	294	0.98
n-Pr	361	343	343	339	331	409	301	293	0.98
i-Pr	358	338	339	332	317	401	298	291	0.99
t-Bu	351	331	331	317	299	388	-	284	0.99
Ph	426	408	409	401	388	475	389	-	0.99

a Bond dissociation enthalpies have been calculated from eq [63]. The standard heat of formation of RX, X^e and R^e are from references. 82, 29 and 32, respectively.

b All values in kJ mol⁻¹.

c Uncertainty $\pm 6-8$ kJ mol⁻¹.

d The standard heat of formation of the radical is given in parentheses.

e Bz = benzyl; Al = Allyl.

f Correlation coefficient for the linear regression analysis of $\text{DHO}(\text{R-X})$ vs. $\text{DHO}(\text{R-H})$ as a function of X.

Table 12. The effect of the X group on relative $\text{DHO}(\text{R-X})$ at 300 K.^{a,b}

X	R							
	Me	Et ^c	n-Pr	i-Pr	t-Bu	Ph	Bz ^d	Al ^d
H	29	0	0	-11	-21	54	-42	-49
Cl	8	0	0	0	-2	57	-39	-
Br	13	0	1	3	-2	54	-35	-53
I	14	0	3	-1	-9	50	-17	-48
OH	6	0	0	6	6	82	-42	-55
Me	18	0	1	-2	-9	66	-42	-49
Et	17	0	0	-5	-12	65	-43	-49
n-Pr	18	0	0	-4	-12	66	-42	-50
i-Pr	20	0	1	-6	-21	63	-40	-47
t-Bu	20	0	0	-14	-32	57	-	-47
Ph	18	0	1	-7	-20	67	-19	-

^a Bond dissociation enthalpies are given in Table 11.

^b All values are in kJ mol^{-1} .

^c Zero by definition.

^d Bz = benzyl; Al = Allyl.

Table 13. The standard enthalpy change, for reaction [70]
 $(R = C_2H_5)$, at 300K. The variation of relative $\Delta H^\circ(R-X)$
 values with X.^{a,b}

X	R				
	Me	n-Pr	i-Pr	t-Bu	Ph
Cl	-20.6±0.8	-0.2±0.9	12.4±0.9	19.5±1.4	3.5±0.9
Br	-15.6±1.4	1.7±1.2	15.5±1.4	19.6±1.7	0.3±3.3
I	-14.9±1.3	3.0±2.0	12.2±2.0	12.5±2.4	-4.3±4.7
OH	-23.7±0.5	-0.5±1.1	17.2±0.6	27.1±2.9	28.4±0.9
Me	-11.0±0.6	1.5±0.6	9.5±0.7	12.4±0.9	12.3±0.6
Et	-12.5±0.7	-0.5±1.1	6.8±0.7	9.4±1.0	11.2±0.7
i-Pr	-9.8±0.8	0.5±1.1	5.1±0.9	0.2±1.4	9.1±1.2
t-Bu	-9.5±1.2	-0.3±1.1	-2.4±1.5	-11.2±1.5	3.1±1.4
Ph	-11.4±0.7	0.8±0.9	4.7±1.2	1.3±1.3	13.8±1.5

^a All values in kJ mol^{-1} .

^b The enthalpy changes were calculated using standard heats of formation (of species involved) from reference 82.

Table 14. The relative enthalpy of interaction a, b, c between two groups R and X, ($\Delta H^0(R/X)$), attached to a common moiety (CH_2) in the gas phase.

X	R			
	Me	Et	Ph	Allyl
Cl	-20.6 $\pm$ 0.8	-20.4 $\pm$ 0.7	-23.9 $\pm$ 3.1	-
Br	-15.6 $\pm$ 1.4	-17.3 $\pm$ 1.1	-23.8 $\pm$ 4.8	-11.9 $\pm$ 4.4
I	-14.9 $\pm$ 1.3	-17.9 $\pm$ 2.0	-39.9 $\pm$ 5.5	-18.6 $\pm$ 2.5
OH	-23.7 $\pm$ 0.5	-23.2 $\pm$ 1.1	-23.4 $\pm$ 1.3	-17.3 $\pm$ 2.1
Me	-11.0 $\pm$ 0.6	-12.5 $\pm$ 0.7	-11.4 $\pm$ 0.7	-11.1 $\pm$ 0.8
Et	-12.5 $\pm$ 0.7	-12.0 $\pm$ 0.7	-12.2 $\pm$ 0.9	-12.1 $\pm$ 1.4
Ph	-11.4 $\pm$ 0.7	-12.2 $\pm$ 0.9	-34.7 $\pm$ 3.1	-56.8 $\pm$ 8.4

^a The standard enthalpy change, at 300 K, for reaction [64]; Z = CH_2 and Y = R.

^b All values in $kJ\ mol^{-1}$.

^c The enthalpy changes were calculated using standard heats of formation (of species involved) from reference 82.

Figure 8. A comparison of the bond dissociation enthalpies of 1,4-pentadiene(1) and 1,3-pentadiene(2).

In fact, the difference in the $DH_o(R-H)$ values of 1 and 2 to give the same delocalized radical 3 has been attributed (32) to substituent effects on neutral closed shell species (i.e. extra stabilization of 2 due to the conjugated double bonds). However, the difference in the intrinsic bond strengths of the dissociated C-H bonds of 1 and 2 will also be a factor causing the unequal DH_o values. It must be noted that this ambiguity will be present for all π -delocalized radicals that can be represented by at least two non-identical resonance forms.

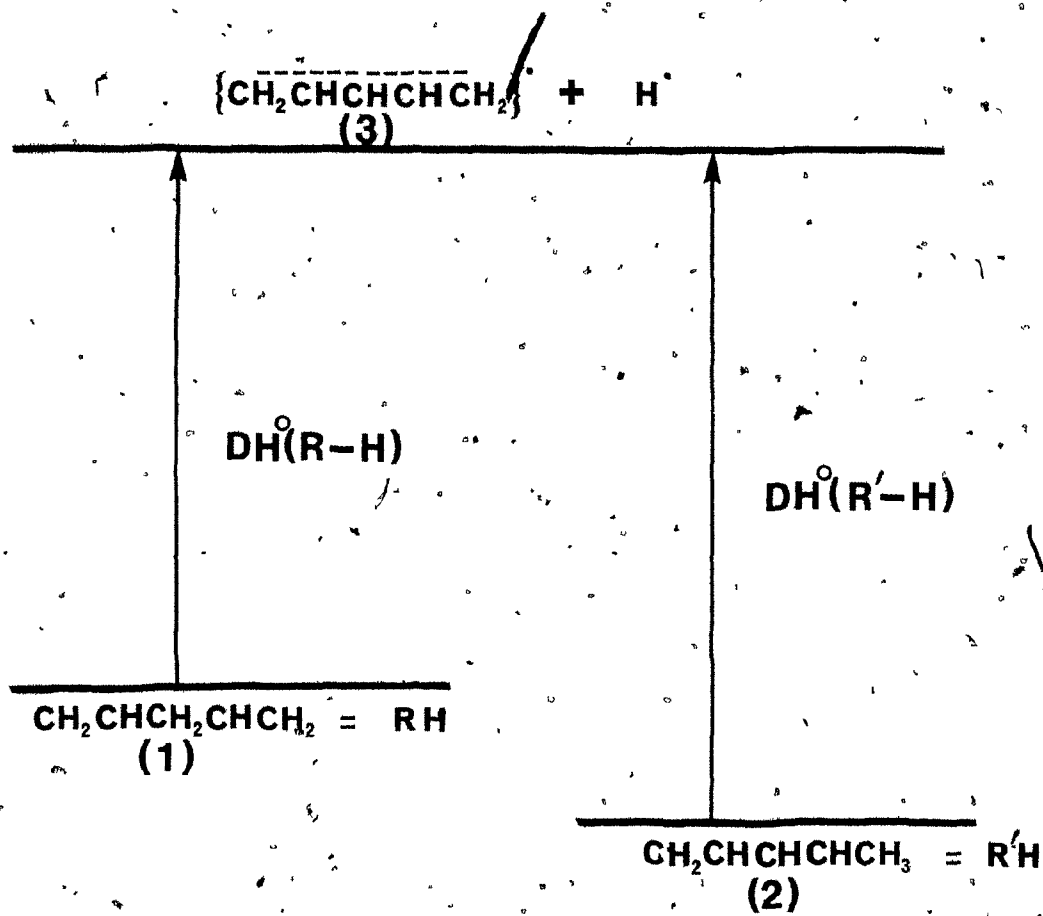
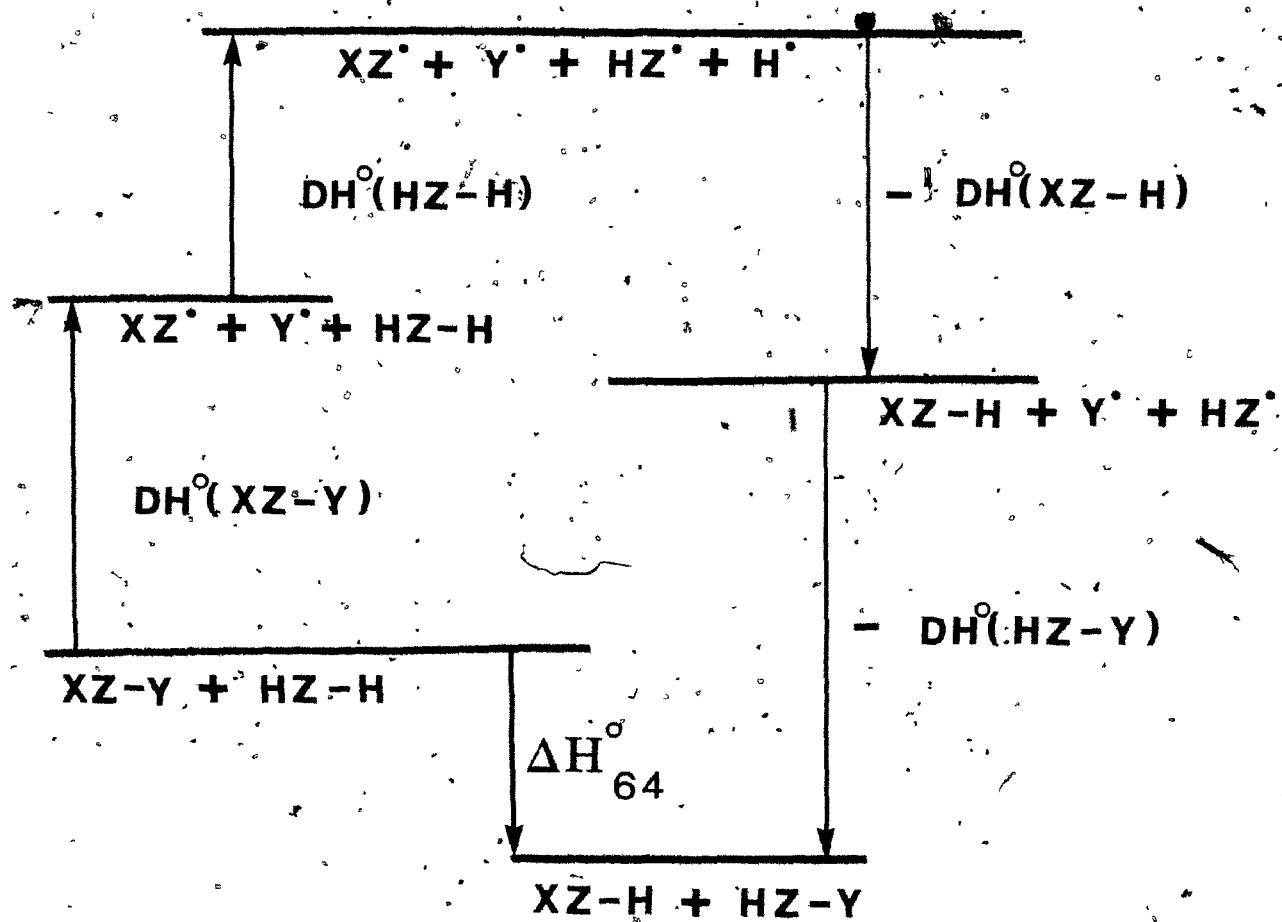


Figure 9. A thermochemical cycle relating the enthalpy change in the isodesmic reaction [64] to ΔH° values of the participating species.



The involvement of substituent effects on the stability of undissociated molecules, is also shown in Table 14, with reference to reaction [64]. In Figure 8, an example of how ambiguities can arise by equating relative DHO values to radical stability, is illustrated.

An analysis of the general isodesmic reaction (reaction [64]):

Using the thermochemical cycle given in Figure 9, the enthalpy change for reaction [64], ΔH_{64} , can be expressed by, eq. [72], where $\delta(\text{DHO}(\text{XZ-Y}))$ and $\delta(\text{DHO}(\text{XZ-H}))$ are substituent effects on the DHO values of the Z-Y and Z-H bonds, respectively.

$$\begin{aligned} [72] \quad \Delta H_{64} &= \text{DHO}(\text{XZ-Y}) - \text{DHO}(\text{HZ-Y}) - \text{DHO}(\text{XZ-H}) + \text{DHO}(\text{HZ-H}) \\ &= \delta(\text{DHO}(\text{XZ-Y})) - \delta(\text{DHO}(\text{XZ-H})) \end{aligned}$$

Equation [72] shows that, for a fixed Y, ΔH_{64} is a measure of only a relative interaction energy between X and Y with respect to X and H. This can also be readily seen by considering reaction [64], with Y=H, in which case $\Delta H_{64}=0$. It must be noted, that the applicability of reaction [64] cannot be tested by the success or failure of any group additivity methods (33a) of obtaining the standard heat of formation of XYZ from HZY, XZH and HZH. This is because in these methods any type of interaction between X and H, say in XZH, is included in the group values for

X(ZH) and ZH(X). Thus, the suitability of using reaction [64], when Y is simply an electron, (or, alternatively eq. [66]) to directly assess radical stability depends on the magnitude of the interaction between a substituent (X) and H in a molecule of the type of XZH.

Factors governing bond dissociation energies:

The bond dissociation energy (DEO) of a bond (C-X) at 0 K has been given by :

$$[73] \quad \text{BDE (C-X)} = \Delta V + \Delta R + \Delta Z$$

where ΔV is the bond potential energy (the energy needed to break the bond at 0 K when the fragments retain their valence state pertaining to bonding); ΔR is the energy change when fragments revert to the standard state at 0 K and ΔZ is the difference between the zero point energies before and after bond scission (83). Even if individual ΔV , ΔR and ΔZ values can be estimated, the use of eq. [73] to obtain radical stabilities will be biased by effects on the parent species (C-X).

In an entirely different approach Leroy and co-workers (84) have estimated the stabilization energy (SE) of radical (or closed shell) species using :

$$[74] \quad \text{SE} = \Delta H_a - \sum N_{AB} E_{AB}$$

where ΔH_a is the heat of atomization of the species

(radical or closed shell) and E_{AB} 's are standard bond energy terms derived from ΔH_a values of reference compounds. However, an unambiguous quantitative assessment of radical stability still cannot be made, because this method too, requires an assumption regarding reference bonds.

2.3. THE ESTIMATION OF THE STABILITY OF ALKYL RADICALS

2.3.1. Charge effects on bond strengths

A bond by bond insight into the various factors contributing to the stability of hydrocarbons has been made possible by a suitable partitioning of the total energy of these species in terms of constituent bonds. Such an analysis in terms of electron distributions has been developed by Fliszar and co-workers (eqs. [75-79] (79, 85-92). Using this approach they have been able to calculate the energy of atomization, $\Delta_{at}E^*$, of several series of organic molecules at 0 K in the hypothetical vibrationless state which show good agreement with experiment (79, 85-92).

Equation [75] shows the relationship between $\Delta_{at}E^*$ and E_{ij} , where E_{ij} and E_{nb}^* gives the energy contributions to $\Delta_{at}E^*$ from the ij bond and the nonbonded interactions, respectively.

$$[75] \quad \Delta_{at} E^* = \sum E_{ij} - E_{nb}^*$$

$$[76] \quad E_{ij} = E_{ij}(Q_i, Q_j)$$

$$\begin{aligned}
 [77] \quad E_{ij} &= E_{ij}^0 + \Delta Q_i \left(\partial E_{ij} / \partial Q_i \right)_{Q_i^0, Q_j^0} + \\
 &\quad \Delta Q_j \left(\partial E_{ij} / \partial Q_j \right)_{Q_i^0, Q_j^0} \\
 &= E_{ij}^0 - \Delta q_i \left(\partial E_{ij} / \partial Q_i \right)_0 \\
 &\quad - \Delta q_j \left(\partial E_{ij} / \partial Q_j \right)_0
 \end{aligned}$$

Equation [76] can be postulated, provided that for a given bond ij the variations in Q_i and Q_j (the total electron populations of the bond forming atoms i and j respectively) due to changes in molecular environment are small. The E_{ij} terms can be expressed as standard E_{ij}^0 terms (of eq. [77]) if eq. [76] is assumed (85).

In eq. [77], Δq_i and Δq_j are net (i.e., $Z-Q$) atomic charges relative to standard charges q_i^0 and q_j^0 . By defining E_{CC} and E_{CH} with respect to the ethane CC and CH bonds, and consequently, q_C and q_H , expressed relative to the net atomic charges of C and H, of ethane, application of eq. [77] gave:

$$[78a] \quad E_{CC} = E_{CC}^0 + a_{CC} (\Delta q_{C_i} + \Delta q_{C_j})$$

$$[78b] \quad E_{CH} = E_{CH}^0 + a_{CH} \Delta q_C + a_{HC} \Delta q_H$$

In these equations a_{CC} , a_{CH} and a_{HC} represent the appropriate $-(\partial E_{ij} / \partial Q_i)_0$ values of eq. [77]. The

significance of eqs. [75-78] is that the individual bond contributions to the differences in the relative stability of two species can be determined, if the required a_{ij} and q values are known (79, 85-91).

Useful information about charge effects on intrinsic bond strengths have been obtained from the application of eqs. [75-78] to a variety of organic molecules. Studies by Fliszar and co-workers (79) of linear and branched paraffins and of compounds containing chair or boat cyclohexane rings have given the following a_{ij} values in the units $\text{kJ mol}^{-1} \text{me}^{-1}$ (where the unit of charge is expressed in millielectrons and symbolized by me (79)):

- [79a] $a_{\text{HC}} = 2.64$
- [79b] $a_{\text{CH}} = 1.03$
- [79c] $a_{\text{CC}} = 2.04$

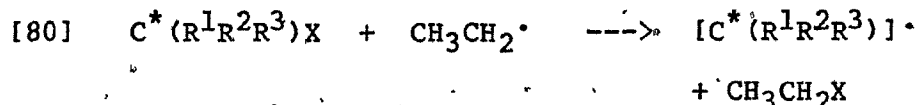
These values indicate that 0.001 electron (= 1 me) added to a hydrogen ($\Delta q_{\text{H}} = -1 \text{ me}$) stabilized a CH bond by 2.64 kJ mol^{-1} , whereas 1 me added to carbon had a stabilizing effect of 1.03 and 2.04 kJ mol^{-1} on a CH and a CC bond, respectively (79). Thus, any electron enrichment on a carbon atom, at the expense of the electron population at the hydrogen atoms of a CH bond in these alkanes, results in a gain in molecular stability but a concomitant weakening of that CH bond.

The relationship between charges on atoms and stabilities provides a method of estimating substituent effects on the intrinsic C-H and C-C bond strengths of several types of organic molecules (RX) independent of the standard heat of formation of the corresponding radicals ($\Delta_f H^\circ(R^\bullet)$ and $\Delta_f H^\circ(X^\bullet)$). The intrinsic bond strength is defined as the contribution of that bond to the energy of atomization of the molecule.

Next this approach is applied to assess changes in the intrinsic C-H and C-C bond strengths of a few representative alkanes. These estimations then enable the calculation of relative net stabilization energies of alkyl radicals via the use of appropriate DH° values (vide infra).

2.3.2 Relative net stabilization energies of a radical (SE^o [R[•], RX])

Consider the isodesmic reaction:

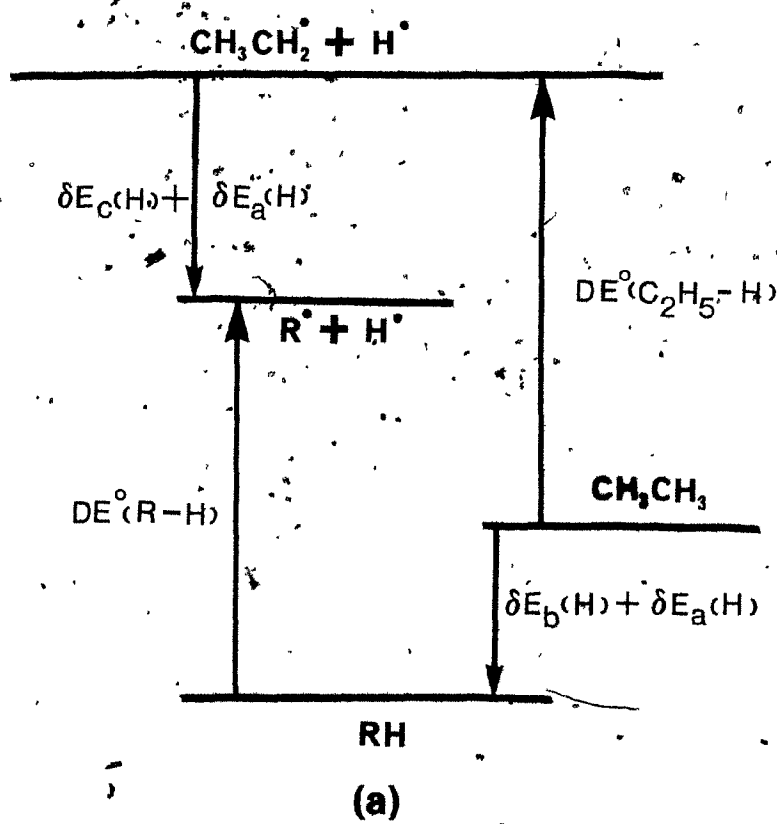


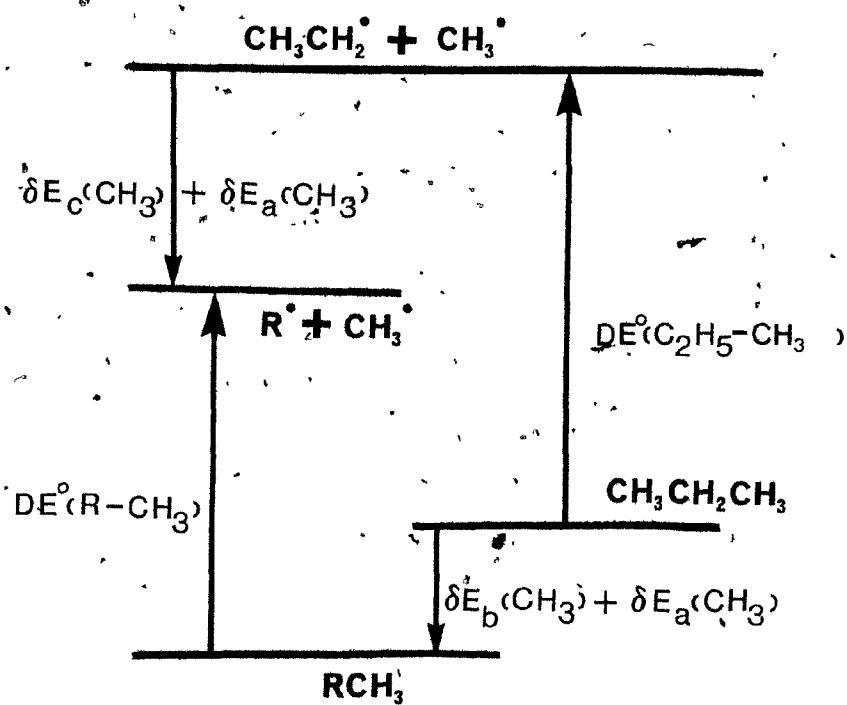
where X is a fixed group (alkyl group or hydrogen) for the series of R groups considered, and $R = C^*(R^1R^2R^3)$.

