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Stephen J. Blanksby

University of Wollongong, blanksby@uow.edu.au

John H. Bowie

University of Adelaide

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Carbanions: Formation, Structure and Thermochemistry

Stephen J. Blanksby¹ and John H. Bowie²

1. Department of Chemistry, University of Wollongong, New South Wales, Australia, 2522.
Phone: +61-2-4221 5484, Fax: +61-2-4221 4287, e-mail: blanksby@uow.edu.au
2. Department of Chemistry, The University of Adelaide, South Australia, 5005
Phone: +61-8-8303 5767, Fax: +61-8-8303 4358, e-mail: john.bowie@uow.edu.au

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Abstract

This chapter deals with even-electron carbanions: their formation, structure and thermochemical properties in the gas phase. There are a number of excellent reviews already available on the chemistry of carbanions: these discuss in the main, reactivity and anion molecule chemistry.¹⁻⁴ In this chapter we focus primarily on the formation, structure and thermochemistry of simple hydrocarbon anions while other chapters in this encyclopaedia cover the broader aspects of carbanion chemistry (see Volume 1, “Strained Ring and Highly Basic Carbanions” and this volume, Reactions of Organic Molecules with Organic Ions: “Reactions of Anions with Carbonyl Centres: C–C Bond Forming Reactions”, and Unimolecular Dissociations of Organic Ions: “Fragmentations of Carbanions and Enolate Anions Directed From the Anionic Centre: an Aid to Structure Determination”, and “Negative Ion Mass Spectra of Underivatised Peptides: an Aid to Sequence Determination”).

Keywords: carbanions, hydrocarbon anions, gas phase acidity, electron affinity, anion stability

1. The Formation of Carbanions

The majority of organic molecules have acidic hydrogens somewhere in the molecule which may be removed by deprotonation to form $[M-H]^-$ anions in the ion source of a mass spectrometer.² This method of ion formation is a form of negative ion chemical ionization and usually employs strong anionic gas phase bases such as NH_2^- , HO^- and MeO^- to bring about deprotonation (eq. 1). When the proton is abstracted from a carbon centre then the resulting anion is a *carbanion*.



Numerous gas phase carbanions, such as acetylenic, allylic and benzylic anions, are readily formed by deprotonation with a gas phase base (*cf.* eq. 1). The carbon centres of some molecules, however, possess only poorly acidic hydrogens which cannot be removed by anionic bases of the type described above. This situation exists for all saturated hydrocarbons. For example, the deprotonation of methane by the amide anion, $CH_4 + NH_2^- \rightarrow CH_3^- + NH_3$, is calculated to be endothermic by *ca.* 13 kcal mol⁻¹ (see later discussion of gas phase acidity) and thus the methyl carbanion cannot be formed by deprotonation.

A further disadvantage of the deprotonation method is observed for molecules with more than one potentially acidic centre. In such instances, deprotonation can lead to a mixture of isomeric anions or, in cases where there exists sufficient differences in acidity between the centres, only a single isomer which does not possess the desired regiochemistry may be formed. For example, the benzylic protons of ethyl benzene ($PhCH_2CH_3$) are substantially more acidic (> 20 kcal mol⁻¹) than either the homobenzylic protons ($PhCH_2CH_3$) or the ring protons and thus only the benzylic anion ($Ph\dot{C}HCH_3^-$) can be formed by deprotonation.⁵ Clearly, alternate methods of carbanion formation are required which (a) form carbanions from organic molecules which lack suitably acidic hydrogens and (b) are regioselective.

The most common alternatives to deprotonation for the generation of carbanions include; (i) the collision induced decarboxylation of a carboxylate anion (eq. 2), where the precursor carboxylate anion is generated by deprotonation of a carboxylic acid (RCO_2H), or by an $S_N2(C)$ reaction between a suitable nucleophile (NH_2^- , HO^- or MeO^-) and an ester (RCO_2R' , where R' is usually Me); (ii) the

collision induced elimination of formaldehyde from a primary alkoxide anion (eq. 3), where the precursor anion is formed by deprotonation of a suitable primary alcohol; and (iii) the gas phase $S_N2(\text{Si})$ reaction first used in the gas phase by DePuy and outlined in eq. 4 ($\text{Nu} = \text{F}, \text{RO}$).^{6,7} These three methods can be used to generate carbanions which cannot be formed by direct deprotonation and generally produce a single regioisomer with the charge site occupying the position of the displaced substituent.



2. Thermochemistry of carbanions

The gas phase acidity of a molecule RH is a particularly important thermochemical property because, among other things, it provides vital information concerning the reactivity of the corresponding anion R^- (see General Concepts: “Gas-phase Acidities, Experiment and Theory”). The gas phase acidity of a molecule RH is, by definition, the molar Gibbs free energy ($\Delta_{\text{acid}}G_{298}$) necessary to heterolytically dissociate it into a proton and an anion at 298 K according to eq. 5. In the case where heterolytic cleavage is of a C–H bond, a carbanion is produced. The enthalpy of eq. 5 is known as the enthalpy of deprotonation ($\Delta_{\text{acid}}H_{298}$) and is related to the gas phase acidity via $\Delta_{\text{acid}}G_{298} = \Delta_{\text{acid}}H_{298} - T\Delta_{\text{acid}}S_{298}$.^{8,9} The enthalpy of deprotonation can also be considered as the proton affinity (*PA*) of the anionic base R^- (i.e., the enthalpy of the reverse reaction in eq. 5). A large number of gas phase acidities have been measured and the values for a few selected hydrocarbons are listed in Table 1 (in units of kcal mol^{-1}). A regularly updated and readily searchable compilation of gas phase acidity data may be found on the NIST database.¹⁰