If all participating species are in the hypothetical vibrationless state at 0 K, the energy change for reaction [80] can be expressed in terms of DE° values :

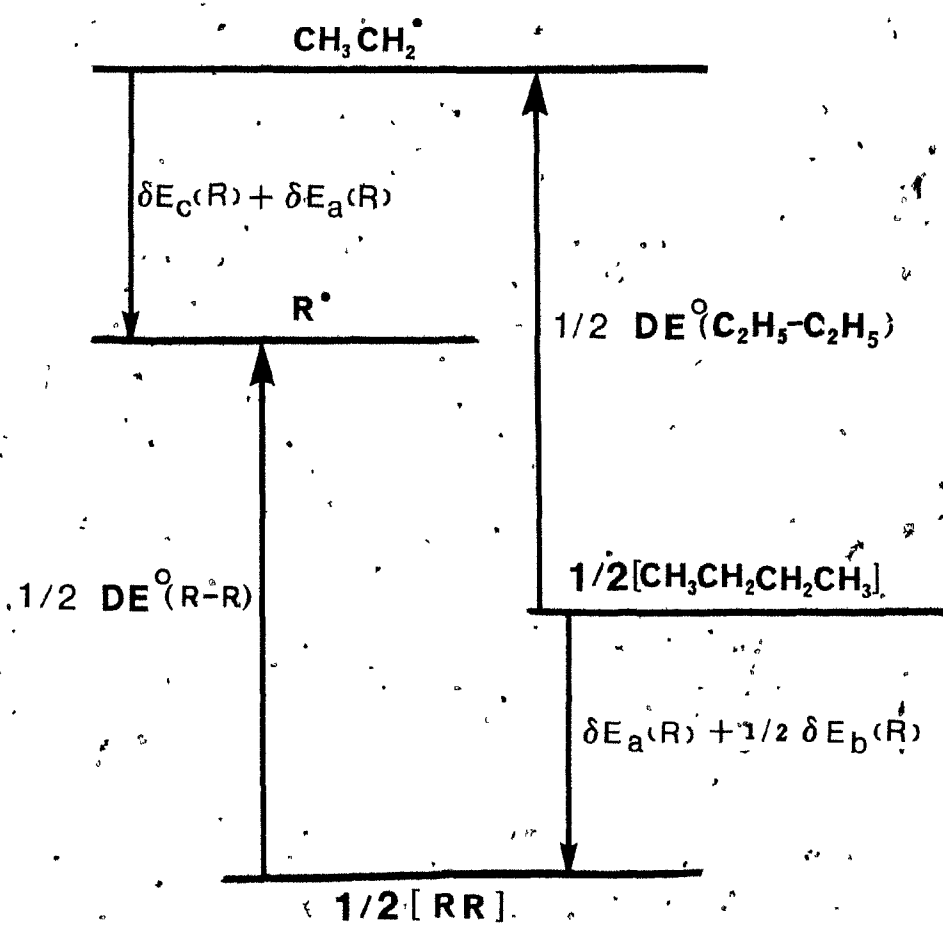
Figure 10. A schematic representation of substituent effects on an open-shell species (CH_3CH_2) and closed shell species $(\text{CH}_3\text{CH}_2\text{X})$, at 0 K, in the hypothetical vibrationless state, where non-bonded interactions have been ignored. (a) $\text{X} = \text{H}$ (b) $\text{X} = \text{CH}_3$ (c) $\text{X} = \text{R}$.

$$\begin{aligned}
 -\delta E_a(\text{X}) &= E^0\{\text{R}(\text{RX})\} - E^0\{\text{C}_2\text{H}_5(\text{C}_2\text{H}_5\text{X})\} \\
 -\delta E_b(\text{X}) &= SE^0(\text{C}^*/\text{X}) \quad (\text{for } \text{X} = \text{H} \text{ and } \text{CH}_3) \\
 &= SE^0(\text{C}^*/\text{C}^*) \quad (\text{for } \text{X} = \text{R}) \\
 -\delta E_c(\text{X}) &= SE^0[\text{R}^*, \text{RX}]
 \end{aligned}$$





(b)



(c)

$$[81a] \quad \Delta E^{\circ}_{80} = DE^{\circ}(R-X) - DE^{\circ}(CH_3CH_2-X)$$

If non-bonded interactions are neglected, from Figure 10(a) and (b) it is clear that, ΔE°_{80} , is given by:

$$[81b] \quad \Delta E^{\circ}_{80} = -\delta E_C(X) - \delta E_A(X) + \delta E_B(X) + \delta E_A(X) \\ = SE^{\circ}[R^{\cdot}, RX] - SE^{\circ}(C^*/X).$$

In eq.[81b], $-\delta E_A(X)$ is the energy of the R component of RX, measured relative to the $C_2H_5^{\cdot}$ component of C_2H_5X . Thus, $-\delta E_C(X)$, is a measure of the stability of the R moiety as a radical with reference to it being a part of RX; (in this thesis the R component of RX is denoted by $R(RX)$) and $SE^{\circ}[R^{\cdot}, RX]$, is referred to as a net stabilization energy because it is measured with reference to $R(RX)$.

Values of $-\delta E_B(X) (= SE^{\circ}(C^*/X))$ are measures of the stabilization energy of the C^*/X interaction in RX relative to that in C_2H_5X . Hence, it is clear that, ΔE°_{80} , depends not only on effects of R^1 , R^2 and R^3 (R^1 , R^2 and R^3 are alkyl groups or hydrogen) on the stability of $R^{\cdot}$ relative to $C_2H_5^{\cdot}$, $SE^{\circ}[R^{\cdot}, RX]$, but also on $SE^{\circ}(C^*/X)$.

Under standard conditions, the enthalpy change for eq. [80], ΔH°_{80} is related to $SE^{\circ}[R^{\cdot}, RX]$ by:

$$[82a] \quad SE^{\circ}[R^{\cdot}, RX] = \Delta H^{\circ}_{80} + SE^{\circ}(C^*/X) \\ + (\Delta E^{\circ}_{nb})_{80} - \Delta(ZPE + H_T - H_O)_{80}$$

Values of $\Delta(ZPE + H_T - H_O)$ for isodesmic reactions

are generally expected to be small. To a first approximation, by neglecting such effects and $(\Delta E^{\circ}_{nb})_{80}$, eq. [82a] simplifies to :

$$[82b] \quad SE^{\circ}[R^{\cdot}, RX] = \Delta H^{\circ}_{80} + SE^{\circ}(C^*/X)$$

For $X=H$ or CH_3 , the neglect of $(\Delta E^{\circ}_{nb})_{80}$ will not lead to any serious error, because $E^{\circ}_{nb}(RX)$ values have been shown to be small (79,93).

Notice that the radical $R^{\cdot}$ and the reference state, $R(RX)$, contain the same number of atoms and approximately the same net charge; hence their total energies or atomization energies will reflect their relative stabilities. However, the structure and charge distribution of the reference states, $R(RX)$ (and hence $SE^{\circ}[R^{\cdot}, RX]$), can vary with the choice of reference state.

To test the magnitude of this variation three types of reference states, $\{R(RX) ; X=H, CH_3 \text{ and } R\}$, have been studied.

Case (i) : $X = H$

Substitution of $X = H$, in eq.[82b] gives eq.[83], where $SE^{\circ}(C^*/H^*)$ is the substituent effect on the intrinsic C^*-H^* bond of RH^* . Equation [83] expresses $SE^{\circ}[R^{\cdot}, RH]$ in terms of known $DH^{\circ}(R-H)$ values and $SE^{\circ}(C^*/H^*)$ which can be calculated using eqs.[79 and 84].

$$[83] \quad SE^{\circ}[R^{\cdot}, RH] = \Delta H^{\circ}_{80}(X=H) + SE^{\circ}(C^*/H^*)$$

$$[84] \quad SE^{\circ}(C^*/H^*) = SE^{\circ}(C^*-(H^*)) + SE^{\circ}(H^*-(C^*))$$

$$= a_{C^*H^*} [\Delta q_{C^*}] + a_{H^*C^*} [\Delta q_{H^*}]$$

In equation [84] $a_{C^*H^*} [\Delta q_{C^*}]$ and $a_{H^*C^*} [\Delta q_{H^*}]$ are the respective contributions to the stabilization of the C^*-H^* bond ($SE^{\circ}(C^*/H^*)$), from changes in the charges (in the units of me) on the C^* and H^* atoms relative to the carbon and hydrogen atoms of ethane. Similar equations can be developed to assess $SE^{\circ}(C^*/H^*)$ values in carbonyl compounds (89), ethers (89), and ethylenes (90).

Case (ii) $X = CH_3$

Substitution of $X = CH_3$ in eq. [82b] gives :

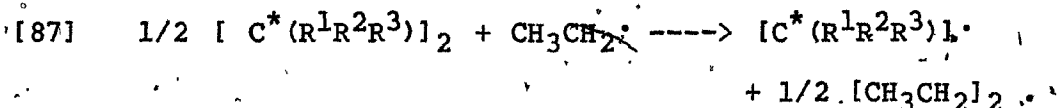
$$[85] \quad SE^{\circ}[R^*, RCH_3] = \Delta H^{\circ}_{80}(X=CH_3) + SE^{\circ}(C^*/CH_3)$$

where $SE^{\circ}(C^*/CH_3)$ is the substituent effect on the interaction between C^* and the whole CH_3 group (eq. [86]). Equation [85] expresses $SE^{\circ}[R^*, RCH_3]$ in terms of known $\Delta H^{\circ}(R-CH_3)$ values and $SE^{\circ}(C^*/CH_3)$ which can be calculated using eq. [86]. In eq. [86], $SE^{\circ}(Y-(Z))$ symbolizes the substituent effect on the stabilization of the Y-Z bond due to changes in the charges on the atom Y. q_Y symbolizes the charge on atom Y relative to that on the same atom (Y) when $R = C_2H_5$. Thus, (C^*/CH_3) involves the interactions in one C-C bond and three C-H bonds.

$$\begin{aligned}
 [86] \quad SE^{\circ}(C^*/CH_3) &= SE^{\circ}\{C^*-(C)\} + SE^{\circ}\{C-(C^*)\} \\
 &\quad + 3SE^{\circ}\{C-(H)\} + 3SE^{\circ}\{H-(C)\} \\
 &= a_{C^*C} [\Delta q_{C^*}] + a_{CC^*} [\Delta q_C] \\
 &\quad + 3a_{CH} [\Delta q_C] + 3a_{HC} [\Delta q_H] \\
 &= a_{CC} [\Delta q_{C^*}] + 3a_{HC} [\Delta q_H] \\
 &\quad (a_{CC} + 3a_{CH}) [\Delta q_C]
 \end{aligned}$$

Case (iii): $X \equiv R$

The need for considering terms such as $SE^{\circ}(C^*/X)$ in eqs. [83 and 85] implies the presence of, and the variation in, charge on X (and hence $R(RX)$). Thus, the choice of reference state in defining radical stability using eqs. [81, 83 and 85] will be biased by this charge effect. Such charge effects can be overcome by choosing the reference state $R(RR)$, where $q_{R(RR)}$ is zero by symmetry. To define $SE^{\circ}[R^{\cdot}, RR]$, let us consider the following isodesmic reaction:



If all participating species are in a hypothetical vibrationless state at 0 K, ΔE°_{87} depends not only on the effects of R^1 , R^2 and R^3 (R^1 , R^2 and R^3 are alkyl groups or hydrogen) on the stability of $R^{\cdot}$ relative to $C_2H_5^{\cdot}$, $SE^{\circ}[R^{\cdot}, RR]$, but also on, $SE^{\circ}(C^*/C^{\cdot})$ (eqs. [88 and

89]), the stabilization of the central C*-C* bond in RR relative to that in CH₃CH₂CH₂CH₃ (i.e. the central C-C bond in n-butane). This is illustrated in Figure 10(c).

$$[88] \quad \Delta E^{\circ}_{87} = 1/2 [DE^{\circ}(R-R) - DE^{\circ}(CH_3CH_2-CH_2CH_3)] \\ = SE^{\circ}[R^{\bullet}, RR] - 1/2 SE^{\circ}(C^*/C^*)$$

In eq.[88] the symbolism adopted (at 0.K) is the same as in eq. [81]. Thus, the descriptions of terms in eq. [81] are also applicable to eq. [88]. The standard enthalpy change for eq. [87], ΔH°_{87} is related to $SE^{\circ}[R^{\bullet}, RR]$ by :

$$[89a] \quad SE^{\circ}[R^{\bullet}, RR] = \Delta H^{\circ}_{87} + 1/2 SE^{\circ}(C^*/C^*) \\ + (\Delta E^{\circ}_{nb})_{87} - \Delta(ZPE + H_T - H_O)_{87}$$

Values of $\Delta(ZPE + H_T - H_O)$ for isodesmic reactions are small and can be neglected in a first approximation, but $(\Delta E^{\circ}_{nb})_{87}$ may not be small (for example when R=t-Bu (85)). However if neglected, it simplifies eq. [89a] to:

$$[89b] \quad SE^{\circ}[R^{\bullet}, RR] = \Delta H^{\circ}_{87} + 1/2 SE^{\circ}(C^*/C^*)$$

Equation [89b] expresses $SE^{\circ}[R^{\bullet}, RR]$ in terms of known $\Delta H^{\circ}(R-R)$ values and $SE^{\circ}(C^*/C^*)$ which can be calculated using eq. [90], where Δq_{C^*} is the charge on the C* atom of RR relative to that in RR(R=C₂H₅).

$$[90] \quad SE^{\circ}(C^*/C^*) = 2 SE^{\circ}\{C^* - (C^*)\}$$

$$\begin{aligned}
 &= 2 a_{CC} [q_C^*(RR) - q_C^*(n-C_4H_{10})] \\
 &= 2 a_{CC} [\Delta q_C^*]
 \end{aligned}$$

2.3.3. Variation of $SE^\circ[R^\cdot, RX]$ with choice of X

The variation in $SE^\circ[R^\cdot, RX]$, for $X=CH_3$ and $X=R$ (with reference to $X=H$), can be represented by:

$$[91a] \quad \delta(SE^\circ[R^\cdot, RX]) = SE^\circ[R^\cdot, RCH_3] - SE^\circ[R^\cdot, RH]$$

$$[91b] \quad \delta'(SE^\circ[R^\cdot, RX]) = SE^\circ[R^\cdot, RR] - SE^\circ[R^\cdot, RH]$$

Substitution of eqs. [83, 85 and 89b] in eq. [91], yields:

$$\begin{aligned}
 [92a] \quad \delta(SE^\circ[R^\cdot, RX]) &= \Delta H^\circ_{80}[(X=CH_3) - (X=H)] \\
 &\quad + SE^\circ(C^*/CH_3) - SE^\circ(C^*/H) \\
 &= \delta'(\Delta H^\circ_{80}) + (SE^\circ(C^*/X))
 \end{aligned}$$

$$\begin{aligned}
 [92b] \quad \delta'(SE^\circ[R^\cdot, RX]) &= \Delta H^\circ_{87} - \Delta H^\circ_{80}(X=H) + \\
 &\quad 1/2 SE^\circ(C^*/C^*) - SE^\circ(C^*/H)
 \end{aligned}$$

In eq. [92] $\Delta(ZPE + H_T - H_O)$ and $\delta(\Delta E^\circ)_{nb}$ terms have been ignored. Although individual, ΔH°_{80} or ΔH°_{87} values have large uncertainties (ca. 8 kJ mol⁻¹), the difference $\delta(\Delta H^\circ_{80})$ values are known more precisely (uncertainty < 1 kJ mol⁻¹) (Table 13). Thus, the differences in the $SE^\circ[R^\cdot, RX]$ values can be calculated using eqs. [92(a) and 92(b)].

While individual $\Delta(ZPE + H_T - H_O)$ values for eqs. [80

and 87], are not readily calculated their differences can usually be obtained (92). Similarly differences in (ΔE_{nb}°) values are generally estimable (79, 93). Using eqs. [81] and 89(a)], the differences in the $SE^{\circ}[R^{\cdot}, RX]$ values can be expressed by:

$$[93a] \quad \delta(SE^{\circ}[R^{\cdot}, RX]) = (\Delta H^{\circ}_{80}) + \delta(SE^{\circ}(C^{\cdot}/X)) \\ - \Delta(ZPE+H_T-H_O)_{80} [(X=CH_3)-(X=H)] \\ + (\Delta E_{nb}^{\circ})_{80} [(X=CH_3)-(X=H)]$$

$$[93b] \quad \delta(SE^{\circ}[R^{\cdot}, RX]) = [\Delta H^{\circ}_{87} - \Delta H^{\circ}_{80}(X=H)] + \\ 1/2 SE^{\circ}(C^{\cdot}/C^{\cdot}) - SE^{\circ}(C^{\cdot}/H) - \\ \Delta(ZPE+H_T-H_O)_{87} + \Delta(ZPE+H_T-H_O)_{80} [X=H] \\ + (\Delta E_{nb}^{\circ})_{87} - (\Delta E_{nb}^{\circ})_{80} [X=H]$$

From Figure 10, it is clear that for any X the total substituent effect on the stability of a radical is a constant. Consequently, by assuming $E_{nb}^{\circ}[R(RX)] = E_{nb}^{\circ}[R(RH)]$ equality [94] can be obtained.

$$[94] \quad \delta E_a(CH_3) + SE^{\circ}[R^{\cdot}, RCH_3] \\ = \delta E_a(H) + SE^{\circ}[R^{\cdot}, RH] \\ = \delta E_a(R) + SE^{\circ}[R^{\cdot}, RR]$$

The differences $\delta[E_a(CH_3)-E_a(H)]$ and $\delta[E_a(R)-E_a(H)]$ can be estimated by considering the charges on the atoms of the $R(RCH_3)$ and $R(RR)$ relative to that in $R(RH)$.

$$\begin{aligned}
 [95a] \quad \delta[E_a(\text{CH}_3) - E_a(\text{H})] &= \delta E_a(\text{CH}_3) - \delta E_a(\text{H}) \\
 &= [E_a(\text{CH}_3) - E_a(\text{H})]_R - \\
 &\quad [E_a(\text{CH}_3) - E_a(\text{H})]_{\text{C}_2\text{H}_5}
 \end{aligned}$$

$$\begin{aligned}
 [95b] \quad \delta[E_a(\text{R}) - E_a(\text{H})] &= [E_a(\text{R}) - E_a(\text{H})]_R - \\
 &\quad [E_a(\text{C}_2\text{H}_5) - E_a(\text{H})]_{\text{C}_2\text{H}_5}
 \end{aligned}$$

$$\begin{aligned}
 [96] \quad -(E_a(\text{X}) - E_a(\text{H}))_R \\
 &= \sum_i [(n_{\text{C}_i} a_{\text{CC}} + n_{\text{H}_i} a_{\text{CH}}) \Delta q_{\text{C}_i}] + \sum_j [a_{\text{HC}} \Delta q_{\text{H}_j}] \\
 &= \sum_i [(n_{\text{C}_i} a_{\text{CC}} + n_{\text{H}_i} a_{\text{CH}} - a_{\text{HC}}) \Delta q_{\text{C}_i}] + \\
 &\quad a_{\text{HC}} [q[\text{R}(\text{RX})] - q[\text{R}(\text{RH})]]
 \end{aligned}$$

In eq. [96] n_{C_i} and n_{H_i} are, the number of carbon and hydrogen atoms attached to C_i ; Δq_{C_i} and Δq_{H_j} are, charges on the i carbon and j hydrogen atom of $\text{R}(\text{RX})$ relative $\text{R}(\text{RH})$.

From eqs. [94-96] an expression for the $\delta(\text{SE}^\circ[\text{R}^\bullet])$ values is obtained:

$$[97a] \quad \delta(\text{SE}^\circ[\text{R}^\bullet, \text{RX}]) = \delta\{E_a(\text{CH}_3) - E_a(\text{H})\}$$

$$[97b] \quad \delta(\text{SE}^\circ[\text{R}^\bullet, \text{RX}]) = \delta\{E_a(\text{R}) - E_a(\text{H})\}$$

2.4. RESULTS AND DISCUSSION

The stabilization energy of a radical must be an invariant quantity. Tables 11 and 12 clearly show, therefore that relative DH° values cannot be directly equated to radical stability. For example, by considering the C-OH bond cleavage it might be concluded that the stabilities of the simple alkyl radicals are in the order, $i\text{-C}_3\text{H}_7^\bullet \approx t\text{-C}_4\text{H}_9^\bullet < \text{C}_2\text{H}_5^\bullet$. This is a complete reversal in the order of stabilities, $\text{C}_2\text{H}_5^\bullet < i\text{-C}_3\text{H}_7^\bullet < t\text{-C}_4\text{H}_9^\bullet$, obtained by considering C-H bond cleavage.

It might be argued that the relatively poor correlation of DH° values (when X is an electronegative atom or group) in Table 11 is due to the uncertainty in some of the data used in the analysis. However, it must be noted that a good correlation in the DH° data is a necessary but not a sufficient criterion to propose that relative DH° (R-X) values are a suitable measure of radical stability.

The differences obtained in Table 12 are independent of the standard enthalpy of formation of any radical species and are equal to the ΔH°_{70} values in Table 13. Most of these values have uncertainties that are smaller than the differences in Table 12 (82). The ambiguities in the order of stabilities inferred from Table 12 are a result of neglecting effects on the parent undissociated molecules of these radicals (see Table 14). Thus, even

when more accurate determinations of DH° values are available they will not change the apparent discrepancies in the values in Table 12 and may not significantly improve the correlation in Table 11.

The poor correlation obtained in the DH° values when X is an electronegative atom is not surprising (Table 11) (94). This is because the polarity of the $C \delta^+ \text{---} X \delta^-$ bond will certainly affect the strength of the other bonds in the molecule. On dissociation of the C-X bond the effects of X on R will be absent. In addition, an X, that had a partial negative charge when attached to R, leaves as a neutral species. Thus, in the radical state the R component will have to accommodate the excess electrons. Furthermore, there will be effects on the C-X bond (and where X contains more than one atom; there will be an effect on the individual bonds in X) from the groups attached to (CX). One of the reasons for the poor correlation in Table 11 and the large ΔH°_{64} values, when X = OH, is possibly because of effects on the O-H bond.

The relatively better correlation, when X = alkyl is probably due to the fact that substituent effects on RX are very similar in nature when X is an alkyl group or a hydrogen atom. However, Table 12 clearly shows that even when X = alkyl the magnitude of relative DH° values change appreciably relative to X = H. Alternatively, it can be suggested that, due to the variation in the relative DH°

values, only $RH^\bullet$ be used to define radical stability.

However, such an a priori choice is unjustified, unless the effects of substituents on the intrinsic R-H bond strengths are known.

Studies by Fliszar and co-workers have shown that charge effects are the dominant factor influencing the stabilities of alkanes (79). From Table 15 it is evident that such effects can be as large as -17 kJ mol^{-1} for the tertiary C-H bond in 2-methyl propane. These effects are a result of the variation in the charges on both atoms (carbon and hydrogen) involved in the bond. In the alkanes studied, except for the primary C-H bond in propane, the variation of charge on hydrogen had a greater effect ($a_{HC} \Delta q_{H^*}$) than the corresponding variation on carbon ($a_{CH} \Delta q_{C^*}$). From Table 15 we see that the C-H bond in methane is 8 kJ mol^{-1} weaker than in ethane. The primary and secondary C-H bonds of propane and the tertiary C-H bond of 2-methyl propane are found to be, respectively, 2.6, 8.0 and 17 kJ mol^{-1} more stable than the C-H bond of ethane.

Charge effects on the total interaction between a methyl group and the carbon atom at the point of attachment for selected alkanes are given in Table 16. These values show that there is a greater contribution from charge variations on the carbon atoms than the hydrogen atoms to the total effect. It is also evident that the C^* atom shows a greater effect in the C/CH_3 system compared to the

Table 15. Charge effects on the relative intrinsic C-H bond strengths in alkanes (RH), $SE^0(C^*/H^*)$.^{a,b,c}

$R-H^*$	$a_{CH} \Delta q_C^*$	$a_{HC} \Delta q_H^*$	$SE^0(C^*/H^*)$ eq. [84]
$C^*H_3-H^*$	1.12	7.00	8.12
$CH_3C^*H_2-H^*$	0 ^d	0 ^d	0 ^d
$CH_3CH_2C^*H_2-H^*$	-1.50	-1.06	-2.56
$C^*H(CH_3)_2-H^*$	-1.67	-6.31	-7.98
$C^*(CH_3)_3-H^*$ ^e	-3.08	-14.04	-17.12

^a All values in kJ mol^{-1}

^b Unless stated otherwise, charges on atoms are obtained from Appendix II of reference 89.

^c Negative (positive) value implies a stabilization and hence a strengthening (weakening) of the bond.

^d Zero by definition.

^e Charges on atoms calculated from Table II ($n = -4.4122$) of reference 88.

Table 16. Charge effects on the relative intrinsic bond strength of the $\text{C}-\text{CH}_3$ bond and $\text{C}-\text{H}$ bonds of the CH_3 group in the alkanes RCH_3 .^{a,b,c}

$\text{R}-\text{H}^*$	$a_{\text{CH}} \Delta q_{\text{C}}^*$	$(a_{\text{CC}} + 3a_{\text{CH}}) \Delta q_{\text{C}}$	$-3a_{\text{HC}} \Delta q_{\text{H}}$	$\text{SE}^0(\text{C}^*/\text{CH}_3)$ eq. [84]
C^*H_3	3.30	7.49	3.17	13.96
$\text{CH}_3\text{C}^*\text{H}_2$	0	0	0	0
$\text{CH}_3\text{CH}_2\text{C}^*\text{H}_2$	-2.45	1.95	-1.98	-2.48
$\text{C}^*\text{H}(\text{CH}_3)_2^{\text{d}}$	-2.79	-6.52	-2.93	-12.24
$\text{C}^*(\text{CH}_3)_3^{\text{d}}$	-3.39	-12.52	-7.52	-23.43

^a All values in kJ mol^{-1}

^b Unless stated otherwise, charges on atoms have been obtained from Appendix II of reference 89.

^c The carbon and hydrogen atoms of the CH_3 group of RCH_3 are indicated by bold type.

^d Charges on atoms calculated from Table II ($n = -4.4122$) of reference 88.

Table 17. The relative net stabilization energies,^a $SE^{\circ}[R^{\bullet}, RX]$, of alkyl radicals ($R^{\bullet}$) in the gas phase.

R	ΔH°_{87} ^b	$1/2 SE^{\circ}(C^{\bullet}/C^{\bullet})$ ^c	$SE^{\circ}[R^{\bullet}, RX]$		
			X = H	X = CH ₃	X = R
CH ₃	17	5.75 ^d	37	32	23
C ₂ H ₅	0	0	0	0	0
n-C ₃ H ₇	0	-2.14 ^{d,e}	-3	-2	-2
i-C ₃ H ₇	-6	-2.84 ^{d,f}	-19	-14	-9
t-C ₄ H ₉	-22	-3.04 ^{d,f}	-38	-32	-25

^a All values in kJ mol⁻¹.

^b Calculated using the standard heats of formation of RR from reference 82 and $R^{\bullet}$ from reference 32.

^c Calculated using charges on carbon from references indicated.

^d Reference 89. Appendix II.

^e Charges for n-hexane estimated using method described in reference 79. ¹³C chemical shifts obtained from D. M. Grant and E. G. Paul, J. Am. Chem. Soc., 86, 2984 (1964).

^f Reference 85, after multiplying by a factor (35.1/69.4) to standardize charges to $q^{\circ}_C(\text{ethane}) = 35.1$ me.

C/H system. This is partly because $a_{CC} > a_{CH}$. The substituent effects observed on the C/CH₃ interaction is in the same order as the C/H interaction, but greater in magnitude. The variation in the relative DH⁰ values observed for the C-CH₃ and C-H cleavages are partly due to differences in SE⁰(C*/CH₃) and SE⁰(C*/H) values. The SE⁰[R[•], RX] values obtained after the appropriate DH⁰ values have been corrected for C/H, C/CH₃ and C/C interactions are given in Table 17.

From Table 17 it is evident that for a given R[•], SE⁰[R[•], RX] varies with the choice of reference state. The uncertainties in the individual SE⁰[R[•], RX] values depend to a large extent on the error in the DH⁰ values used to calculate ΔH⁰₈₀ or ΔH⁰₈₇. Before discussing the relative merits of using the various SE⁰[R[•], RX] values calculated to define radical stability, the reasons for their differences must be given careful consideration. The charge contribution to the energy differences between reference states, is given in Table 18. These values show that for a given R[•] the stability of the reference states are in the order R(RR) > R(RCH₃) > R(RH). This order arises because of the differences in the net charges of the reference states (Table 19).

Table 18. Substituent effects on the stabilization of the $R^\bullet$ component of RX , $R(RX)$, relative to $R(RH)$.

R	$(E_a(X) - E_a(H))^b$		$(E_a(X) - E_a(H))^b$	
	X = R	X = CH_3	X = R	X = CH_3
CH_3	24.4 ^c	24.4 ^c	-13.3	-5.5
C_2H_5	37.7 ^c	29.9 ^c	0	0
n- C_3H_7	37.9 ^d	29.2 ^c	0.2	-0.7
i- C_3H_7	46.4 ^e	33.6 ^{c,f}	8.7	3.7
t- C_4H_9	50.9 ^e	33.7 ^{e,f}	13.2	3.8

^a All values in kJ mol^{-1} .

^b Charges obtained from references indicated.

^c Reference 79, Appendix II.

^d See footnote (e) Table 17.

^e See footnote (f) Table 17.

^f See footnote (b) Table 15.

Table 19. Net charges^{a,b} on the R component (q_R) of RH, RCH₃ and RC₂H₅.

R	q_R (RH)	q_R (RCH ₃)	q_R (RC ₂ H ₅)
CH ₃	9.05	0	-2.66
C ₂ H ₅	11.70	2.66 ^c	0
n-C ₃ H ₇	12.10	3.03	0.40
i-C ₃ H ₇	14.09	5.04	2.40 ^c
t-C ₄ H ₉	17.02 ^d	7.95	5.30 ^c

^a All charges are given in the units me.

^b Unless indicated otherwise charges from reference 89, app II.

^c See footnote (f) Table 17.

^d See footnote (b) Table 15.

Table 20. The variation in the relative net stabilization energies^a of a radical R[•], SE^o[R[•], RX] with reference state^b R(RX).

SE ^o [R [•] , RX] - SE ^o [R [•] , RH]						
R	X = CH ₃			X = R		
	equation			equation		
	[92a] ^c	[93a] ^d	[97a] ^e	[92b] ^f	[93b] ^d	[97b] ^e
CH ₃	-5.1	-2.7	-5.5	-14.1	-12.8	-13.2
C ₂ H ₅	0	0	0	0	0	0
n-C ₃ H ₇	1.6	3.8	-0.7	0.3	3.0	0.2
i-C ₃ H ₇	5.3	5.6	3.7	11.1	10.3	8.7
t-C ₄ H ₉	6.1	4.4	3.8	13.2	11.6	13.3

^a All values in kJ mol⁻¹.

^b R components of RH, RCH₃ and RR.

^c $\delta(\Delta H^o_{80})$ values have been obtained from Table 13.

^d The required (ZPE + H_T - H^o) and E^o_{nb} values have been obtained from references 79, 85, 86 and 92.

^e From Table 18.

^f The difference in ΔH^o values have been obtained using the appropriate heats of formation values from reference 82.

In Table 19, the net charges of the R components RH, RCH₃ and RC₂H₅ are compared. The charges of R(RH) range from 9.05 me [the value for R = methyl] to 17.02 me [R = t-butyl]. The charges of R(RCH₃) and R(RC₂H₅) are of a much smaller magnitude.

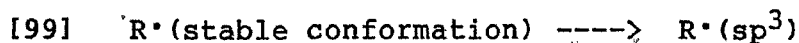
A radical, R[•] is electrically neutral. However, Table 19, shows that q[R(RH)] and q[R(RCH₃)] have non-zero values with the exception of q[CH₃(C₂H₆)]. The closer a reference R component R(RX) is to neutrality, the more suitable it is to be used to define radical stability. This is because if q[R(RX)] is not negligible, then R(RX) and R[•] do not have the same net charge, their energies are not directly comparable. The rationale behind choosing R(RX) to define radical stability, was to use a reference state having the identical arrangement of atoms and same net charge as R[•] and in addition have an inert unpaired electron. All these conditions are met in R(RR), where q[R(RR)] is zero for all R by symmetry. R(RH) and R(RCH₃) have the limitation of having a slight deficiency in the electronic charge. Thus, conceptually the SE⁰[R[•], RR] values are the best parameters that can be used to define radical stability.

It must be noted that these SE⁰ [R[•], RR] values also include stabilization due to change in hybridization (ΔR of eq. [73]). The ΔR term will include stabilization due to changes in one electron, two-electron and non bonded

interactions. It is also interesting to consider to what extent a radical in the hypothetical sp^3 hybridized state can be stabilized. This can be obtained from ;

$$[98] \quad SE^{\circ} [R^{\bullet}(sp^3), RR] = SE^{\circ} [R^{\bullet}, RR] - [\Delta R(R) - \Delta R(C_2H_5)]$$

where ΔR is the energy change for the transformation;



Relative to the ethyl radical in the sp^3 state the following $SE^{\circ}[R^{\bullet}(sp^3), RR]$ values in kJ mol^{-1} are obtained: CH_3 , 21; $i\text{-C}_3\text{H}_7$, -7; $t\text{-C}_4\text{H}_9$, -22. These values indicate that, even in an sp^3 hybridized state, radicals are stabilized. However the origin of this stabilization is not apparent from this study (95, 96).

The dependence of the relative stabilization energies of radicals on the chosen reference state is described by the difference in the $SE^{\circ}[R^{\bullet}, RX]$ values (see Table 20). The advantage of this approach is that these differences in $SE^{\circ}[R^{\bullet}, RX]$ values can be calculated independent of $\Delta_f H^{\circ}$ (radical) values (which may introduce large uncertainties). The differences in the values calculated using eqs. [92] and [93] are due to, respectively, the neglect and inclusion of $(ZPE + H_T - H_O)$ and E_{nb}° terms in the computations. The fair agreement between the two equations suggests that, $SE^{\circ}[R^{\bullet}, RX]$ calculated (eqs. [83],

[85] and [89b]) are reliable. However, the $SE^{\circ}[R^{\bullet}, RR]$ value for $R=i-C_3H_7$ and $t-C_4H_9$ must be used with caution because the required $(ZPE + H_T - H_O)$ and E_{nb}° values are known with less certainty (85). Thus, the $SE^{\circ}[R^{\bullet}, RR]$ values for these R groups may be in error. The close agreement between $\delta(SE^{\circ}[R^{\bullet}, RX])$ (or δ°) values calculated using eqs. [92] and [97] indicate the internal consistency in using linear charge-energy relationships to estimate $SE^{\circ}[R^{\bullet}, RX]$ values.

2.5. CONCLUSIONS

The relationship between radical stability and bond dissociation enthalpies involves several factors that need careful consideration. It is shown that relative DH° values cannot be directly equated to radical stability. The net stabilization energy of a radical $R^{\bullet}$ can be defined relative to the same R group, when present in a closed shell species RX (X is an alkyl group or hydrogen). $R(RR)$ is found to be the most suitable reference state because (like a radical $R^{\bullet}$) it is electrically neutral.

$SE^{\circ}[R^{\bullet}, RX]$ values indicate that the methyl radical is more destabilized and that the n-propyl, iso-propyl and t-butyl radicals are more stabilized, relative to the ethyl radical, than suggested from the corresponding $DH^{\circ}(R-X)$ values. This results from differences in the total C/X interactions (defined independent of any radical species)

of RX as a function of R.

The $SE^{\circ}[R^{\cdot}, RX]$ values obtained in this work do not agree with the SE values reported by Leroy (84). A major reason for these differences is the use of different reference C-C ($E(C-C)$) and C-H ($E(C-H)$) bond energies and the assumption, made by Leroy, of a constant $E(C-C)$ value for all alkanes. This work is based on the intrinsic bond energies obtained by Fliszar and co-workers for ethane: $E(C-C) = 292 \text{ kJ mol}^{-1}$; $E(C-H) = 448.1 \text{ kJ mol}^{-1}$. However, Leroy's work is based on $E(C-C) = 355.8 \text{ kJ mol}^{-1}$, obtained by using an empirical scheme suggested by Laidler (97). The assumption that $E(C-C)$ is constant is an obvious drawback of the Laidler scheme (98). In addition the neglect of charge effects on Fajan's bond energy terms by Leroy can introduce serious error. It is noted that SE values for radicals derived from eq. [74] are also measured relative to closed shell species.

Finally, we have attempted to critically analyse methods of assessing radical stability, in the hope that a clearer understanding of the behaviour of these reactive species will ensue. It is stressed that, with available data a definite separation of radical and charge contributions to the stability of alkyl radicals is not possible.

At present, Fliszar's method of assessing charge effects on bond strengths cannot be extended to the benzenoid systems (99). Hence, the net stabilization energy of benzyl radicals cannot be estimated by the procedures described here for alkyl systems. Alternatively, electron spin resonance hyperfine coupling constants and molecular orbital calculations can be used to assess the importance of unpaired spin interactions in these systems. This will be the topic of the next chapter.

CHAPTER 3. SUBSTITUENT EFFECTS ON THE STABILITY OF BENZYL RADICALS.

3.1. INTRODUCTION

The stability of a radical may be estimated using the total energy, only if a suitable reference state can be defined. In chapter 2 the net stabilization energy, $SE^0[R, R\dot{R}]$, of an open shell species, $R^\cdot$, was defined as a measure of the stability. These SE^0 values are estimates of the stabilization (or destabilization) of a radical, resulting from the bonding interactions of the unpaired electron. However, the data necessary to estimate these values for benzyl radicals is not available. Fortunately, there are alternative approaches for assessing the stabilities of such pi-radicals.

The dominant interaction of the unpaired electron, in a pi-radical, is with the pi-bonds. Such interactions are characterized by the delocalization of the spin throughout the pi-system. The resulting spin density distribution is usually reflected in the electron spin resonance (esr) spectrum of these species. Furthermore, the esr hyperfine coupling constants (hfc's) should be related to the stabilization energy of these radicals. However, a direct relationship between radical stability and esr hfc's will be expected only in systems where the variation in these parameters are governed primarily by changes to the spin density distribution of the molecules.

Dust and Arnold proposed the $\sigma_{\alpha}^{\bullet}$ scale, based on esr hfc's, which reflect the effect of ring substituents on the stability of benzyl radicals (100, 101). This substituent parameter scale is defined by:

$$[100] \quad (\sigma_{\alpha}^{\bullet})_X = 1 - (a\text{-hfc}_X)/(a\text{-hfc}_H)$$

where the alpha-hfc, denoted by a-hfc, is the hfc due to the hydrogens at the benzylic position and the subscript indicates the nature of the substitution. Equation [100] assesses substituent effects on spin delocalization in benzyl radicals (100).

From the relationship, between pi-stabilization energy, based upon partial double bond rotational barriers (102), and the alpha-hfc of the methylene hydrogens for a series of radicals of the general form $ZCH_2^{\bullet}$, where Z is a pi-bonded moiety, it will be shown that these substituent constants reflect substituent effects on the pi-stabilization energy of benzyl radicals.

In this thesis, esr hfc's and rotational barriers (V_2) are used to assess the effects of substituents on the pi-stabilization of benzyl radicals. In the absence of experimentally determined V_2 values, the feasibility of using ab initio calculations to estimate these parameters are examined. Values of $\sigma_{\alpha}^{\bullet}$ and rotational barriers of the CH_2 group in benzyl radicals are related to factors governing the energetics of the delocalization of spin.

Relative V_2 and σ_{∞} values can be regarded as measures of the relative stabilization of these radicals.

In this chapter, it will be shown that the DH° value for the benzylic C-H bond of a toluene is not a true measure of the stability of the corresponding benzyl radical. Also, the difficulties of estimating $SE^{\circ}[R^{\bullet}, RX]$ in benzenoid systems will be discussed.

In closed shell species, a Mulliken population analysis (103) permits an understanding of the charge interactions present in the molecule, albeit, in certain cases this analysis may give unrealistic results (79, 104). However, Mulliken charges can be used in all cases where carbon forms the same number and type of bonds; because, any anticipated error due to an incorrect assignment of overlap populations (e.g. for C-H) cancels in this type of comparison. It will be shown how such an analysis can be useful in rationalizing interaction energies in benzenoid systems. Here, such an approach will be applied to substituted benzyl radicals and toluenes.

In open-shell species, the individual contribution from the alpha- and beta-levels to these charge effects can be obtained. These individual alpha- and beta-charges are essentially estimates of the contribution of alpha- and beta-spins to the total effect. Hence, these charge (or spin) components may be used to make a semi-quantitative analysis of the interactions governing the stability and

reactivity of a radical. Furthermore, a comparison of the σ_{∞} values with these individual charges, should permit an insight into the effects of substituents on spin delocalization.

Also, in this work, the feasibility of using ab initio, single determinant, molecular orbital (MO) calculations adopting the 'unrestricted Hartree-Fock (UHF)' procedure to compute the esr hfc's for benzyl radicals is examined. The UHF spin function used to determine hfc is not an eigen function of the total wave function of the system (26). Consequently, the spin densities computed by the UHF method have not agreed with experiment, because of contamination from higher spin states (105). Nevertheless, since this work involves the comparison of several closely related benzyl radicals, we may expect many of the errors in the UHF method to cancel. Thus, relative hfc, agreeing with experiment, may be computed even though the absolute values are incorrect. The data presented here is a test for such an agreement.

The benzyl radicals studied represent five groups. Substituents were placed at both the meta- and para-positions, and were classified according to their donor-acceptor characteristics in a mono-substituted benzene. Thus any deviations from the behaviour expected according to this classification may be attributed to effects of unpaired spin interactions. The substituents

were chosen only to illustrate the presence of spin related interactions between groups attached to a benzene nucleus and not with a view of establishing an overall picture of such effects (106-108).

The following classification was made:

- (i) H (unsubstituted benzyl radical) representing a sigma-donating and pi-non-interacting group.
- (ii) CH₃, representing a pi- and sigma-donating group.
- (iii) F and OMe, representing pi-donating and sigma-accepting groups.
- (iv) CN, exemplifying pi- and sigma-acceptors.
- (v) Li, representing a pi-accepting and sigma-donating group.

The fluoro group was of special interest because, while the fluoro and methoxy groups are both sigma-accepting and pi-donating, they have behaved differently in benzyl radical systems. For example, esr spectroscopic studies show that fluorine is one of the few para-substituents that increases the spin density at the benzylic position (relative to hydrogen) in benzyl radicals (100). Similar behaviour has been observed for this substituent in the thermal isomerization of 2-aryl-3,3-dimethylmethylenecyclopropane (109). In an attempt to understand the behaviour of a fluoro substituent in greater detail, we have studied the effect of an ortho-fluoro group using esr spectroscopy and ab initio MO theory.

3.2. THE ESTIMATION OF SUBSTITUENT EFFECTS ON THE STABILITY OF BENZYL RADICALS

3.2.1. Relationship between π -stabilization energy and esr hfc's in π -radicals

The interaction energy between the CH_2 group and Z (a π -bonded moiety), $\Delta E^0(\text{CH}_2/\text{Z})$, in a radical of the form $(\text{ZCH}_2)_\text{C}$ or $(\text{ZCH}_2)_\text{P}$, (where the two forms of the radical with the CH_2 group, coplanar with and perpendicular to the π -framework are denoted by subscripts C and P respectively), can be represented by:

$$[101] \quad \Delta E^0(\text{CH}_2/\text{Z})_\text{C} = \text{SE}(\pi\text{-R})_\text{C} + \text{SE}(\sigma\text{-R})_\text{C} + \text{SE}(\text{O})_\text{C}$$

$$[102] \quad \Delta E^0(\text{CH}_2/\text{Z})_\text{P} = \text{SE}(\sigma\text{-R})_\text{P} + \text{SE}(\text{O})_\text{P}$$

where $\pi\text{-R}$ and $\sigma\text{-R}$ are π - and σ -radical stabilizing effects and O stands for all other interactions.

If we assume that, the contribution to the rotational barrier of the methylene group from all effects other than π -stabilization energy of the radical $\text{R}^\bullet$, denoted in this thesis by $\text{SE}(\text{R}^\bullet)$, is independent of Z, from eqs. [101] and [102] we get:

$$[103] \quad \text{SE}(\text{R}^\bullet) = V_2(\text{CH}_2) - V_2^*$$

where, $V_2(\text{CH}_2)$ and V_2^* , are the rotational barriers of the $\text{CH}_2^\bullet$ group of the radical $\text{ZCH}_2^\bullet$, in the presence and absence of spin delocalization (102).

Table 21. Electron spin resonance hyperfine coupling constants of the methylene hydrogens (α -hfc) and π -stabilization energies of π -radicals ($SE(R^\bullet)$).

$R^\bullet$	α -hfc (G)	$SE(R^\bullet)^a$ (kJ mol ⁻¹)
1. Methyl	24.65 ^b	0
2. Acetylmethyl	19.7 ^c	35 ^c
3. Benzyl	16.25 ^d	52 ^e
4. Allyl	14.40 ^f	62 ^f
5. Pentadienyl	10.0 ^g	82 ^h
6. Heptatrienyl	7.55 ^g	<94 ^h
7. $1/2(CH_2--CH_2)^i$	0	146 ^j

^a Unless stated otherwise, SE values were calculated from eq. [103], assuming a V_2^* value of 4 kJ mol⁻¹.

^b For the planar methyl radical (see text). Reference 110.

^c Reference 117.

^d Reference 100.

^e V_2 value assumed to be equal to that of the phenethyl radical and obtained from reference 116.

^f Reference 102.

^g Reference 113.

^h Obtained after correction of value in reference 113, as indicated in the text.

ⁱ A hypothetical radical with a zero $a(H)$ value.

^j π -bond energy from reference 79.

Next, the relationship between SE ($R^\bullet$) and the a -hfc of the methylene hydrogens for a series of radicals of the form ZCH_2 using data in Table 21 is investigated.

The methyl radical, in a planar conformation (110), was taken as a model for a radical with an SE value of zero. The a -hfc for this radical should be equal to the Q value given by the McConnell relationship (111):

$$[110] \quad a\text{-hfc} = Q_a \cdot \rho$$

where ρ is the π -spin density (which is equal to one in this case). Similarly, the algebraic sum of the coupling constants of the allyl radical should also correspond to the Q_a value. It should be noted that the hfc for the methyl radical directly measured from the esr spectrum is not a true measure of Q because of vibrational effects and non-planarity of the radical (110).

The π -bond of ethylene is formed by the interaction of two CH_2 moieties, with unit π -spin density on each of the carbons. Thus, the maximum stabilization resulting from delocalization of an unpaired electron in a π -framework is taken as equal to half the energy of a carbon-carbon π -bond. This should correspond to the SE value of a hypothetical π -radical with a -hfc of zero. Alternatively, the rotational barrier for a methylene group of ethylene could have been used as a measure of SE. However, the close proximity of the unpaired electrons at the transition state

for the isomerization, and the effects of spin multiplicity on the rotational barrier makes this approach less suitable (112).

The SE values for the pentadienyl and hexatrienyl radicals were obtained from reported values for the s-cis - s-trans isomerization energies (E_i) for these radicals (113).

$$[105a] \quad SE(R^\bullet)_P = (E_i)_P + SE(R^\bullet)_A - V^*$$

$$[105b] \quad SE(R^\bullet)_H = (E_i)_H + SE(R^\bullet)_P - V^*$$

where the subscripts, A, P, H are used to denote the allyl, pentadienyl and hexatrienyl radicals respectively and V^* is the E_i value in the absence of spin delocalization. However, the SE values for the polyenyl radicals given in Table 21 differ significantly from those reported by Green and Walton (113). This is primarily because we have used a value of 16 kJ mol^{-1} for V^* , to correct for the intrinsic rotational barrier present in a polyene in the absence of spin delocalization (114).

The SE value for the benzyl radical was assumed to be equal to that of the phenethyl radical, because the hfc for the benzylic and para-hydrogens are approximately equal for these radicals (see chapter 4). Also, ab initio calculations performed at the STO-3G and 4-31G levels ($V_2 = 67 \text{ kJ mol}^{-1}$, Table 22) for the benzyl radicals support this value.

Table 22. Theoretical estimates of the rotational barrier of methylene group ($V_2(\text{CH}_2)$) in the benzyl radical

Method	STO-3G	4-31G// STO-3G ^a	4-31G
$V_2(\text{CH}_2)/\text{kJ mol}^{-1}$	68.1	66.9	66.6

^a Following Pople and co-workers (26) the notation A/B is used to indicate that the energy has been calculated using basis set A at a geometry optimum for basis set B.

The theoretical V_2^* value was obtained as the difference in the energy between the benzyl radical with the benzylic group coplanar with and perpendicular to the ring. All geometrical parameters except those involving the ring were optimized. A standard ring (optimized values for benzene (56)) with hexagonal symmetry was assumed. Comparison of the 3-21G and experimental V_2 values for the allyl radical show that the ab initio value is larger by ca. 10-15 kJ mol^{-1} (115). Thus, the theoretical value for the benzyl radical of ca. 67 kJ mol^{-1} is in good agreement with the assumed barrier of 56 kJ mol^{-1} for this radical (116).

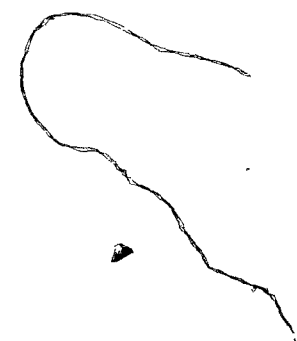
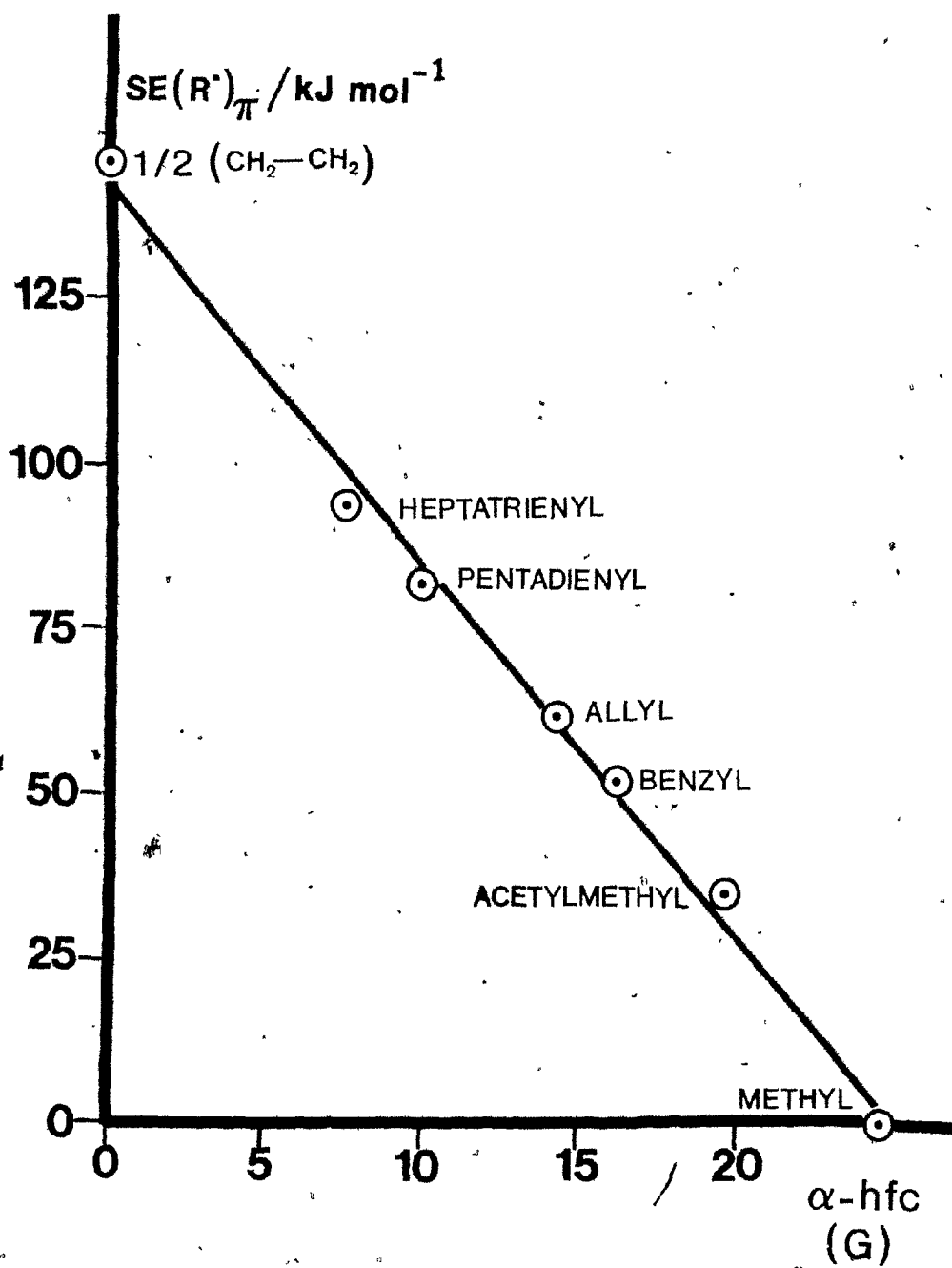


Figure 11. A plot of the π -stabilization energy
($SE(R^\cdot)$) versus the esr hfc of the α -H
of the CH_2 group (a -hfc) in π -radicals of
the form $ZCH_2^\cdot$.



The linear relationship, plotted in Figure 11 is well represented by :

$$[106] \text{ SE (R}\cdot\text{) / kJ mol}^{-1} = 142 \pm 3 - (5.65 \pm 0.21) \text{ } a\text{-hfc / G}$$

which suggests that the $a\text{-hfc}$ of the methylene hydrogens of a π -radical is linearly related to the π -stabilization energy of that species. Consequently, such a relationship should also be valid for a series of ring substituted benzyl radicals.

Green and Walton have alternatively suggested that $\text{SE(R}\cdot\text{)}$ is dependent upon the logarithm of $a\text{-hfc}$. However, the correlation coefficient for the linear plot in Figure 11 is good ($r = 0.997$), significantly better than for the alternative logarithmic relationship ($r = 0.96$). Green and Walton's analysis is heavily biased by the SE values for the pentadienyl and hexadienyl radicals which are too large by the 12 and 24 kJ mol^{-1} , because of the neglect of the intrinsic barrier for the rotation around the carbon-carbon single bond of polyenes. It is significant that acetylmethyl is represented well by eq. [106]. The apparent discrepancy between the SE value for this radical (117) and the bond dissociation enthalpy value (DH°) for acetone (32) is not surprising because, as shown in chapter 2, DH° is not a true measure of radical stability.

3.2.2 Application to benzyl radicals

Application of eq. [103] to benzyl radicals gives:

$$[107] \quad \delta_{SE} (R^\bullet) = \delta V_2 (CH_2)$$

where $\delta_{SE} (R^\bullet)$ is the substituent effect, relative to hydrogen, on the π -stabilization energy of a benzyl radical. Similarly, eqs. [100] and [106] yields:

$$[108] \quad \delta_{SE} (R^\bullet) = K \sigma_\alpha^\bullet$$

where K is a constant. Thus, from eqs. [107] and [108],

$\delta_{SE} (R^\bullet)$ values can be obtained for those substituted benzyl radicals where $\sigma_\alpha^\bullet$ is known. In the absence of experimental rotational barriers, estimates of V_2 using ab initio calculations can be made, where:

$$[109] \quad V_2 = V_2(\text{ab initio}) + \text{BSE.}$$

In eq. [109] BSE represents the basis set error. If we assume that BSE is independent of substituent, substitution of eq.

[109] in eq. [107] yields:

$$[110] \quad \delta_{SE} (R^\bullet) = \delta V_2 (\text{ab initio})$$

Table 23. Relative interaction enthalpies, ΔH°_{111} , for the interaction between X and Y (relative to X and H, and Y and H) for the isodesmic reaction [111] in the gas phase at 300 K.^a

X	Y			
	m-CH ₃	p-CH ₃	m-Z	p-Z
CH ₃	0±0.8	0.7±1.0	1.8±1.3	0.4±1.4 ^b
F	-	1.3±1.9	5.7 ^{c,d}	8.4 ^{c,d}
OCH ₃	-3.3±5.0	-	-	-
CN	-	-	14.2±3.6 ^{d,e,f}	8.6±3.5 ^{d,e,f}
OH	-3.2±1.5	3.8±1.8	3.9±1.9 ^b	5.9±1.3 ^b
NO ₂	-3.8±4.0	-	-	-
I	4.2±7.5	-7.5±7.5	-	-13.4±7.7 ^g
Cl	-	-	-16.5±4.1 ^g	-15.3±3.8 ^g
NH ₂	-	-	7.2±3.7 ^g	-7.2±4.1 ^g

^a All values in kJ mol⁻¹; Unless indicated otherwise interaction energies were calculated using heats of formation of species given in reference 82.

^b Z = C₂H₅.

^c Z = F.

^d Reference 118; uncertainty in the data is not given.

^e Z = CN.

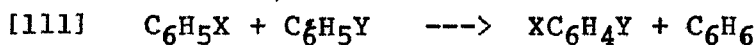
^f Calculated using the heats of formation of the dicyano benzenes from reference 118.

^g Z = COOH.

3.3. CHARGE EFFECTS IN BENZENOID SYSTEMS

The charge-energy relationships were studied with two objectives: first to investigate if charge and energy were linearly correlated; second to show the presence of substituent effects on the strength of the benzylic C-H bond in monosubstituted toluenes.

The interaction energy between two substituents X and Y attached to a benzene ring has been estimated (108) using the isodesmic reaction:



Applying Y=H to reaction [111] it is evident that interaction energies measured using this reaction are only relative to interactions between X (and Y) and the appropriate ring hydrogens.

The proximity of R and X in a molecule of the type RCH_2X and the fact that they are bonded to the same atom is one of the reasons for the large relative interaction energies observed in alkyl systems. However, even in meta- and para-disubstituted benzenes, where the interacting groups are far removed from one another, significant interactions are observed (Table 23). For example, the relative interaction between two cyano groups are 14.2 and 8.6 kJ mol^{-1} , respectively, at the meta- and para-positions (118). These values clearly show significant interactions between two cyano groups and/or between a cyano group and

the hydrogen atom (CN/H) at these positions. The (CN/H) interaction has to be considered because these isodesmic interaction energies are measured relative to X/H and Y/H interactions.

The X/COOH interactions are particularly interesting because the Hammett sigma scale is based on the dissociation of these benzoic acids (119). From Table 23, it is clearly seen that for the benzoic acids, when X = NH₂ and Cl, significant interactions are observed both at the meta- and para-positions (and when X = I at the para-position). These are total group effects; at present no separation into contributions from individual bonds in the COOH group is possible. The importance of such a separation is that it will indicate the presence (or absence) of a substituent effect in the benzoic acids that may not exist in the ionized state.

The interactions are significant even with alkyl groups (X = OH, Z = C₂H₅) and thus can be expected to be general. The significance of these results is that kinetically derived substituent constants reflect interactions in a transition state (or intermediate) relative to a reference state that is also subject to substituent interactions. Undoubtedly, the interactions on the reference state will be smaller than on any ionized state or highly polar transition state; but, may be large enough (not to be disregarded) when effects on non-ionized

open or closed shell states are considered. Thus, ΔE^{σ}_{111} values (rather than Hammett-sigma values) have been used in this work to investigate the relationship between interaction energies and charges on atoms.

Substituent effects on the stability of benzyl radicals have been assessed generally relative to the toluenes (32). Here it will be shown, using ab initio MO calculations at the STO-3G level, that such an approach is unsuitable because of interactions between substituents and the methyl group in toluenes.

In an isodesmic reaction, the formal bond types are conserved on both sides of the equation. This has the advantage that systematic errors inherent in the minimum STO-3G basis set calculations tend to cancel (120). Thus, a fair confidence can be placed in the calculated ΔE^{σ}_{111} values.

3.4. RESULTS

3.4.1. Details of calculations:

Standard single determinant MO theory was used. The ab initio MO calculations described were obtained by the use of the GAUSSIAN 76 program (43) on a Control Data CYBER 170-720 system. The open shell, spin-unrestricted (UHF) procedure was employed (44) to compute the energies of the benzyl radicals with the benzyl group, coplanar with and perpendicular to the benzenoid ring. The closed shell, spin-restricted (RHF) procedure was employed (121) to

compute the energies of the monosubstituted benzenes and toluenes. The minimal STO-3G (46) and the split-valence 4-31G basis sets (48) were used. Partial geometry optimizations, subject to imposed symmetry constraints, were applied. A standard phenyl ring (optimized values for benzene) with hexagonal symmetry was assumed in every case (56). The parameters used were $r_{CC} = 1.38669$ Å, $r_{CH} = 1.08258$ Å (56), for the STO-3G calculations and $r_{CC} = 1.3841$ Å, $r_{CH} = 1.0721$ Å for the 4-31G calculations.

The energy of benzyl radical in the perpendicular form was obtained by using the MO coefficients of the coplanar form as the input for the self consistent field (SCF) procedure. The theoretical rotational barrier of the CH_2 group in a benzyl radical was computed as the difference in the total UHF energies of the coplanar and perpendicular forms of the radical.

3.4.2. Geometries

Substituted benzyl radicals:

Unsubstituted radical: The geometrical parameters of the CH_2 group (r_{CH} , $\angle HCC(\text{ring})$, and r_{CC}) were optimized at the STO-3G and 4-31G levels for both coplanar and perpendicular forms.

Substituted radicals: All geometry optimizations were carried out at the STO-3G level. The r_{CH} of the CH_2 group for, $X=H$, was assumed for all the substituted radicals.

because the optimization of this parameter for the substituents, $X = H$, meta-F, para-F, meta-CN, and para-CN, in the coplanar form of $XC_6H_4CH_2$ affected the total energy by less than 0.03 kJ mol^{-1} . Model CH_3 groups ($r_{CH} = 1.09 \text{ \AA}$ and $\angle HCH = 109.47^\circ$) were used for the methyl and methoxy substituents. For the methoxy radicals the orientation of the OMe group with the C-O bond perpendicular to the benzenoid ring was found to be more stable than when it was coplanar with the ring.

Except in the cases mentioned above all other geometrical parameters of the substituent and the CH_2 group were optimized at the STO-3G level.

Substituted toluenes and benzenes:

Model CH_3 groups ($r_{CH} = 1.09 \text{ \AA}$ and $\angle HCH = 109.47^\circ$) were used for the methyl and methoxy substituents. For the methoxy radicals the orientation of the OMe group with the C-O bond coplanar with the benzenoid ring was assumed.

Except in the cases mentioned above all other geometrical parameters of the substituent and the CH_3 group ($r_{cc(\text{ring})}$) were optimized at the STO-3G level.

Table 24. The total UHF energies of substituted benzyl radicals at the STO-3G level (E_{UHF}).

Substituent	$E_{\text{UHF}} / \text{au}$	
	coplanar	perpendicular
H	265.87735	265.85140
3-Li	272.58456	272.55891
4-Li	272.58466	272.55877
3-Me	304.46068	304.43473
4-Me	304.46064	304.43469
3-CN	356.43598	356.40994
4-CN	356.43646	356.40997
2-F	363.33550	363.30978
3-F	363.33581	363.31002
4-F	363.33574	363.30990
3-OMe	378.29038	378.26468
4-OMe	378.29031	378.26452

3.5. DISCUSSION

3.5.1. The stability of benzyl radicals

Figure 11 and eq. [106] show that SE ($R^\bullet$) can be estimated for radicals of the form $ZCH_2^\bullet$, where Z is a π -bonded moiety, using esr hfc's of the methylene hydrogens. This is useful because hfc's are known for many radicals and can be measured conveniently in most cases.

A reduction of the a-hfc of a benzyl radical by 1.0 G, corresponds to an increase in stabilization of ca. 6 kJ mol⁻¹; or, one $\sigma_\alpha^\bullet$ unit is equivalent to 92 kJ mol⁻¹. The range of known $\sigma_\alpha^\bullet$ values (100), from para-thiomethyl (0.063) to meta-cyano (-0.026) represents a variation in benzyl radical stability of 8 kJ mol⁻¹.

This analysis now allows a more quantitative evaluation of the significance of $\rho(\sigma_\alpha^\bullet)$ values. For example, the $\rho(\sigma_\alpha^\bullet)$ calculated (100) for the thermal isomerization of 2-aryl-3,3-dimethylmethylenecyclopropane (109) indicates that about half of the total possible π -stabilization energy is utilized at the transition state. This, of course, assumes that the entropy of the reaction is unaffected by substitution.

Table 25. Substituent effects on rotational barriers and π stabilization energies of benzyl radicals.^a

Substituent	V_2 (<i>ab initio</i>)	$\delta_{SE} (R^\bullet)^b$		Δ^c
		ESR	RB	
H	68.1	0	0	0
3-Li	67.4	-	-0.7	-
4-Li	68.0	-	0.1	-
3-Me	68.1	0.2	0.0	0.2
4-Me	68.3	1.4	0.2	1.2
3-CN	68.4	-2.4	0.3	-2.7
4-CN	69.5	3.7	1.4	2.3
2-F	67.5	-0.7	-0.6	-0.1
3-F	67.7	-0.8	-0.4	-0.4
4-F	67.8	-1.0	-0.3	-0.7
3-OMe	67.5	-0.1	-0.6	0.5
4-OMe	67.7	1.7	-0.4	2.1

^a All values in kJ mol^{-1} .

^b A positive value indicates a stabilizing effect.

^c Difference in the $\delta_{SE}(R^\bullet)$ values calculated from eqs. [108] and [110].

Table 26. Fermi-Contact hyperfine splitting^a in the carbon atoms of the benzyl radical.

Position	Fermi-contact term conformation	
	Coplanar	Perpendicular
benzylic-	0.232	0.286
<u>ipso</u> -	-0.193	-0.220
<u>ortho</u> -	0.179	0.196
<u>meta</u> -	-0.174	-0.165
<u>para</u> -	0.175	0.166

^aUsing UHF, STO-3G calculations.

In Table 25 substituent effects on rotational barriers of benzyl radicals, using STO-3G calculations, are listed. The perpendicular form is not expected to show any pi-stabilization and should act as essentially a localized radical. Hence, strong pi-spin delocalizing substituents should stabilize (relative to hydrogen) the coplanar form and show positive δV_2 and $\sigma_{\infty}^{\bullet}$ values. Similarly, substituents that destabilize (relative to hydrogen) the coplanar form should have negative δV_2 and $\sigma_{\infty}^{\bullet}$ values.

Table 25 shows that the order in the $\delta SE (R^{\bullet})$ values obtained from esr hfc's and from calculated rotational barriers is different. Also, the V_2 method (eq. [110]) shows smaller stabilization energies for most substituents, although the difference (Δ) between the values calculated by the two methods is $< 3 \text{ kJ mol}^{-1}$ for all substituents. It is useful, however, to examine other causes for the small variation in V_2 values obtained by the MO method.

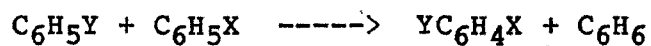
Fermi-contact analysis of the benzyl radical, given in Table 26, indicates extensive spin delocalization in the perpendicular form; this was observed in all cases. This is undoubtedly an artifact of the method, because such an extent of spin delocalization into the ring cannot be solely caused by effects of spin polarization (122). Above all, if such delocalization is possible in the perpendicular form, relative V_2 values will be smaller than the relative pi-stabilization energies of these radicals.

Table 27. Substituent effects on isodesmic interaction energies (ΔE) in benzyl radicals and toluenes.

Substituent (X)	$\Delta E^{a,b,c}$			δDE^o ^d
	Y=CH ₂ [•]		Y=CH ₃	
	benzyl radical coplanar	benzyl radical perpendicular	Toluene	
H	0	0	0	0
3-Li	8.4	7.7	1.0	7.4
4-Li	8.2	8.1	1.2	6.9
3-Me	0.9	0.8	-0.1	1.1
4-Me	1.0	1.1	0.5	0.3
3-CN	-15.0	-14.8	-5.1	-9.9
4-CN	-16.3	-14.9	-6.2	-10.1
2-F	4.0	3.4	-	
3-F	3.2	2.8	-1.0	4.2
4-F	3.4	3.1	0.5	2.9
3-OMe	5.8	5.2	-0.9	6.7
4-OMe	6.0	5.6	1.3	4.7

^aAll values in kJ mol⁻¹.

^b ΔE values for the isodesmic reaction:



where x = substituent and Y = fixed group.

^cNegative (positive) value indicates a stabilizing (destabilizing) interaction.

^dRelative bond dissociation energies.

Table 28. Total STO-3G energies ($E_{\text{RHF}}(\text{au})$) of monosubstituted benzenes and toluenes.

Substituent	- E_{RHF}		

	Toluene		
	Benzene	meta-	para-
H	227.89136	266.47503	
Li	234.60178	273.18506	273.18499
Me	266.47503 ^{a,b} 266.47503 ^{b,c}	305.05875 ^b	305.05849 ^b
CN	318.44427	357.02832	357.02873
F	325.35104	363.93508	363.93452
OMe	340.30661 ^{b,d}	378.89063 ^{b,d}	378.88979 ^{b,d}

^a One of the C-H bonds in the methyl group is assumed to be coplanar with the benzenoid ring.

^b A model methyl group ($r_{\text{CH}} = 1.09 \text{ \AA}$ and $\angle \text{HCH} = 109.47^\circ$) was used.

^c One of the C-H bonds in the methyl group is assumed to be perpendicular to the benzenoid ring.

^d The O-C bond in the OCH_3 group is assumed to be coplanar with the benzenoid ring.

The inability of the UHF procedure to describe the spin distribution in the perpendicular form limits the use of the ab initio method to assess SE (R[•]). However, other useful thermochemical parameters can be obtained using the energy of the coplanar form. For example, the isodesmic interaction energy between a substituent and the CH₂ group or bond dissociation energies may be computed. Although these energy parameters do not measure radical stability they do assess the magnitude of the energy of interaction in radicals relative to that in closed shell species (Table 27 and 28). These energy values may also provide a check on the reliability of the calculations by comparison with experiment. Unfortunately, very few experimental values are available for comparison (24, 32).

3.5.2. Charge effects in toluenes

In Tables 29-31, the feasibility of using ab initio MO calculations, at a minimum STO-3G level, to study charge-energy relationships in benzenoid systems is investigated.

The Mulliken charges given in Tables 29 and 30, show that the donation (or withdrawal) of sigma-or pi-charges by a substituent to (or from) the ring is changed only slightly in the toluenes compared to the benzenes. Thus, the charge contributions of X to the stability of the toluene relative to the benzene will depend on the different sensitivities of the methyl group and the

Table 29. Mulliken group charges in mono-substituted benzenes.

Substituent	$10^3 q_{\sigma}(\text{m-H})^a$	$10^3 q_{\sigma}(\text{p-H})^a$	$10^3 q_{\sigma}(\text{X})^b$	$10^3 q_{\pi}(\text{X})^b$
H	-62.9	-62.9	-62.9	0
Li	-48.3	-50.2	-282.7	100.8
Me	-62.0	-60.9	-6.9	-7.7
CN	-73.1	-73.4	105.7	21.1
F	-68.6	-64.3	203.2	-69.6
OMe	-65.5	-60.4	178.3	-87.7

^a. Values of q_{σ} denote the total sigma-charge donated (withdrawn) by a ring hydrogen to (from) the ring. Negative (positive) q values indicate a donation (withdrawal).

^b $q_{\sigma}(\text{X})$ and $q_{\pi}(\text{X})$ are the total sigma- and pi-charges, respectively, donated (withdrawn) by a substituent, X, to (from) the ring.

Table 30. Total sigma- and pi-Mulliken group charges in mono-substituted toluenes.^a

Substituent	$10^3 q_\sigma(Y)$	$10^3 q_\sigma(X)$	$10^3 q_\pi(Y)$	$10^3 q_\pi(X)$
3-H	-6.9	-62.0	-7.7	0
4-H	-6.9	-60.9	-7.7	0
3-Li	11.2	-280.5	-6.2	100.4
4-Li	8.3	-279.7	-6.1	105.2
3-Me	-5.7	-5.7	-7.7	-7.7
4-Me	-4.6	-4.6	-7.2	-7.2
3-CN	-19.6	107.3	-8.6	21.0
4-CN	-19.7	107.5	-9.8	23.3
3-F	-13.7	204.4	-8.5	-70.0
4-F	-8.9	203.6	-7.3	-68.0
3-OMe	_b	_b	_b	_b
4-OMe	_b	_b	_b	_b

^a $q_\sigma(Y)$, $q_\sigma(X)$, $q_\pi(Y)$, and $q_\pi(X)$ are the total sigma- and pi-charges respectively donated (withdrawn) by a substituent, Y or X to (from) the ring; Y = CH₃ and X = meta- or para-substituent. Negative (positive) q values indicate a donation (withdrawal).

^b Values not calculable since neither substituent is coplanar with the ring.

hydrogen atom to the charge effects of X. If the stabilizing effects of X was independent of Y (including H atoms) ΔE^0_{111} would be zero. However, Table 27 shows significant interactions between substituents and the meta- and para-methyl groups (and/or hydrogen atoms). In Table 31 the importance of charge effects in these interactions is investigated.

In an extensive and incisive study of substituent interactions in substituted benzenes, Pross and Radom (108) outlined factors governing the stability of disubstituted benzenes, and reached qualitative conclusions about sigma- and pi-interactions. Their study indicated that the dominant sigma-effects were the lowering (or raising) of the energy levels of the ring orbitals by a deshielding (or shielding) process caused by sigma-acceptors (or donors). It was also found that sigma-effects cause changes to π^* -energy levels and hence affect pi-charges. The pi-effects (especially in the para-position) were found to be dominated by resonance type interactions. In this study the relationship between interaction energies and sigma- and pi-charges is investigated on a quantitative basis. Results in Table 31 support the above conclusions reached in the study by Pross and Radom (108).

Table 31. The relationship between isodesmic interaction energies (ΔE_{111}^0) and Mulliken group charges (q). A linear regression analysis of ΔE_{111}^0 vs. q_σ and q_π values of meta- and para-substituted toluenes.^{a,b}

Correlation coefficients(r), and regression coefficients (K and C) for eq. [112]		
Type of substituent (n) ^c	K_1, K_2 (r, C_{12}) ^d	K_1, K_2, K_3 (r, C_{123}) ^e
<u>meta</u> - (5)	281, -31 (0.96, 1.18)	175, -46, -11 (0.999, 0.50)
<u>para</u> - (5)	361, -33 (0.98, 1.86)	290, -47, -8 (1.00, 1.51)
<u>meta</u> - and <u>para</u> - (10)	318, -32 (0.97, 1.51)	236, -47, -9, (0.984, 1.05)

^a q_σ and q_π values from Table 30. $q_1 = q_\sigma$ (Y); $q_2 = q_\pi$ (X); $q_3 = q_\sigma$ (X).

^b [112] ΔE_{111}^0 (Y=CH₃) = $\sum_i K_i q_i + C_{jk}$ (or C_{jkl})

where $i = j, k$ (or j, k and l).

^c Number of data points.

^d Equation [112]: $i = 1, 2$.

^e Equation [112]: $i = 1, 2, 3$.

Table 32. Total sigma- and pi-Mulliken group charges^a in mono-substituted benzyl radicals.

Substituent	$10^3 q_{\sigma}^{\text{Y}}$	$10^3 q_{\sigma}^{\text{X}}$	$10^3 q_{\pi}^{\text{Y}}$	$10^3 q_{\pi}^{\text{X}}$
3-H	-2.4	-61.1	-1.3	0
4-H	-2.4	-61.1	-1.3	0
3-Li	9.7	-250.1	6.9	81.5
4-Li	6.6	-250.6	6.7	83.4
3-Me	-1.5	-3.5	-0.5	-6.1
4-Me	-1.7	-3.5	0.1	-6.0
3-CN	-9.8	96.2	-7.1	13.9
4-CN	-8.2	95.9	-7.5	14.2
2-F	-12.6	202.0	-3.6	-65.9
3-F	-6.9	202.4	-3.5	-65.5
4-F	-5.1	202.5	-1.9	-65.9
3-OMe	-5.4	178.7	-2.4	-79.4
4-OMe	-3.1	178.9	0.1	-80.1

^a q_{σ}^{Y} , q_{σ}^{X} , q_{π}^{Y} , and q_{π}^{X} are the total sigma- and pi-charges respectively donated (withdrawn) by a substituent, Y or X to (from) the ring; Y = CH₂ and X = meta-or para-substituent. Negative (positive) q values indicate a donation (withdrawal).

Table 33. Total sigma- and pi-Mulliken group alpha-charges^a in mono-substituted benzyl radicals.

Substituent	<u>alpha</u> -charges			
	$10^3 q_{\sigma}(Y)$	$10^3 q_{\sigma}(X)$	$10^3 q_{\pi}(Y)$	$10^3 q_{\pi}(X)$
3-H	54.7	-1.9	-72.4	0
4-H	54.7	-60.1	-72.4	0
3-Me	55.1	26.1	-72.0	-9.1
4-Me	55.0	-30.5	-71.8	3.4
3-CN	51.1	103.6	-75.7	-27.1
4-CN	51.9	-8.4	-76.6	42.7
2-F	49.3	78.6	-74.0	-11.9
3-F	52.4	121.1	-73.3	-52.4
4-F	53.3	80.5	-72.7	-12.3
3-OMe	53.1	108.6	-72.3	-63.4
4-OMe	54.3	69.4	-71.4	-15.0

^a $q_{\sigma}(Y)$, $q_{\sigma}(X)$, $q_{\pi}(Y)$, and $q_{\pi}(X)$ are the total sigma- and pi-alpha-charges respectively donated (withdrawn) by a substituent, Y or X to (from) the ring; Y = CH₂ and X = meta- or para- substituent. Negative (positive) q values indicate a donation (withdrawal).

Table 34. Total sigma- and pi-Mulliken group beta-charges^a in mono-substituted benzyl radicals.

Substituent	<u>beta</u> -charges			
	$10^3 q_{\sigma}(Y)$	$10^3 q_{\sigma}(X)$	$10^3 q_{\pi}(Y)$	$10^3 q_{\pi}(X)$
3-H	-57.1	-59.2	71.1	0
4-H	-57.1	-0.9	71.1	0
3-Me	-56.6	-29.6	71.5	3.1
4-Me	-56.7	26.9	71.8	-9.4
3-CN	-60.9	-7.4	68.6	40.9
4-CN	-60.1	103.9	69.1	-28.4
2-F	-61.9	123.4	70.4	-54.1
3-F	-59.3	81.3	69.7	-13.1
4-F	-58.4	122.0	70.7	-53.6
3-OMe	-58.5	70.1	70.2	-16.0
4-OMe	-57.3	109.4	72.0	-65.2

^a $q_{\sigma}(Y)$, $q_{\sigma}(X)$, $q_{\pi}(Y)$, and $q_{\pi}(X)$ are the total sigma- and pi-beta-charges respectively donated (withdrawn) by a substituent, Y or X to (from) the ring; Y = CH₂ and X = meta-or para-substituent. Negative (positive) q values indicate a donation (withdrawal).

It is clear from Table 31, that a linear Mulliken charge-energy relationship has been established for both meta- and para-substituted toluenes. Thus, the Mulliken population analysis is a useful approach to assess and rationalize substituent effects in benzenoid systems. However, we have studied the effects of substituents on the whole methyl group and not on individual bonds. Hence, this method cannot be used to correct DH° values to yield $SE^\circ[R^\cdot, RX]$ values of benzyl radicals. Nevertheless, Mulliken group charges in benzyl radicals can provide useful information about interactions in these systems.

3.5.3. Charge and spin interactions in benzyl radicals

Table 32 lists sigma- and pi-charges donated by the substituent and the CH_2 group of benzyl radicals in the coplanar form. These charge effects should account for charge related interactions between a substituent and the fixed group (methyl or benzyl). In Table 27 we have shown that the interaction energy between the groups X and CH_3 for a series of substituted toluenes of the form $XC_6H_4CH_3$ is related to the sigma- and pi-charges donated (or withdrawn) from the ring by X and Y. However, such charge effects will not reflect interactions resulting from spin redistribution. For example, the group charges for the benzyl radicals (Table 32) are smaller than those observed for the corresponding toluenes (Table 30). However, the

isodesmic interaction energies are generally larger in the benzyl radicals (Table 27), because of spin related effects not included in the charge analysis in Table 32.

Table 32 shows that the net charge effect for all substituents are similar to that observed in closed shell systems (see introduction). For example, the net charge effect of both meta- and para-cyano substituents is strongly pi- and sigma-accepting although their ability to delocalize spin from the benzylic position is very different in nature (100). This is true for all the substituents considered. A better understanding of the effects of spin delocalization in benzyl radicals is obtained by separating the total charge effects into the individual contributions of the alpha- and beta-levels.

Table 33 shows the effects of substituents on interactions involving alpha-charges. These charges are estimates of the donation (or withdrawal) of alpha-spin by a group attached to the benzenoid ring. The benzylic group is shown to be a strong pi-alpha-spin donor and sigma-alpha-spin acceptor. Thus, substituents that are strong pi-alpha-spin acceptors and sigma-alpha-spin donors should favourably interact with the benzyl group and stabilize the radical in the alpha-level. Differences between the behaviour of meta- and para-cyano substituents are evident from Table 33. However, para-methoxy, with a positive value (100), shows destabilizing interactions in the alpha-

level. Thus, both alpha- and beta-levels must be considered to gain a complete understanding of unpaired spin interactions in benzyl radicals.

Table 33 shows the effects of substituents on interactions involving beta-charges. The benzylic group is shown to be a strong pi-beta-spin acceptor and sigma-beta-spin donor. Thus, substituents that are strong pi-beta-spin donors and sigma-beta-spin acceptors should favourably interact with the benzyl group and stabilize the radical in the beta-level. The reasons for the spin delocalizing power of the para-methoxy group is now evident.

The effects of alpha-substituents of the benzylic group on the spin delocalizing power of ring substituents can be predicted from the charge/spin analysis presented in Tables 32 and 33. For example, side chain substituents that are strong pi-donors (acceptors) will increase (decrease) the pi-alpha-spin donating power and decrease (increase) the pi-beta-spin accepting power of the benzylic group, and thereby, increase (decrease) and decrease (increase) the effectiveness of spin-delocalizing pi-alpha-acceptors and -donors respectively. Such effects, have been observed even when the variation at the benzylic position is substitution by a methyl group(s), as in the phenethyl and cumyl radical systems. These effects have been discussed in terms of merostabilization (123) and captodative stabilization (124).

Next, we compare the Mulliken population analysis for the alpha- and beta-levels with the relevant σ_x values so that the effects of substituents on benzyl radical hyperfine coupling constants can be rationalized.

The Mulliken analysis shows that all substituents are stronger pi-alpha-acceptors (or weaker pi-alpha-donors) at the para position relative to the meta-position. Similarly, in the beta-level the meta-derivatives are the better acceptors. This may be understood in terms of the excess of pi-alpha-spin at the para-carbon and the excess of pi-beta-spin at the meta-carbon. Similar effects are observed in the sigma-framework.

Cyano substituent: This substituent is predicted to delocalize spin strongly in the para-position and localize spin (relative to hydrogen) in the meta-position (100). This is well described by the Mulliken analysis, because, while para-cyano shows stabilizing interactions, meta-cyano displays destabilizing interactions with the benzylic groups at both levels. Also, depending on electron demand (that is the nature of the donor/acceptor power of the benzylic group) the nature of the substituent can vary significantly from the behaviour observed in closed shell systems. Thus, while the cyano substituent is defined as a strong pi-acceptor in terms of the sigma-value, in a benzyl radical it can act as a pi-alpha-donor in the meta-position and a pi-beta-donor in the para-position.

Furthermore, calculated dipole moments of the benzyl radicals, toluenes and benzenes, listed in Tables 35 and 36, show that the nature of the cyano substituent is very different in the benzyl radical system compared with the behaviour in the closed-shell system.

Table 35. Comparison of experimental and theoretical dipole moments (D) of mono-substituted benzenes.

Substituent	STO-3G	Experimental ^a	
		gas phase	solution
Li	4.99	-	-
Me	0.25	0.37	0.37
CN	3.65	4.35	4.05
F	1.02	1.61	1.47
OMe	1.17	1.35	1.28

^a Reference 125.

 Table 36. Comparison of dipole moments (D) in toluenes and
 benzyl radicals.

Substituent	Toluene	benzyl radical	
		coplanar	perpendicular
H	0.25	0.00	0.05
3-Li	-	4.85	4.82
4-Li	-	4.88	4.82
3-Me	0.21	0.18	0.15
4-Me	0.04	0.18	0.13
3-CN	3.85	3.21	3.26
4-CN	4.02	3.25	3.30
2-F	-	1.02	1.02
3-F	1.17	1.10	1.12
4-F	1.27	1.09	1.14
3-OMe	0.97	1.18	1.13
4-OMe	1.22	1.18	1.19

Methoxy substituent: This group delocalizes spin in the para-position (100). Tables 33 and 34 show that the para-methoxy has a positive $\sigma_{\alpha}^{\bullet}$ value because of stabilizing interactions in the beta-level. This substituent shows a similar type of interaction at the meta-position; but, now the stabilizing interactions are weaker and the destabilizing interactions in the alpha-level are much stronger (and probably dominate) to make this radical slightly destabilized relative to the unsubstituted benzyl radical (100). All pi-effects due to a lone pair of electrons involve rehybridization of the electronegative atom and consequently will be susceptible to effects due to sigma-interactions. In fact, in comparison to the cyano substituent, the methoxy derivatives show larger sigma-effects. Also, the most stable orientation of the methoxy group is with its C-O bond perpendicular to the benzenoid ring. Thus, C-O type hyperconjugative spin delocalization is possible. It is clear that the effect of this substituent, although regarded simply as a two centre - three electron interaction, is actually the net result of both sigma- and pi- effects at the alpha- and beta-levels.

Fluoro substituent: This is one of the few substituents that is predicted, from esr hfc's to show destabilizing interactions at all positions (Table 37). The population analysis suggests that this is because the destabilizing interaction in the alpha-level more than compensates for the stabilizing effects in the beta-level. Although both fluoro and methoxy act as pi-donors in closed shell species their behaviour in the benzyl radical system is very different. The data in Tables 33 and 34 suggest that this results from weaker pi- and stronger sigma-effects in the fluoro radicals. Also, the charge/spin analysis predicts that the behaviour of this substituent should be similar at the para- and ortho-positions, as observed in their esr spectra.

Methyl substituent: The $\sigma_{\alpha}^{\bullet}$ value is positive for this group at both the para- and meta-positions; although, at the meta-position the value is close to zero (0.002 ± 0.003). The Mulliken analysis correctly predicts that the methyl group will delocalize spin strongly at the para-position, but the meta-methyl group is shown as destabilizing at all levels. However, meta-methyl is a weaker sigma-beta-donor than meta-hydrogen. Thus, the sigma-beta-interaction in meta-methyl will be stabilizing relative to the benzyl radical; this may account for the mild stabilizing power of this substituent. The magnitude of the pi-charge effects of this substituent are relatively

small, and hence may change in sign on small perturbations. Furthermore, the assumption of equal partitioning, intrinsic to the Mulliken scheme, may cause incorrect assignments of charges to be made in this case.

Tables 33 and 34 show that, in general, para-substituents can delocalize spin through the pi-framework better than their meta counterparts. Thus, in the absence of sigma-effects, a substituent will have a more positive value at the para-position.

Substituent effects on the esr hfc's of the benzyl radicals could not be assessed from the STO-3G (UHF) calculations, because the computed hfc's were very sensitive to the geometry of the molecule. For example, variation in the benzylic C-C bond by 0.001 Å, which corresponded to a change of less than 10^{-6} au in energy, resulted in large changes in the hfc's. Thus, a consistent set of values could not be extracted from the calculations.

Table 37. Electron spin resonance hyperfine coupling constants (hfc) and $\sigma_{\alpha}^{\bullet}$ values of fluorobenzyl radicals.

Position	hfca,b		
	Type a derivative		
	ortho-Fc	meta-Fd	para-Fd
ortho-(i)	5.28	5.15	5.30
(ii)	8.18e	4.95	5.30
meta-(i)	1.75	1.80	1.75
(ii)	1.70	4.72e	1.75
para-	6.32	6.19	14.43e
benzylic (i)	16.42	16.39	16.42
(ii)	16.32	16.39	16.42
valuef	-0.007g	-0.009d	-0.010d

a Unless stated otherwise hfc's are due to hydrogen and are in G.

b Uncertainty in hfc's ca. ± 0.03 G.

c This work. Determined by the procedure described in reference 100.

d Reference 100.

e 19F.

f Uncertainty ca. ± 0.003 .

g Calculated from eq. [100] using the average of the two benzylic hfc's.

3.6. CONCLUSIONS

This study has shown that esr hfc values of π -radicals can be used to predict the stability of these species, and that the $\sigma_{\alpha}^{\bullet}$ scale is a suitable measure of substituent effects on benzyl radical stability. As a result, $\sigma_{\alpha}^{\bullet}$ values can be considered as pseudo thermochemical parameters which can be used to predict substituent effects on the π -stabilization of benzyl radicals.

The STO-3G (UHF) method is found to be unsuitable in assessing substituent effects on the rotational barrier and the esr hfc of the benzylic group. However, other useful parameters, such as isodesmic interaction energies and bond dissociation energies, can be derived from these calculations.

Mulliken charges at the α - and β -levels are found to provide valuable information about factors governing the effects of substituents on spin delocalization in benzyl radicals. These effects can be rationalized by considering four types of unpaired spin interactions involving σ - and π -spins in the α - and β -levels.

The present work shows that ab initio MO calculations, even at the minimum STO-3G level, can provide a quantitative analysis of interactions in benzenoid systems.. Relative interaction energies between a substituent and the methyl group in meta- and para- substituted toluenes are found to be linearly related to Mulliken sigma- and pi-charges. Further work needs to be done to determine if these linear relationships are generally applicable. It is hoped that the present approach of analysing isodesmic interaction energies in terms of sigma and pi charges will stimulate further work in this area.

CHAPTER 4 SUBSTITUENT EFFECTS ON BENZYL RADICAL HYPERFINE COUPLING CONSTANTS.

4.1. Introduction

The study of substituent effects on radical reactivity and stability is a topic of great interest. Several linear free-energy (σ) scales based upon relative reactivity have been proposed (126). Most of these scales have failed to unambiguously separate radical and polar effects.

Dust and Arnold have suggested that the $\sigma_{\alpha}^{\bullet}$ scale, based upon electron spin resonance (esr) α -hydrogen hyperfine coupling constants (denoted a -hfc) is a true reflection of the nature of the radical and is therefore free from complications caused by steric and polar effects inherent at a transition state (100). The validity and utility of the $\sigma_{\alpha}^{\bullet}$ scale was demonstrated by the satisfactory correlation obtained between $\sigma_{\alpha}^{\bullet}$ and the logarithm of the rate constant for the thermal isomerization of a series of 2-aryl-3,3-dimethylmethylenecyclopropanes studied by Creary (100, 109).

In chapter 3 it was shown that these $\sigma_{\alpha}^{\bullet}$ values represent the substituent effect on the component of energy that may be attributed to spin delocalization in these benzyl radicals. The $\sigma_{\alpha}^{\bullet}$ scale offers major advantages over other $\sigma^{\bullet}$ scales, because the substituent effects are attributable only to effects on the radical and not on

any closed shell species.

In chapter 2 it was shown that the effects of charge on the stability of even relatively non-polar species, like hydrocarbons and hydrocarbon radicals, is not negligible. Consequently, the other $\sigma^{\bullet}$ scales, which have ignored effects on neutral closed shell species, cannot be used as an indication of radical stability.

Wayner and Arnold extended the $\sigma_{\alpha}^{\bullet}$ scale to over thirty substituents. They also described in detail the mode of action of sulphur-containing substituents on benzyl radical delocalization. Several para-substituted benzyl radicals of the general form $R(O_n)SC_6H_4CH_2^{\bullet}$ ($n = 0, 1, 2$; $R = Me, Ph, Tol, COMe, OMe$) were studied (101).

In this thesis, these studies of substituent effects on benzyl radical hfc's are extended to the alpha-methylbenzyl (phenethyl) and alpha, alpha-dimethylbenzyl (cumyl) systems.

This study is significant, because it enables the comparison of the substituent effects on the a- and b-hfc's of three closely related series of radicals. Since both a- and b-hfc's depend primarily on spin density they will correlate, if the major effect of substituents is on spin delocalization. Moreover, if such a correlation exists between these two parameters it will add considerable strength to the argument that the $\sigma_{\alpha}^{\bullet}$ scale is primarily a measure of spin density. It will give

confidence to the $\sigma_{\alpha}^{\bullet}$ values that have already been established. In addition, if the substituent effect on both a - and b -hfc's are in general the same, specific deviations from a linear correlation between these two parameters may provide valuable information about the factors which influence spin density and hence stabilization of a radical by spin delocalization.

While the overall change in a -hfc's is large ($>10\%$), the small effects ($<0.03G$) caused by some substituents cannot be readily distinguished. It would therefore be useful to have a scale with a larger variation in hfc's as a function of substitution. Studies of carbon based radicals, containing hydrogens both alpha and beta to the radical centre show that b -hfc's are frequently greater than the corresponding a -hfc's (see Table 38).

Consequently, we may find that the phenethyl and cumyl series, where b -hfc's are being measured, will be more sensitive to changes in spin density. On the other hand, the significant decrease in the delocalization of spin into the ring, caused by the alpha-methyl groups, will attenuate the substituent effect. The relative importance of these two opposing factors cannot be predicted a priori.

Table 38. A comparison of the isotropic hyperfine coupling (hfc) constants of the alpha- and beta-hydrogens of hydrocarbon radicals.^a

Radical	hfc(G)	
	alpha-H	beta-H
CH ₃ •	23.07	-
CH ₃ CH ₂ •	22.38	26.87
CH ₃ CH ₂ CH ₂ •	22.08	33.2
(CH ₃) ₂ CH•	22.11	24.68
(CH ₃) ₃ C•	-	22.72
CH ₂ =CHCH ₂ CH ₂ •	22.3	29.7
cyclo-C ₃ H ₅ •	6.51	23.42
cyclo-C ₄ H ₇ •	21.2	36.66
cyclo-C ₅ H ₉ •	21.48	35.16
C ₆ H ₅ CH ₂ •	16.25 ^b	-
C ₆ H ₅ CH•(CH ₃)	16.25 ^b	17.69 ^b
C ₆ H ₅ C•(CH ₃) ₂	-	16.28 ^b
CH ₂ =CH•	13.4	102.4

^aUnless otherwise indicated the hfc's are from Table 8.7 in reference 127.

^b This work.

4.2. RESULTS

The phenethyl and cumyl radicals ($R^\bullet$) were generated photochemically in the microwave cavity of the esr spectrometer, either by hydrogen atom abstraction from the corresponding hydrocarbon (RH) or by bromine atom abstraction from the appropriate bromide (RBr) (100). The esr spectra were recorded with the aid of a signal averager and the hfc's were determined by computer simulation of the spectra.

The data (Tables 39 and 40), represents consistent series, produced under similar conditions, by procedures used previously by Dust and Arnold in their studies of benzyl radicals (100). Best signal to noise ratio was obtained at the lowest temperature possible, above the freezing point of the solution. But, most of the phenethyl radical and cumyl radical spectra were recorded at 213 K and 253 K, respectively, to maintain a consistency in the conditions. The h -hfc of three phenethyl and two cumyl radicals have been reported previously (128); the agreement between our values and those reported is shown in Table 41. In several cases, (*para*-chloro, acetyl, benzoyl, isopropyl, and carbomethoxy), the effect of variation of the spectra as a function of temperature was studied; the hfc's were found to be independent of temperature over the range 213 to 333 K. Details are reported in the Experimental Section.

Table 39. ESR hyperfine coupling constants for para-substituted phenethyl radicals^a.

X	a _α ^b	a _β ^b	a _o ^b	a _m ^b	a _x ^b
1. COMe	15.03	16.65	4.70	1.65	0.30 ^c
2. CPh	15.08	16.69	4.70	1.65	-
3. CN	15.35	16.97	4.88	1.65	0.80 ^d
4. COOMe	15.43	16.96	4.79	1.60	0.30 ^c
5. OCH ₃	15.60 ^e	17.25	4.85 ^f 4.95 ^f	1.50 ^f	0.70 ^{c,f}
6. Et	16.06	17.51	4.72 ^f 5.12 ^f	1.60 ^f	2.95 ^{f,g}
7. H	16.25	17.69	4.95	1.65	5.90
8. OCOMe	16.30	17.78	4.85 5.15	1.70	-
9. F	16.33	17.89	5.00 5.30	1.69	13.46 ^h

^aAll values are in G. Unless indicated otherwise the uncertainty is ± 0.03 G. ^b Subscript indicates position; o = ortho, m = meta, and x = substituent. ^c Hydrogens of methyl. ^d Nitrogen of CN. ^e Uncertainty is ± 0.10 G.

^f Uncertainty is ± 0.06 G. ^g Alpha-hydrogens of ethyl.

^h ¹⁹F.

Table 40. Hyperfine coupling constants for para-substituted cumyl radicals^a.

Substituent	a_{β}^b	a_o^b	a_m^b	a_x^b
1. COCH ₃	15.07	4.55	1.55	<0.50 ^c
2. CPh	15.07	4.52	1.53	-
3. CN	15.37	4.60 ^d	1.60 ^d	0.80 ^{d,e}
4. COOCH ₃	15.40	4.57	1.55	<0.35 ^c
5. SPh	15.60	4.72	1.65	-
6. S(O) ₂ Ph	15.76	4.61	1.55	-
7. Cl	16.03	4.85	1.65	0.36 ^f , 0.30 ^g
8. OCH ₃	16.10	4.75 ^d	1.50 ^d	0.60 ^{c,d}
9. OPh	16.10	4.82	1.62	-
10. CH ₃	16.10	4.70 ^d	1.60 ^d	5.8 ^{c,d}
11. Et	16.13	4.60 ^d	1.60 ^d	2.90 ^{d,h}
12. CF ₃	16.15	4.70	1.58	8.40 ⁱ
13. i-Pr	16.17	4.75	1.55	2.35 ^j
14. t-Bu	16.17	4.75	1.55	-
15. OCOPh	16.24	4.83	1.65	-
16. H	16.28	4.70	1.65	5.55
17. OCOCH ₃	16.30	4.85	1.65	-
18. F	16.35	4.75	1.55	12.65 ^k

^aAll values are in G. Unless indicated otherwise the uncertainty is ± 0.03 G. ^b Subscript indicates position. ^c Hydrogens of methyl. ^d Uncertainty is ± 0.06 G. ^e Nitrogen of CN. ^f ³⁵Cl. ^g ³⁷Cl. ^h α -Hydrogens of ethyl. ⁱ Fluorine of CF₃. ^j α -Hydrogen of isopropyl. ^k ¹⁹F.

Table 41. A comparison of the β -hfc's of phenethyl and cumyl radicals with reported values.^a

Series	Substituent	This work	Literature
Phenethyl:	4-CN	16.97	16.90
	4-OCH ₃	17.25	17.25
	H	17.69	17.70
Cumyl:	4-CH ₃	16.10	16.04, 16.09
	H	16.28	16.30, 16.23,
			16.0b, 15.89b 16.5 ^b

^a Unless specified otherwise hfc's are from reference 128.

All values are in G.

^b Reference 129.

4.3. Discussion

4.3.1. Mechanism of spin delocalization

In general, an α -hfc is believed to arise primarily from a spin-polarization mechanism, while a β -hfc results mostly from a hyperconjugative type of interaction (127, 130-131). Thus, α - and β - hyperfine coupling interactions need not show the same sensitivity to substituent effects. In fact, it has been shown that α - and β -hfc in hydrocarbon radicals are affected differently by, such factors as deviation from planarity (i.e., the state of hybridization of the radical centre, Table 38). β -Hfc values are also known to be very dependent on torsional angle, so, conformation of the singly occupied orbital relative to the β -carbon-hydrogen bond is important (131). However, within a closely related series of substituted benzyl, phenethyl or cumyl radicals, factors other than spin density that could influence hfc, should remain constant. So, if the major function influencing the α - and β -hfc's is spin density they should correlate.

The esr spectra of all the phenethyl and cumyl radicals studied showed a single hfc for all the hydrogens of the α -methyl groups. This indicates that all of the methyl hydrogens are equilibrated, throughout the temperature range (213 to 333 K) used in this work. Thus, the methyl groups must be rapidly rotating so that torsional effects are averaged. Consequently, substituent

effects on h -hfc's of the phenethyl and cumyl radical series, can be expected to be related, primarily, to spin delocalization. Nevertheless, a more detailed discussion of how the difference in the mechanism of spin delocalization to the alpha- and beta-hydrogens may affect the relationship between the corresponding hfc values may be useful.

The a -hfc interactions in planar conjugated hydrocarbon radicals arise from a spin polarization mechanism and the resulting isotropic proton hyperfine coupling (a -hfc) has been shown to be dependent on spin density (111) (See eq. [104]).

The h -hfc's of carbon-based radicals can be represented by the empirical relationship :

$$[113] \quad h\text{-hfc} = A + B \cos^2 \theta.$$

In eq. [113] the value of A represents that part of the hfc that is due to bond polarization; this interaction, through two bonds for a beta-hydrogen, is considerably smaller than the corresponding one-bond interaction for an alpha-hydrogen. (132). In the other term, θ , is the torsional angle, between the beta-carbon-hydrogen bond and the axis of the singly occupied $C 2p_z$ orbital. Equation [113], has been used to study torsional effects on hfc's in a series of radicals where the spin density on the radical centre is assumed to remain constant. In such systems, the

terms A and B of eq. [113] also can be considered as constants. Such is not the case in benzyl radicals, where the spin density at the benzylic carbon varies significantly as a function of ring substitution (100). Hence, both the A and B terms, for these radicals, will depend on spin density. Furthermore, if the substituents affect the A and B terms differently, the b-hfc's of cumyl radicals may vary non-linearly with spin density (and hence with the a-hfc's of benzyl radicals). However, the present study does not provide any evidence to suggest that such a situation prevails.

It has been suggested that the coupling due to hydrogens of a methyl group (b-hfc) in a radical $\text{CH}_3\text{CH}^\bullet\text{X}$ is proportional to the spin density, ρ_α , at the alpha-carbon atom:

$$[114] \quad \text{b-hfc} = Q_b \cdot \rho_\alpha$$

where Q_b is believed to be an unique constant (133, 134).

From eqs. [112 and 114] we get:

$$[115] \quad \text{a-hfc} / \text{b-hfc} = Q_a / Q_b = K.$$

Thus if both a- and b-hfc's are linearly related to spin density the ratio K will be a constant. However, for a series of radicals of the type $\text{CH}_3\text{CH}^\bullet\text{X}$ studied by Fisher (134), the K value varied with the substituent X, according to the chemical shift of the methylene group of

the corresponding molecule $\text{CH}_3\text{CH}_2\text{X}$. By implicitly assuming the validity of eq. [114] for these radicals, Fisher then concluded that, Q_a was dependent on the polar character of the group X, since the chemical shift is affected by the electron withdrawing capacity of the substituent X and Q_a was dependent on the polarity of the C-H sigma-bond. However, the only conclusion that can be drawn from Fisher's results is that α - and / or β -hfc's are affected by polar substituents. Hence, this radical system has been reinvestigated, and the results are given in Table 42.

Table 42 shows that, whereas the K values for X groups that can act as π -acceptors are between 0.8 and 0.9, the corresponding value for substituents containing a lone pair of electrons is much smaller (ca. 0.6 - 0.8).

It has been shown that alpha-substituents with a non-bonding pair of electrons cause extensive out-of-plane bending of the radical centre in alkyl radicals (96b). This causes a large decrease (to less negative values) in the magnitude of the α -hfc. Thus, the variation of the K values for such X groups may be dominated by effects on α -hfc. Although variations to Q_b cannot be ruled out, because β -hfc's are also known to be affected by the nature of the hybridization of the radical centre.

Table 42. A comparison of esr hyperfine coupling constants^a of alpha- and beta-hydrogens of the radicals $\text{CH}_3\text{CH}\cdot\text{X}$ with the Nmr chemical shifts^b of the methylene group in the corresponding molecules of the type $\text{CH}_3\text{CH}_2\text{X}$.

X	a-hfc	b-hfc	Q_a/Q_b	$\delta(\text{CH}_2)^b$
H	22.4	26.9	0.833	0.87
CH_3	22.1	24.7	0.895	1.17
CH_2OH	21.7	25.3	0.858	1.49
COOH	20.2	25.0	0.808	2.37
COOR	20.3	24.9	0.815	2.27
Br	20.5	24.7	0.830	3.34
CN	20.3	23.0	0.883	2.34
COC_2H_5	18.6	22.5	0.823	2.25
COCH_3	18.8	22.3	0.843	2.40
OH	15.0	22.6	0.664	3.58
OPh	14.2	22.4	0.634	3.89
OC_2H_5	13.9	21.6	0.644	3.38
NH_2	15.3	20.2	0.757	2.61
$\text{N}(\text{C}_2\text{H}_5)_2$	13.7	19.6	0.699	2.42
r^c	0.74	0.50	0.75	

^a All hfc's (given in G) are from reference 129.

^b Nmr chemical shifts from reference 135.

^c Correlation coefficient.

For electron acceptors, with unsaturated groups that can delocalize spin, the deviation of the radical centre from planarity will be small. Hence, any variations in the K value will probably arise from charge effects on both a- and b-hfc's.

The poor correlation between ratio of the hfc's (K) and the chemical shift of the methylene group of the ethyl derivatives ($\text{CH}_3\text{CH}_2\text{X}$), when a wider range of substituents are considered is not surprising. This is because the causes for the variation of K are not the same for all substituents. Furthermore, chemical shifts are not the best parameters to assess charge effects.

From these observations it is clear that both a- and b-hfc's may be expected to be related to spin density in planar conjugated radicals not affected by this type of charge effect. A system where such a relationship can be studied conveniently is the alpha-methyl benzyl (phenethyl) radical system. In this thesis, a study of the effects of para-substituents on the esr benzylic a- and b-hfc's of this system, is reported.

4.3.2. The phenethyl radical system

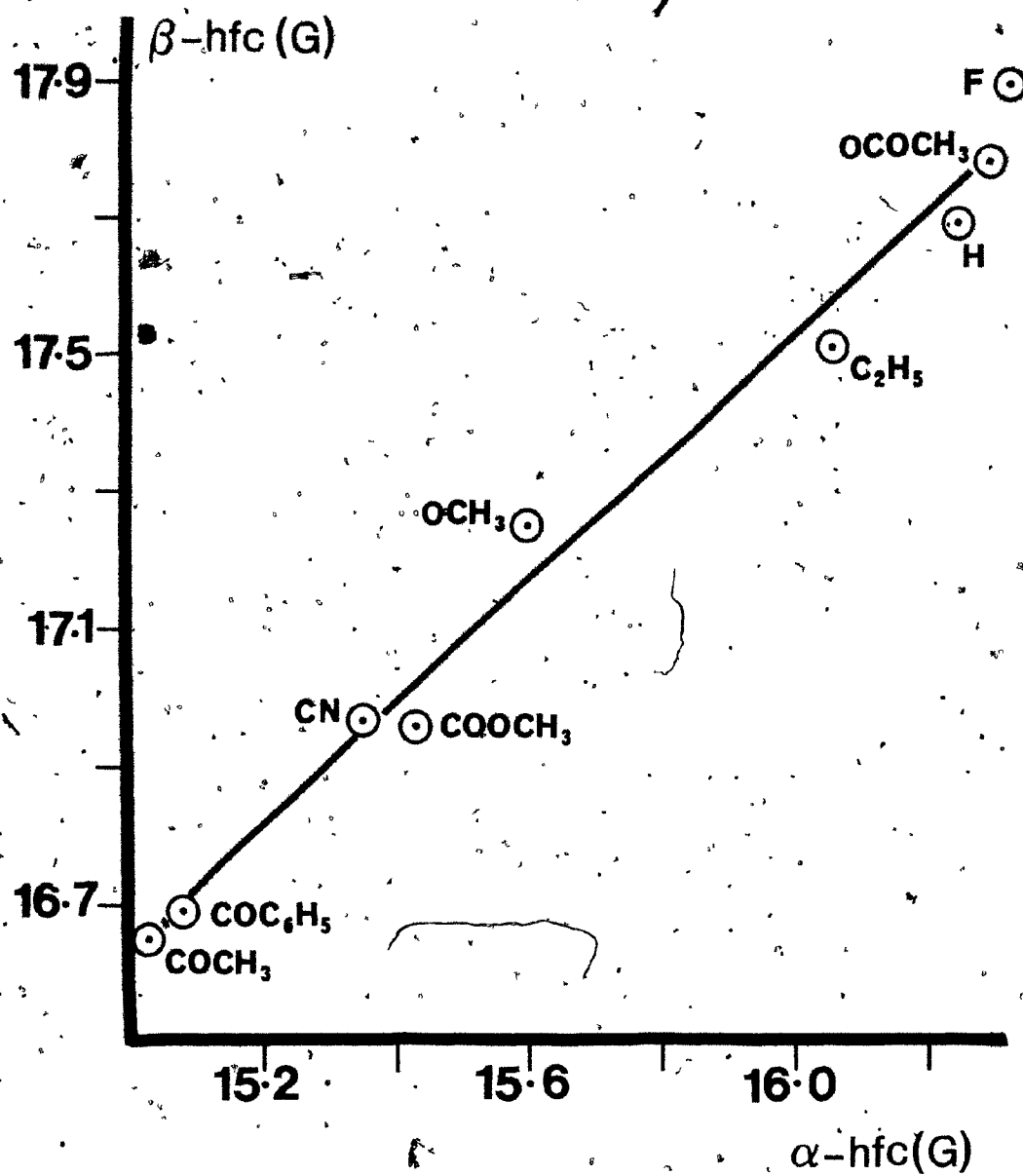
In the phenethyl system the alpha- and beta-benzylic hydrogens are on the same radical. Thus, spin density related substituent effects will be the same for both the a- and b-hfc's.

Table 38 shows that the b-hfc of the phenethyl radical is the largest out of the benzylic radicals considered. Hence, this system should show the greatest sensitivity to substituent effects. So, an added attraction for studying this system will be that it will be most suited for revealing small differences between effects of substituents.

The correlation between the a- and b-hfc's of the phenethyl radicals, and, that between these hfc's and the a- and b-hfc's of, respectively, the corresponding benzyl and cumyl radicals are given in Tables 43 and 44.

The relationship between the b- and a-hfc's of the phenethyl radicals is illustrated in Figure 12. The hfc's are found to correlate well ($r = 0.993$). These results indicate that substituent effects on spin delocalization by either hyperconjugation or spin polarization is linearly related. Furthermore, it gives confidence to the argument that benzylic a- and b-hfc's are linearly related to spin density.

Figure 12. A linear regression analysis of the relationship between beta-hfc (β -hfc) and alpha-hfc (α -hfc) of phenethyl radicals.



The correlation between the ρ - and α -hfc. of the phenethyl radicals does not improve with inclusion of the Hammett σ substituent constant. This shows that, charge effects, if present, affect α - and ρ -hfc's in a similar manner.

In Figure 13, the relationship between the ρ -hfc of a phenethyl radical and the α -hfc of the corresponding benzyl radical is illustrated. The correlation is slightly better ($r = 0.995$) with α -hfc of the benzyl series than with the α -hfc of phenethyl itself. A possible cause for this is the smaller uncertainty in the benzyl values (Table 44).

The excellent correlation obtained for the plot in Figure 13, and the absence of any improvement in the correlation coefficient with inclusion of the Hammett σ substituent constant in the regression analysis, indicates that charge related effects on spin delocalization are similar for the benzyl and phenethyl systems.

The correlation between the α -hfc's of the phenethyl and benzyl radicals is not as good as that between the α -hfc's and the ρ -hfc of phenethyl radicals. This is probably because of the larger uncertainty in the α -hfc of the phenethyl radicals (Table 43).

Figure 13. A linear regression analysis of the relationship between beta-hfc of phenethyl radicals (β -hfc) and the benzylic alpha-hfc (α -hfc) of benzyl radicals. The points are numbered according to Table 39.

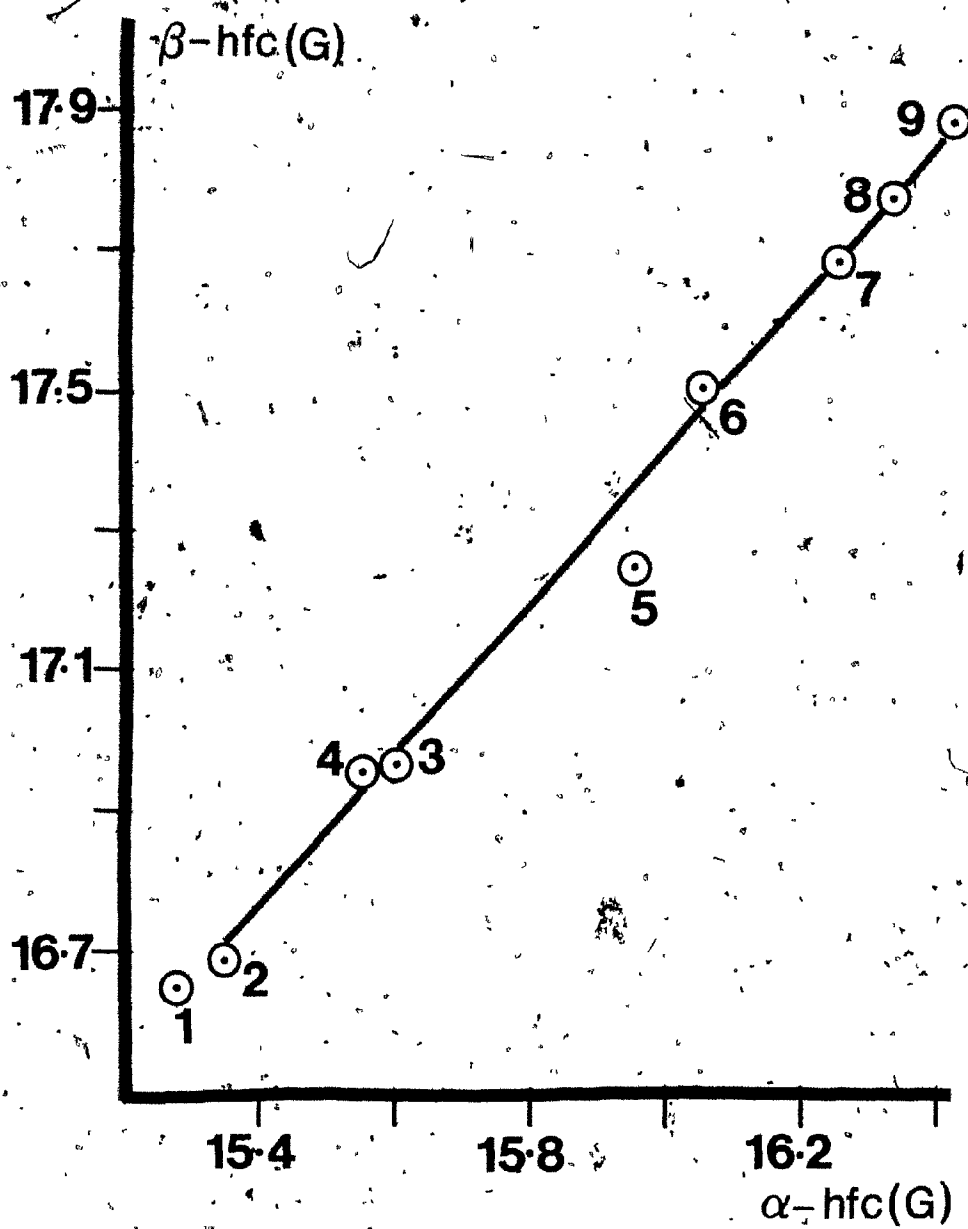


Table 43. A linear regression analysis of the relationship between the benzylic *h*-hfc values of phenethyl radicals and the benzylic *a*- and *h*-hfc values of benzylic radicals.^a

Regression coefficients (*K*), correlation coefficients (*r*) and constants (*c*) for eq. [116] *b, c, d*

Series	<i>K_i</i>	<i>K_i, K_σ</i>
	(<i>r_i, C</i>)	(<i>r, C*</i>)
<i>a</i> -hfc ^e (phenethyl)	0.89±0.09 (0.993, 3.32±1.4)	0.87±0.13, 0.05±0.15 (0.992, 0.0±2.1)
<i>a</i> -hfc ^f (benzyl)	1.09±0.09 (0.995, -0.02±1.47)	1.14±0.12, 0.10±0.17 (0.995, -0.85±2.00)
<i>h</i> -hfc ^g (cumyl)	0.84±0.19 (0.963, 4.06±3.07)	1.08±0.21, 0.52±0.36 (0.986, 0.12±3.3)

^a Hyperfine coupling values (hfc's) from Tables 39 and 40.

σ_p values from reference 136. The number of data points are nine in all cases.

^b [116a] *h*-hfc(phenethyl) = *K_i* *a_i* + *C*.

[116b] *h*-hfc(phenethyl) = *K_i* *a_i* + *K_σ* *σ* + *C**.

^c *a₁* = *a*-hfc(phenethyl); *a₂* = *a*-hfc(benzyl);

a₃ = *h*-hfc(cumyl).

^d Standard error at 95% confidence level.

^e Eq. [116]; *i* = 1. ^f Eq. [116]; *i* = 2. ^g Eq. [116];

i = 3.

Table 44. A linear regression analysis of the relationship between the benzylic a-hfc values of phenethyl radicals and the benzylic a- and b-hfc values of benzylic radicals.^a

Regression coefficients (K), correlation coefficients (r) and constants (c) for eq. [117].^{b, c, d}

Series	K_i (r, C)	K_i, K_σ (r, C*)
a-hfc ^e (benzyl)	1.20 ± 0.21 (0.979, -3.37 ± 3.31)	$1.27 \pm 0.31, 0.13 \pm 0.42$ (0.978, -4.45 ± 4.96)
b-hfc ^f (cumyl)	0.92 ± 0.26 (0.948, 1.14 ± 4.09)	$1.21 \pm 0.34, 0.61 \pm 0.58$ (0.971, -3.45 ± 5.42)

^a Hyperfine coupling values (hfc's) from Tables 39 and 40.

σ_p values from reference 136. The number of data points are nine in all cases.

^b [117a] a-hfc(phenethyl) = $K_i a_i + C$.

[117b] a-hfc(phenethyl) = $K_i a_i + K_\sigma \sigma + C^*$.

^c a_1 = a-hfc(benzyl); a_2 = b-hfc(cumyl).

^d Standard error at 95% confidence level.

^e Eq. [117] ; $i = 1$. ^f Eq. [117] ; $i = 2$.

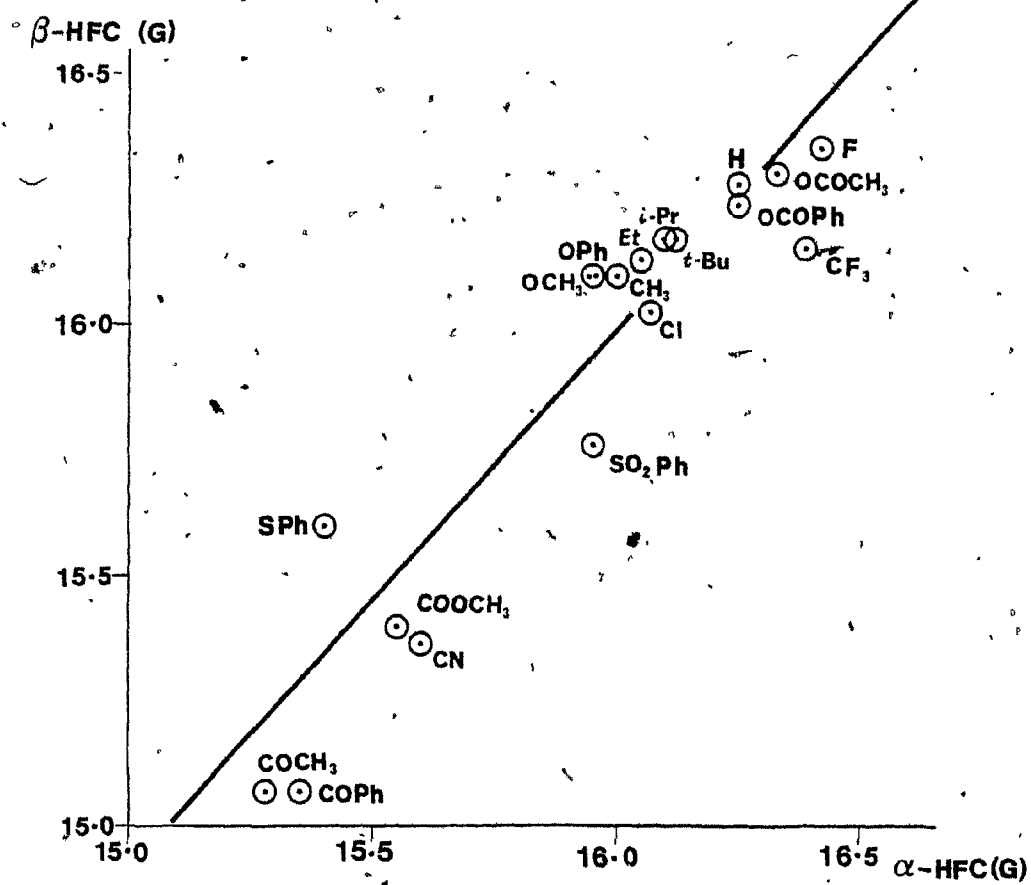
The ρ -hfc's of the cumyl radicals correlate better with both ρ - and ρ -hfc's of the phenethyl radicals when the Hammett σ constants are included in the regression analysis. This clearly indicates the presence of, or the variation in, charge related effects on hfc's with substitution of the benzylic hydrogens with methyl groups. If the origin of these charge effects are related to the donor-acceptor characteristics of the α -methyl substituents, the relationship between the ρ -hfc of the cumyl radicals and the ρ -hfc of the benzyl radicals should be most sensitive to this type of effect. Thus, substituent effects on the ρ -hfc's of eighteen ρ -substituted cumyl radicals were studied and compared to the corresponding effects on the ρ -hfc's of the benzyl radicals. The results are discussed in the next section.

Table 45. The effect of para-substituents (X) on alpha- and beta-hyperfine coupling constants of benzylic radicals.^a

X	a ^b	c	a / a _H
COCH ₃	15.07	15.28	0.986
COPh	15.07	15.35	0.982
CN	15.37	15.60	0.985
COOCH ₃	15.40 ⁹⁰	15.55	0.990
SPh	15.60	15.30 ^d	1.020
S(O) ₂ Ph	15.76	15.95 ^d	0.988
Cl	16.03	16.07	0.998
OCH ₃	16.10	15.95	1.009
OPh	16.10	15.95 ^d	1.009
CH ₃	16.10	16.00	1.006
Et	16.13	16.05 ^d	1.005
CF ₃	16.15	16.39	0.985
i-Pr	16.17	16.10 ^d	1.004
t-Bu	16.17	16.12	1.003
OCOPh	16.24	16.25 ^d	0.999
H	16.28	16.25	1.002
OCOCH ₃	16.30	16.33	0.998
F	16.35	16.42	0.996

^aAll values are in G. The uncertainty is ± 0.03 G. ^bbeta-hfc values of cumyl radicals from Table 39. ^calpha-hfc values of benzyl radicals; unless stated otherwise from reference 100. ^d Reference 101.

Figure 14. A linear regression analysis of the relationship between beta-hfc of cumyl radicals (β -hfc) and the benzylic alpha-hfc of benzyl radicals (α -hfc).



4.3.3. General trends and specific deviations in the relationship between the b-hfc's of cumyl radicals and the a-hfc of benzyl radicals.

In Table 45 the benzylic a-hfc constants of para-substituted benzyl radicals are compared with the b-hfc constants of the corresponding cumyl radicals. If both of these hfc's correlate, a constant ratio, $a\text{-hfc}/b\text{-hfc}$, is expected. Table 45 shows that for most substituents this ratio is close to the value for the unsubstituted radicals ($a\text{-hfc}/b\text{-hfc} = 1.002$). Thus, there is a general trend for the b-hfc's in cumyl radicals to vary in a similar manner to that of the a-hfc's in benzyl radicals. However, Table 46 and Figure 14 clearly show that significant deviations, much larger than the experimental error of ± 0.03 G, from a linear correlation between the a- and b-hfc values are observed for some substituents. Due to these specific deviations, the correlation between the two types of hfc's is far from satisfactory ($r = 0.92$, 18 data points, see Figure 14 and Table 46).

In the plot shown in Figure 14 the substituents that lie below (above) the least-squares regression line have a relatively lower (higher) ratio of $a\text{-hfc}/b\text{-hfc}$ and hence show an unexpectedly large (small) effect in the cumyl series with respect to the benzyl series. Figure 14 also shows that, all electron-withdrawing (donating) groups

Table 46. A linear regression analysis of charge effects on the relationship between the benzylic β -hfc values of cumyl radicals (a_β) and the benzylic α -hfc values of benzyl radicals (a_α).^a

Regression coefficients (ρ), correlation coefficients (r) and constants (c) for eq. [118] b, c, d, e

ρ_1 ^f (r, C_1)	ρ_1, ρ_2 ^g (r, C_{12})	ρ_1, ρ_3 ^h (r, C_{13})
1.06 ± 0.23 ($0.92, -0.9 \pm 3.7$)	$0.92 \pm 0.13, -0.45 \pm 0.15$ ($0.98, 1.3 \pm 2.1$)	$0.88 \pm 0.24, 0.41 \pm 0.33$ ($0.94, -3.3 \pm 3.7$)

^a Hyperfine coupling (hfc) values from Tables 39 and 40. σ_p values from reference 136.

^b [118] $a_\beta(\text{cumyl}) = \sum \rho_i Q_i + C_j$ (or C_{jk}); where $i = j$ or j, k .

^c $\rho_1 = \rho_\alpha$; $\rho_2 = \rho_\sigma$; $\rho_3 = \rho_{om}$

^d $Q_1 = a_\alpha(\text{benzyl})$; $Q_2 = \sigma_p$; $Q_3 = 2(|a_o| + |a_m|)(\text{cumyl})$

^e Standard error at 95% confidence level.

^f Equation [118]; $i = 1$.

^g Equation [118]; $i = 1, 2$.

^h Equation [118]; $i = 1, 3$.

Figure 15. A plot of Δ versus the Hammett
substituent constant σ_p

$$\Delta = (\beta - \text{hfc}) - 1.06 (\alpha - \text{hfc}) + 0.93$$

(Points are numbered according to Table 40).

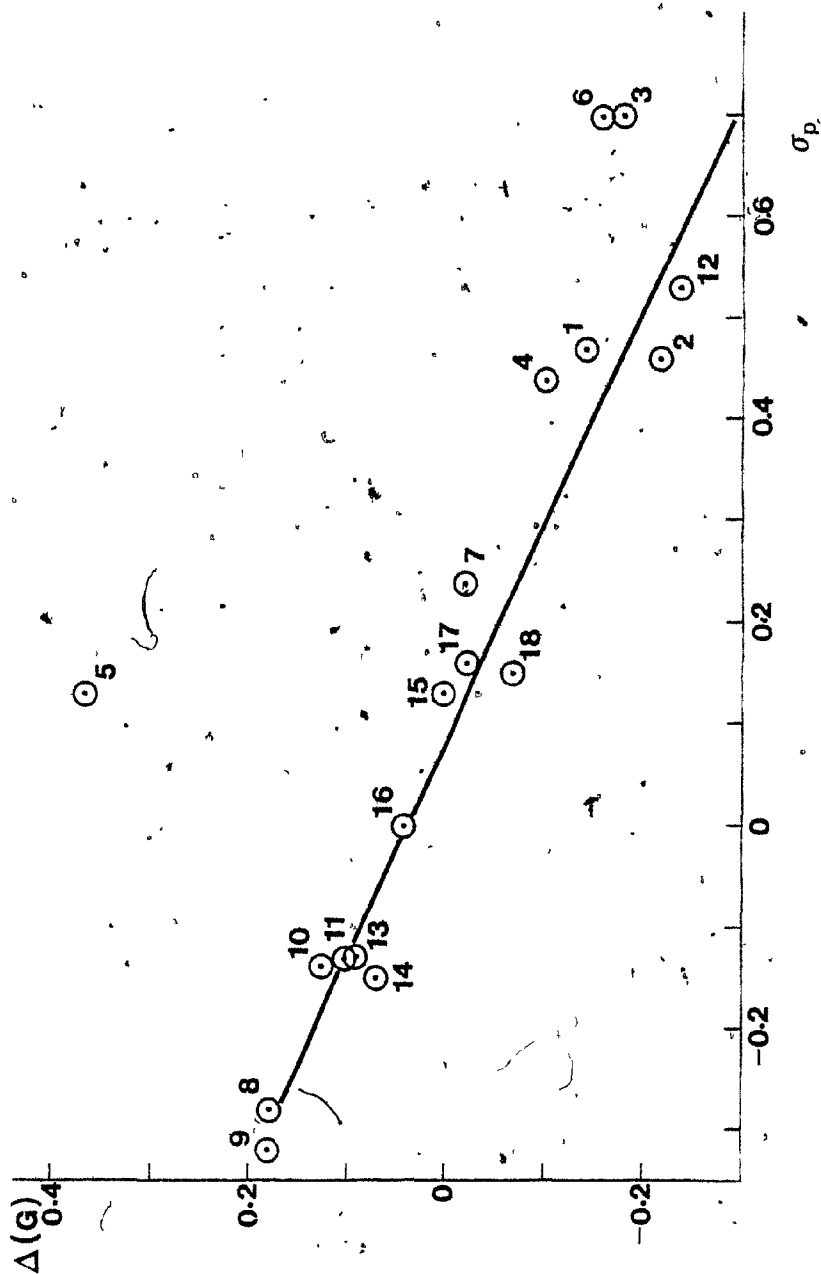
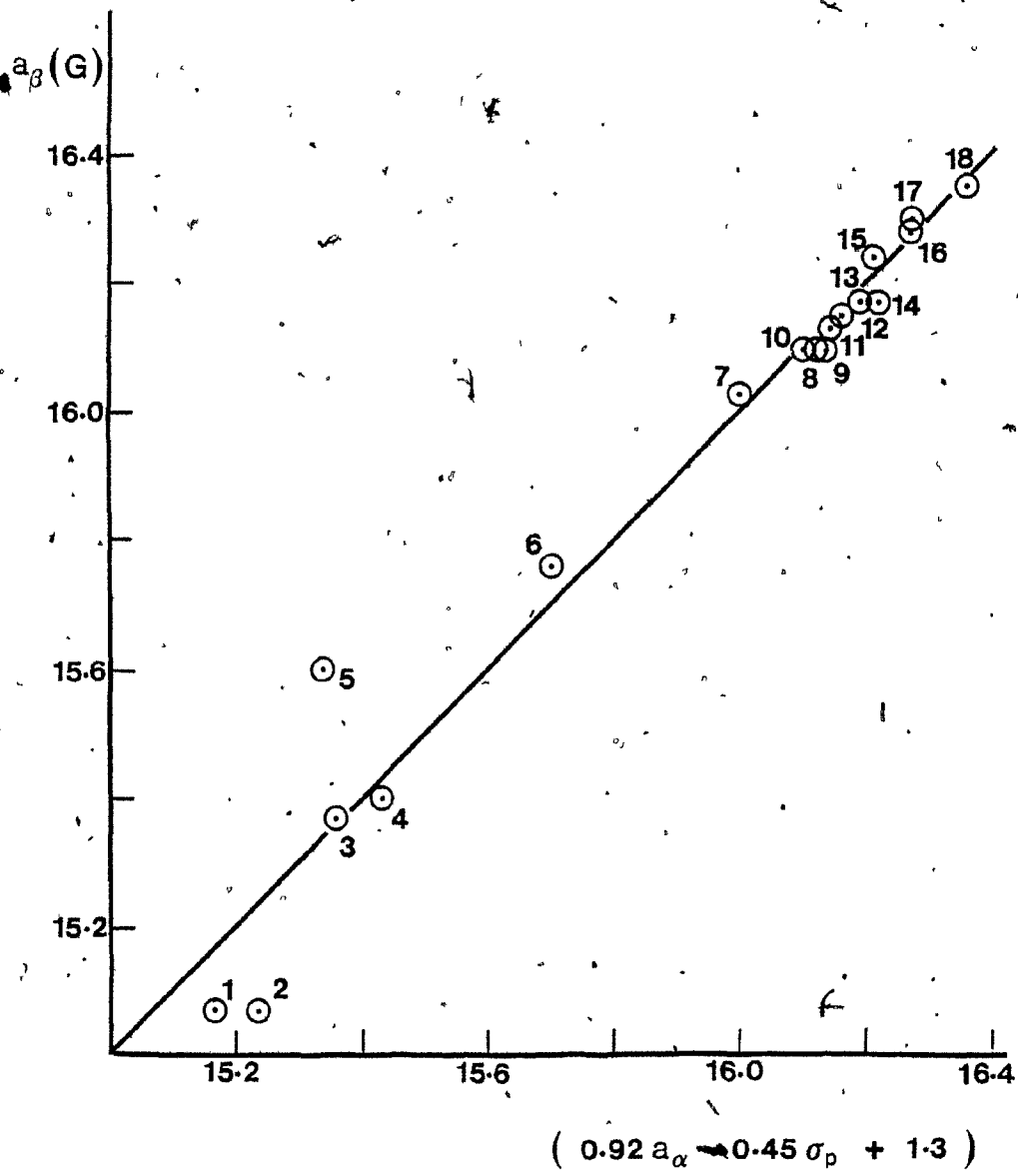


Figure 16. Two-parameter Hammett correlation: A plot of β -hfc values of cumyl radicals (a_β) vs. ρ 0.92
 $a_\alpha(\text{benzyl}) = 0.45 \sigma_p + 1.3$ l. Points are numbered according to Table 40.

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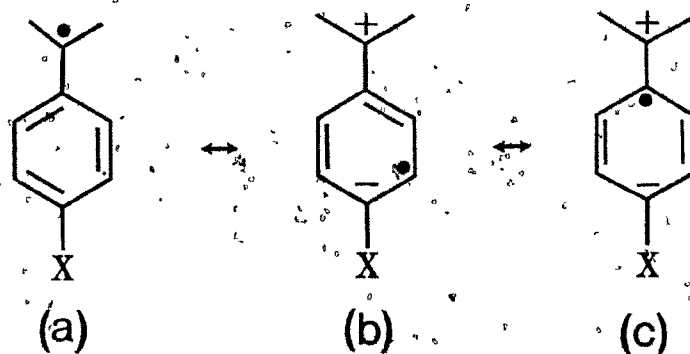


cause a larger (smaller) spin delocalizing effect on the β -hfc in the cumyl than the α -hfc of the benzyl radical system. Consequently, it will be important to consider how charge effects may influence spin delocalization in these systems.

4.3.4. Charge effects on spin delocalization

The presence of charge effects on spin delocalization have been proposed by several workers and discussed in terms of merostabilization (123) and captodative stabilization (124).

In chapter 3 we discussed briefly the effects of α -substituents of benzylic radical systems on the spin delocalizing power of a ring substituent. Relative to the benzyl radical series, the corresponding phenethyl and cumyl systems are obtained by substituting, respectively, one and two benzylic hydrogens with methyl groups. Table 32 shows that, at positions of excess α -spin, a methyl group will act as a weak π - β -donor. Thus, substitution of methyl groups at the benzylic position will make the benzylic group a weaker acceptor of π - β -electrons from the ring, and diminish the effect of para -substituents that delocalize spin by donating π - β -electrons.



Scheme 3.

Scheme 3 shows how the electron withdrawing nature of a para-substituent can affect spin delocalization. Effects resulting from the development of a negative charge on the benzylic carbon have been ignored in the absence of electron-withdrawing alpha-substituents. However, such effects, if present, will be opposite to the charge effects described in scheme 3 (b) and (c). From these charge separated valence-bond structures it is evident that alpha-substituents that can stabilize an incipient positive charge on the benzylic carbon will enhance spin delocalization by electron withdrawing groups at the para-position. Therefore, the cumyl system, with two alpha-methyl substituents that stabilize a positive charge better than the alpha-hydrogens in the benzyl radicals, should be more sensitive than the corresponding benzyl system to charge effects. Hence, the deviations observed in Figure

14 can be a result of a greater contribution of charge separated valence-bond structures, such as scheme 3(b) and (c), in the cumyl than in the benzyl radicals.

From the above discussion it is clear that, depending upon the donor-acceptor characteristics, a substituent can either be more or less effective in delocalizing spin in a cumyl radical relative to that in a benzyl radical. The specific deviation of each point, from the correlation line shown in Figure 14, is plotted against the Hammett substituent constant σ in Figure 15. This parameter was chosen because a consistent set of values were available (136). The correlation coefficient for the least squares line in Figure 15 is $r = 0.79$.

The sign of the slope of the line in Figure 15 reflects the fact that electron-withdrawing groups generally have a greater influence increasing spin delocalization in the cumyl series relative to the benzyl series. This is consistent with a greater contribution of the charge separated valence-bond structures (scheme 3(b) and (c)) in the cumyl series, where the alpha-methyl groups stabilize the positive charge.

Dust and Arnold (100) have defined the substituent effect on spin delocalization ($\sigma_{\alpha}^{\bullet}$) based upon the a -hfc of the benzyl radical. Of course, there must be some inherent charge effect on this system as well. A quantitative indication of the increased importance of

charge effects on the cumyl radical series, relative to the benzyl series, can be obtained by plotting the h -hfc's against the two parameters a -hfc and ρ_p (Figure 16). For the data plotted in Figure 16, the correlation coefficient is $r = 0.98$.

The ρ_p value reflects the balance between the inherently larger h -hfc, and the diminished delocalization into the ring; since considerable spin is distributed among the alpha-methyl groups.

The magnitude of ρ_p indicates the increased importance of spin delocalization away from the benzylic position through a greater contribution of the valence-bond structures (scheme 3 (b) and (c)); in the cumyl series relative to the benzyl series.

The importance of charge effects on the relationship between the benzylic hfc's is now clear. Therefore, it will be useful to determine if there are any other manifestations of charge effects on spin delocalization in the esr spectra of the cumyl radicals.

The valence-bond structures (b) and (c) in scheme 3 clearly show that spin delocalization induced by charge effects will cause an increase in alpha-spin at the meta- and ipso-positions. This will result in a concomitant decrease in alpha-spin at the benzylic position. Moreover, such changes in spin distribution will undoubtedly affect the hfc's at the ortho- and meta-ring positions.

It is well known that in benzylic radicals, while there is an excess of alpha-spin at the ortho- and para-positions, there is an excess of beta-spin at the meta- and ipso-positions (137). Thus, the increase in alpha-spin (or decrease in beta-spin) at the meta- and ipso-positions will lead to a decrease in the alpha-spin at the ortho-position. Consequently, all substituents showing a greater efficiency in delocalizing spin due to charge effects in the cumyl radicals should also show relatively lower hfc's for the ring hydrogens at the ortho- and meta-positions, which are represented by a_o and a_m , respectively, in Table 40. All substituents displaying enhanced delocalizing effects in the cumyl system do indeed have relatively lower a_o and a_m values. Moreover, the hypothesis that the variation in the a_o and a_m values are a manifestation of charge effects, can be tested by the multiple linear regression analysis of a - and b -hfc's (denoted a_α and a_β respectively in Table 46), with the inclusion of an additional parameter, namely, the sum of the absolute values of the ortho- and meta- hyperfine coupling constants (i.e. $2(|a_o| + |a_m|)$):

$$[119] \quad a_\beta = \rho_\alpha a_\alpha + \rho_{om} 2(|a_o| + |a_m|) + C$$

In eq. [119], ρ_α , ρ_{om} and C are constants. This is admittedly a semi-quantitative approach to correct for charge effects on spin delocalization. However, the

improvement in the correlation coefficient (r) when all points are considered ($r = 0.92$ becomes $r = 0.94$), suggests that this is a valid analysis (Table 46). Consequently, $2(|a_o| + |a_m|)$, can be regarded as a useful parameter, in describing the charge related effects on spin delocalization.

4.4 CONCLUSION

The present study shows that there is a general trend: b -hfc's of phenethyl and cumyl radicals vary in a similar manner to the a -hfc's of phenethyl and benzyl radicals. However, specific deviations are observed from a linear correlation between these a - and b -hfc's. These deviations are rationalized by considering charge effects on spin delocalization. Electron-withdrawing (donating) substituents show a greater (smaller) delocalizing effect in the cumyl radicals relative to the phenethyl and benzyl radicals.

Charge effects on spin delocalization should be general, and should depend upon the electron-withdrawing and donating ability of the groups attached to the radical centre (124b).

It has been shown that the variations in the hfc's at the ortho- and meta-position, reflect the changes in the spin delocalizing efficiency of a substituent in the cumyl radicals relative to the corresponding benzyl system.

Since the extent of spin delocalization of a radical

is inherently dependent upon charge effects, it will be difficult to assess the relative importance of radical stabilizing effects and polar factors from studies of relative reactivity.

Finally, this study of the esr spectra of para-substituted phenethyl radicals, and the significant improvement in multiple correlation coefficient, for the linear regression analysis of the b-hfc's of cumyl radicals and the a-hfc's of benzyl radicals, when parameters reflecting charge effects on spin delocalization are included, leads us to believe that both a- and b-hfc's of benzylic radicals are linearly related to spin density.

4.5. EXPERIMENTAL

4.5.1. General Information

Esr spectra were recorded on a Varian Associates E-109 B electron paramagnetic resonance spectrometer, equipped with a liquid nitrogen variable temperature accessory, at 0.5-mW microwave power and 0.5-0.8 G modulation amplitude. All spectra were recorded with the aid of a Nicolet 1170 signal averager. Typically, twelve, 100 G wide, scans were accumulated (0.5 min. per scan). Coupling constants were measured directly from the oscilloscope and refined by computer simulation (138) using an IBM-PC.

^1H nmr spectra were recorded on a Varian CFT-20 spectrometer or a Nicolet Model 360 NB spectrometer, coupled to an Oxford Instruments Superconducting Magnet and a Nicolet 192 K word Data Acquisition System, and are reported in parts per million downfield from TMS. Infrared spectra were recorded on either an air-purged Perkin-Elmer 180 grating infrared spectrometer, a Pye Unicam SP1000, a Perkin-Elmer 283B or 237B Infrared spectrometer and are reported in wavenumbers (relative to the 1601.8 cm^{-1} absorption of polystyrene). Mass spectra were obtained on a modified Du Pont CEC Model 21-104 mass spectrometer. Melting points were recorded on a Sybron Corporation Thermodyne hotstage apparatus and are uncorrected.

Substituted ethylbenzenes and cumenes (liquids) were purified by gas chromatography. A 5' x 3/8" column packed

with 5% SE-30 on Chromosorb-W (60/80) incorporating helium as the carrier gas was used.

4.5.2. Materials

Di-tert-butyl peroxide (DTBP) and triethylsilane were obtained from Pfaltz and Bauer Inc. and were used without further purification. Hexamethylditin and hexabutylditin were obtained from Alpha Products and used without further purification. Chlorobenzene (J. T. Baker Chemicals, Inc.) was stirred over concentrated sulphuric acid, washed successively with water, saturated sodium bicarbonate and water; dried over anhydrous magnesium sulphate and distilled through a Vigreux column. All solvents were distilled prior to use.

4.5.3. Synthesis (139)

4-Ethylacetophenone

4-Ethylacetophenone was prepared by the reaction of ethylbenzene and acetyl chloride in the presence of aluminum chloride, using carbon disulphide as the solvent (140). The reaction mixture was purified by vacuum distillation. 4-Ethylacetophenone was obtained as a colourless oil. ^1Hmr (80 MHz, CDCl_3) δ 7.85(d, 2H), 7.23(d, 2H), 2.66(q, 2H), 2.53(s, 3H), 1.22(t, 3H); IR PE1320 (neat) cm^{-1} 1680, 1610, 1270, 835.

4-Ethylbenzophenone

4-Ethylbenzophenone was prepared by a procedure similar to that used for the acetophenone except using benzoyl chloride. Vacuum distillation afforded 4-ethylbenzophenone as a colourless oil. ^1Hmr (80 MHz, CDCl_3) δ 7.20-7.82(m, 9H), 2.68(q, 2H), 1.23(t, 3H); IR PE1320 (neat) cm^{-1} 1660, 1610, 850, 705.

Methyl 4-ethylbenzoate

In a 250 mL 3-necked flask equipped with a magnetic stirrer, reflux condenser and a constant pressure dropping funnel, was placed 12.2 g (91 mmol) of aluminum chloride. To the aluminum chloride was added 8.0 g (83 mmol) of ethylbenzene dissolved in 175 mL of carbon disulphide. The flask was cooled in an ice bath; to the cooled mixture was added a solution of 11.6 g (91 mmol) of oxalyl chloride in 25 mL of carbon disulphide. After the evolution of gases had ceased, the mixture was allowed to warm to room temperature. The mixture was then refluxed for 2.0 h and the cooled mixture was poured into 200 mL of methanol. The carbon disulphide was removed by distillation and the residue was poured into water and extracted with ether. The combined organic layers were washed with 5% sodium hydroxide, saturated salt solution, dried with magnesium sulphate and evaporated. The yield of a pale yellow oil was 8.2 g (60%). The product was distilled under vacuum to yield a colourless oil. ^1Hmr (80 MHz, CDCl_3) δ 7.94

(d,2H), 7.20(d,2H), 3.85(s,3H), 2.65(q,2H), 1.21(t,3H); IR
PE 1320 (neat) cm⁻¹ 1725, 1610, 1280, 1110.

4-Ethylphenyl acetate

4-Ethylphenyl acetate was prepared by the reaction between 4-ethylphenol and acetyl chloride in 3M aqueous sodium hydroxide (140). ¹Hmr (80 MHz, CDCl₃) δ 6.88-7.19(m,4H), 2.58(q,2H), 2.16(s,3H), 1.17(t,3H); IR 1320 (neat) cm⁻¹ 1770, 1515, 1375, 1220, 1025, 920, 855.

4-Cyanoethylbenzene

4-Cyanoethylbenzene was prepared by a Sandmeyer reaction using the diazonium salt formed from 4-ethylaniline and cuprous cyanide(140). IR SP1000 cm⁻¹ 2240, 1610, 840.

4-Methoxyethylbenzene

4-Methoxyethylbenzene was prepared by the reaction of 4-ethylphenol with dimethyl sulphate in 5% aqueous potassium hydroxide. The product was purified by vacuum distillation. ¹Hmr (80 MHz, CDCl₃) δ 7.10(d,2H), 6.79(d,2H), 3.74(s,3H), 2.57(q,2H), 1.19(t,3H); IR PE 1320 (neat) cm⁻¹ 1615, 1590, 1515, 1250, 1180, 1040, 915, 830, 735.

4-Fluoroethylbenzene

4-Fluorethylbenzene was prepared by the thermal decomposition of the diazonium fluoroborate salt formed from 4-ethylaniline with fluoroboric acid. ^1Hmr (80 MHz, CDCl_3) δ 7.03(m, 4H), 2.60(q, 2H), 1.20(t, 3H); IR PE 233B (neat) cm^{-1} 1505, 1230, 1155, 830.

4-Isopropyldiphenyl ether

4-Isopropyldiphenyl ether was prepared by refluxing a mixture of 4-isopropylphenol, bromobenzene, cuprous oxide and γ -collidine (141, 142). The yield of 4-isopropyldiphenyl ether was 87% as a colourless oil. ^1Hmr (80 MHz, CDCl_3) δ 7.34-6.87(m, 9H), 2.90(m, 1H), 1.24(d, 6H); IR PE 180 (neat) cm^{-1} 1600, 1500, 1250, 875, 760.

4-Isopropylacetophenone

4-Isopropylacetophenone was prepared by the reaction of cumene and acetyl chloride in the presence of aluminum chloride, using carbon disulphide as the solvent. The reaction mixture was purified by vacuum distillation. 4-Isopropylacetophenone was obtained as a colourless oil (143). ^1Hmr (361.1 MHz, CDCl_3) δ 7.90(m, 2H), 7.31(m, 2H), 2.97(m, 1H), 2.59(s, 3H), 1.27(d, 6H); IR SP1000 (neat) cm^{-1} 1680, 1610, 830.

4-Isopropylbenzophenone

4-Isopropylbenzophenone was prepared by a procedure similar to that used for the acetophenone except using benzoyl chloride. Vacuum distillation afforded 4-

isopropylbenzophenone as a colourless oil (144). ^1Hmr (361.1 MHz, CDCl_3) δ 7.32-7.81 (m, 9H), 2.99 (m, 1H), 1.29 (d, 6H); IR SP1000 (neat) cm^{-1} 1660, 1610, 850, 700.

4-Isopropyldiphenyl sulphone

4-Isopropyldiphenyl sulphone was prepared in essentially quantitative yield by the addition of 4-isopropylsulphonyl chloride to a solution of benzene and aluminum chloride (141). The sulphonyl chloride was prepared in 94% yield by the addition of chlorosulphonic acid to cumene at 0 C (145). Recrystallization of the crude product from alcohol, with added Norite, produced colourless needles mp 101-101.5 C (lit. (146) 98.5-99.5 C)

^1Hmr (80 MHz, CDCl_3) δ 7.81-8.00 (m, 4H), 7.28-7.53 (m, 5H), 2.94 (m, 1H), 1.22 (d, 6H); IR PE 180 (KBr) cm^{-1} 1610, 1325, 1170, 840, 760, 690, 650.

4-Isopropyldiphenyl sulphide

4-isopropyldiphenyl sulphone, 2.0 g (7.7 mmol), was placed in a 50 mL round bottom flask equipped with a reflux condenser and septum inlet. The flask was purged with dry nitrogen and 5.5 g of diisobutylaluminum hydride (DIBAL-H) (38.4 mmol) in toluene (20 mL) was added through the septum via a syringe. The solution was refluxed under a nitrogen atmosphere until the sulphone had reacted (3-4 days). The reaction mixture was poured into aqueous ammonium chloride and extracted with ether. The combined

organic layers were washed with a saturated salt solution, dried with magnesium sulphate and evaporated(147). The residue was chromatographed on a silica gel column using methylene chloride as the eluent. The yield of the purified product was 1.57 g (90%). ^1Hmr (361.1 MHz, CDCl_3) δ 7.16-7.32(m,9H), 2.88(m,1H), 1.24(d,6H); IR PE 180 (neat) cm^{-1} 2980, 1595, 1490, 1450, 1395, 1375, 830, 745, 695.

Methyl 4-isopropylbenzoate

In a 250 mL 3-necked flask equipped with a magnetic stirrer, reflux condenser and a constant pressure dropping funnel, was placed 12.2 g (91 mmol) of aluminum chloride. To the aluminum chloride was added 10.0 g (83 mmol) of cumene dissolved in 175 mL of carbon disulphide. The flask was cooled in an ice bath; to the cooled mixture was added a solution of 11.6 g (91 mmol) of oxalyl chloride in 25 mL of carbon disulphide. After the evolution of gases had ceased, the mixture was allowed to warm to room temperature. The mixture was then refluxed for 1.5 h and the cooled mixture was poured into 200 mL of methanol. The carbon disulphide was removed by distillation and the residue was poured into water and extracted with ether. The combined organic layers were washed with 5% sodium hydroxide, saturated salt solution, dried with magnesium sulphate and evaporated. The yield of a pale yellow oil was 11.3 g (76%). The product was distilled under vacuum to

yield a colourless oil (148). ^1Hmr (80 MHz, CDCl_3) δ 7.91-8.01(m, 2H), 7.22-7.32(m, 2H), 3.89(s, 3H), 2.95(m, 1H), 1.25(d, 6H); IR PE 283B (neat) cm^{-1} 1735, 1620, 1285, 1120.

4-Fluorocumyl alcohol

4-Fluorocumyl alcohol was prepared by the reaction of ethyl 4-fluorobenzoate with methyl magnesium iodide. mp 36-37 C uncorrected (lit. (149) 37.8 C). ^1Hmr (80 MHz, CDCl_3) δ 6.99-7.53(m, 4H), 1.89(s, 1H), 1.56(s, 6H); IR 283B (neat) cm^{-1} 3400, 1605, 1510, 1235, 1160, 835.

4-Trifluoromethylcumene

Method a: 4-trifluoromethylcumene was prepared by catalytic hydrogenation of 4-trifluoromethyl- α -methylstyrene using palladium on carbon (49% overall yield from the cumyl alcohol). The styrene was prepared by the acid catalyzed dehydration of 4-trifluoromethylcumyl alcohol (150, 151) using 4-toluenesulphonic acid in refluxing benzene.

Method b: 4-trifluoromethylcumene was prepared by the reduction of 4-trifluoromethylcumyl alcohol using hydriodic acid and red phosphorus (refluxing overnight) (152). The yield was 58%. ^1Hmr (80 MHz, CDCl_3) δ 7.18-7.59(m, 4H), 2.96(m, 1H), 1.25(d, 6H); IR 283B (neat) cm^{-1} 1625, 1335, 1175, 1135, 1080, 1020, 845.

4-Methylcumyl alcohol

4-Methylcumyl alcohol (149, 152) was prepared by the reaction of methyl 4-toluate with methyl magnesium iodide.

^1Hmr (361.1 MHz, CDCl_3) δ 7.37(m, 2H), 7.15(m, 2H), 2.34(s, 3H), 1.79(s, 1H), 1.57(s, 6H); IR 283B (neat) cm^{-1} 3420, 1520, 1370, 960, 820.

4-Chlorocumene

4-Chlorocumene was prepared by a Sandmeyer reaction using the diazonium salt from 4-isopropylaniline and cuprous chloride (153). ^1Hmr (80 MHz, CDCl_3) δ 7.06-7.32(m, 4H), 2.87(m, 1H), 1.21(d, 6H); IR 283B (neat) cm^{-1} 1500, 1100, 1020, 830. Mass Spec. m/e (rel intensity) 154(M^+ , 30), 139(100).

4-Isopropylphenyl benzoate

4-Isopropylphenyl benzoate was prepared by the reaction between 4-isopropylphenol and benzoyl chloride in 3 M aqueous sodium hydroxide (140). mp 75 C (lit.(154) 72-74 C) ^1Hmr (361.1 MHz, CDCl_3) δ 8.20(m, 2H), 7.11-7.62(m, 7H), 2.94(m, 1H), 1.27(d, 6H); IR 283B cm^{-1} 1735, 1200, 1055, 880, 720.

4-Isopropylphenyl acetate

4-Isopropylphenyl acetate (155) was prepared by a procedure similar to that used for the benzoate. ^1Hmr (80 MHz, CDCl_3) δ 6.92-7.28(m, 4H), 2.90(m, 1H), 2.27(s, 3H), 1.23(d, 6H); IR 283B (neat) cm^{-1} 1780, 1510, 1375, 1225, 1205, 1020, 915, 850.

4-Ethylcumyl alcohol

4-Ethylcumyl alcohol was prepared by the addition of 4-ethylacetophenone to methyl magnesium iodide (149). ^1Hmr (80 MHz, CDCl_3) δ 7.10-7.45(m, 4H), 2.62(q, 2H), 1.88(s, 1H), 1.55(s, 6H), 1.23(t, 3H); IR 283B (neat) cm^{-1} 3400, 1510, 1460, 1365, 1170, 955, 830.

4-tert-Butylcumyl alcohol

4-~~tert~~-Butylcumyl alcohol was prepared by the addition of methyl 4-~~tert~~-butylbenzoate to a solution of methyl magnesium iodide. mp 78 C (lit. (149) 79 C) ^1Hmr (80 MHz, CDCl_3) δ 7.38(s, 4H), 1.73(s, 1H), 1.57(s, 6H), 1.31(s, 9H); IR 283B (neat) cm^{-1} 3350, 1370, 960, 830.

4-Cyanocumene

4-Cyanocumene (156) was prepared by a Sandmeyer reaction using the diazonium salt formed from 4-isopropylaniline and cuprous cyanide (140). ^1Hmr (361.1 MHz, CDCl_3) δ 7.59(m, 2H), 7.33(m, 2H), 2.97(m, 1H), 1.27(d, 6H); IR 237B cm^{-1} 2240

4-Methoxycumene

4-Methoxycumene was prepared by the reaction of 4-isopropylphenol with dimethyl sulphate in 5% aqueous potassium hydroxide. The product was purified by column chromatography using silica gel. ^1Hmr (361.1 MHz, CDCl_3) δ 7.15(m, 2H), 6.85(m, 2H), 3.79(s, 3H), 2.86(m, 1H), 1.23(d, 6H);

IR 283B (neat) cm^{-1} 1620, 1520, 1250, 1040, 830.

Preparation of Cumyl bromides

The method of Grice and Owen (157) was used for the conversion of substituted cumyl alcohols to the bromides. Typically, the cumyl alcohol (0.02 mol) was dissolved in pentane or benzene (100 mL). Hydrogen bromide gas was passed through the solution for 0.5 h. The solution was then dried over anhydrous magnesium sulphate, filtered and the solvent removed at reduced pressure.

4.5.4. ESR Experiments

Hydrocarbon: A static solution of DTBP (0.3 mL) (158) and the hydrocarbon (30-60mg) was irradiated in the esr spectrometer cavity using filtered (methanol in a quartz tube) light from a 1 kW Hanovia Xe-Hg high pressure lamp. All samples were purged with nitrogen for 5 minutes prior to irradiation and examined at 253 K .

The observed spectra of the 4-methoxycumyl and 4-methoxyphenethyl radicals, generated by this procedure, were complicated by the competitive hydrogen abstraction from the methoxy methyl group. Simulation indicated a ratio of benzylic to α -aryloxymethyl radical of ca. 1 : 1. The α -aryloxy radicals were simulated by $a(\text{CH}_2) = 17.40 \pm 0.1$ and 17.65 ± 0.1 G, for the para-isopropyl and para-ethyl, respectively.

Cumylbromides. Three procedures were used to generate the cumyl radicals from the bromide.

In procedure 1, a static solution of DTBP (0.2 mL), triethylsilane (0.2 mL) and the bromide (50-100 mg) diluted if necessary with chlorobenzene was purged with nitrogen and irradiated as described above in the esr spectrometer cavity. The 4-tert-butylcumyl radical was generated by this procedure at 233 K.

In procedure 2, a solution of the bromide (50-100 mg) in tert-butylbenzene or chlorobenzene was continuously purged with nitrogen while hexamethylditin (0.1 mL) was injected via the purge tube. It was necessary to have a glass wool plug in the purge tube to filter the hexamethylditin. This solution was irradiated as described above. The use of chlorobenzene allowed cooling of the sample to temperatures as low as 233 K without precipitation of the hexamethylditin. The 4-fluoro and 4-ethyl derivatives were generated by this method at 263 K and 233 K, respectively.

In procedure 3, the bromide (100mg) was purged with nitrogen and hexabutyliditin(0.1mL) added in a glove box under an inert atmosphere. This solution was irradiated as described above. The 4-methyl derivative was generated by this method at 253 K.

Control experiments: Linearity of field was checked against the lines of $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ doped with 2%

[Co(NH₃)₅Cl]Cl₂ (158). Accuracy of the field was checked against the couplings for Wurster's blue perchlorate in ethanol (159). The effects of moderate temperature changes on the spectra of six representative cumyl radicals: 4-chloro, 4-isopropyl, 4-acetyl, 4-carbomethoxy, 4-benzoyl and 4-phenylsulfonyl were studied, by recording the spectrum at, 213, 233, 253, 273 and 333 K for 4-chloro; 233, 253 and 333 K for 4-acetyl; 213, 253 and 293 K for 4-isopropyl; 213 and 253 K for 4-carbomethoxy; 253 and 293 K for 4-benzoyloxy and 4-phenylsulfonyl. In all cases the benzylic ~~beta~~-hfc value was invariant. However, for the 4-isopropyl derivative, a change in the hfc value for the isopropyl group with a lowering of temperature was observed; indicating the hindered rotation of the isopropyl group.

EPILOGUE

The major objective of obtaining thermochemical parameters for open-shell systems has been realized in this work.

This work is the first example of the use of thermochemical cycles to obtain a direct estimate of the acidity of any closed- or open-shell organic species. It is also the first report of an acidity constant for a hydrocarbon radical cation. This method has been used recently to obtain the pK_a values of the radical cations of tetraphenylcyclopropane (160) and HMB (35), and should prove to be useful in the future.

A new definition of radical stability with special consideration of the effects of reference molecules is proposed. It is hoped that this approach will lead to a better understanding of the interactions in open-shell species.

The first quantitative evidence for linear relationships between esr hfc's and π -stabilization energy in π -radicals and the α - and β -hfc's in benzylic radicals is presented.

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Publications:

1. Thermochemical parameters for organic radicals and radical ions. 1. An estimation of the pK_a of radical cations based on thermochemical calculations. A.M. de P.Nicholas and D.R.Arnold. Can.J.Chem. 60, 2165 (1982).
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3. Radical ions in photochemistry. D.R.Arnold.* Gordon Research Conference. Organic Photochemistry. Andover, New Hampshire, U.S.A. 1983.
4. The stability of open-shell species. The relative net stabilization energy of alkyl radicals in the gas phase. A.M. de P.Nicholas and D.R.Arnold. 8th Canadian Symposium on Theoretical Chemistry. Halifax, N.S. Canada. 1983.
5. Substituent effects on ESR α - and β -hyperfine coupling constants in benzylic radicals. A.M. de P.Nicholas, D.R.Arnold and R.Subramanian. 67th Canadian Chemical Conference. Montreal, P.Q., Canada. 1984.

* A part of this presentation described my work on the acidity of radical cations.