The measurement of the gas phase acidity of a molecule provides a convenient pathway for the determination of the heat of formation of the corresponding anion, which is critical for predicting the

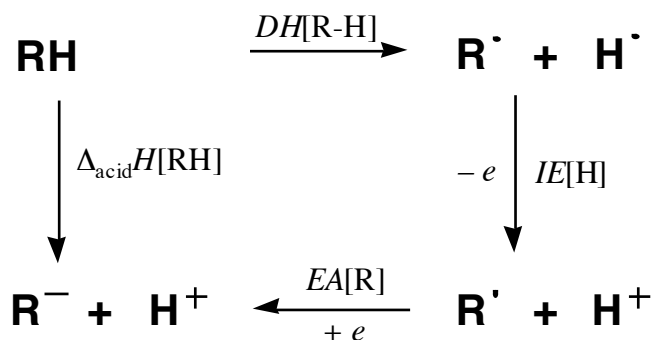
thermochemically favoured outcomes of anionic reactions. In the case of eq. 5, if the gas phase acidity is measured, then $\Delta_{\text{acid}}H_{298}[\text{RH}]$ can be determined, which is related to the heat of formation of the R^- anion via the relation, $\Delta_{\text{f}}H_{298}[\text{R}^-] = \Delta_{\text{acid}}H_{298}[\text{RH}] + \Delta_{\text{f}}H_{298}[\text{RH}] - \Delta_{\text{f}}H_{298}[\text{H}^+]$. In this expression, $\Delta_{\text{f}}H_{298}[\text{RH}]$ is the heat of formation of RH, which is usually available from calorimetry and $\Delta_{\text{f}}H_{298}[\text{H}^+] = 365.7 \text{ kcal mol}^{-1}$ is the precisely known heat of formation of H^+ .



Another important thermochemical property of carbanions (and anions generally) is the electron binding energy, which corresponds to the energy required to remove an electron from an anion. For an even-electron anion, such as that depicted in eq. 6, removal of an electron results in a neutral radical and a free electron. The enthalpy of this reaction is the electron binding energy, which is more commonly referred to as the electron affinity (*EA*) of the corresponding radical and is usually reported in units of electron volts. The electron affinity of a neutral is often used as an indicator of the “stability” of the corresponding anion. That is, if the electron affinity of R is positive, then the anion R^- is said to be “bound” or stable with respect to electron detachment, whereas if the electron affinity of R is negative, then the anion R^- is “unbound” or unstable with respect to electron detachment. In the latter case, a nascent anion formed by one of the methodologies discussed above (eq. 1-4) will spontaneously lose its electron to generate the neutral radical. The electron affinities of numerous carbon centred radicals are listed in Table 1 (in units of eV). It is apparent from these data that many carbanions – especially those formed from saturated hydrocarbons – are unbound and thus cannot be directly detected by mass spectrometry.

The enthalpy of deprotonation, $\Delta_{\text{acid}}H[\text{RH}]$, and the electron affinity, *EA*[R], are related to the homolytic R-H bond dissociation energy, *DH*[R-H], by the simple Hess relationship shown in Scheme 1, which includes the well established ionization energy of the hydrogen atom, *IE*[H].¹¹ The utility of this thermochemical relationship lies in the fact that if two of the key properties can be measured then the third can be derived. The negative-ion thermochemical cycle (Scheme 1) has provided much of the thermochemical information currently available for carbanions.

Scheme 1.



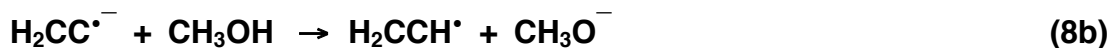
3.1 Thermochemistry of carbanions: gas phase acidity

Experimental methods for measuring gas phase acidities have been discussed in detail in a recent review.⁹ Some of the methods applicable to carbanion chemistry are briefly outlined here. Kinetics for the forward and reverse proton transfer reactions of an acid-base equilibrium can be measured using an ion cyclotron resonance or flowing afterglow mass spectrometer. These measurements provide the difference in gas phase acidity between the two acids (i.e. $\Delta\Delta_{\text{acid}}G_{298}$) and, where one of the acids is a reference of known gas phase acidity, the $\Delta_{\text{acid}}G_{298}$ of the target acid can be determined. For example, proton transfer kinetics were used to determine the gas phase acidity of acetylene by using hydrogen fluoride as a reference acid (eq. 7).¹²



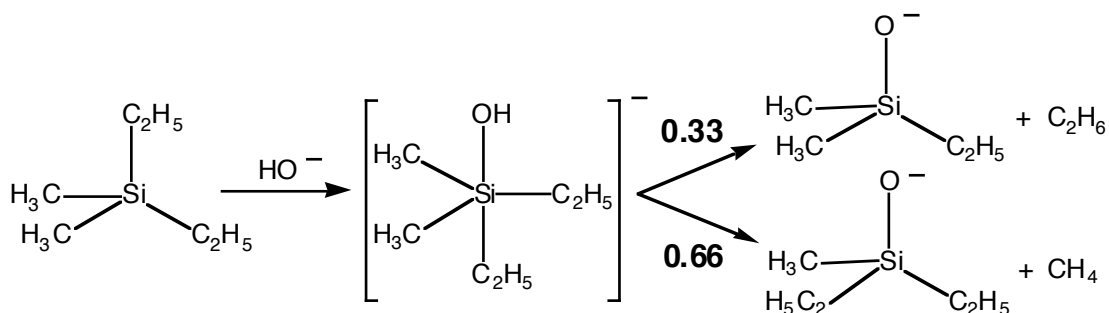
Proton transfer kinetics is perhaps the most precise method for measuring gas phase acidities but it suffers from two key limitations: namely, (i) the target carbanion must be stable and (ii) the conjugate acid must also be available as a stable, volatile reagent. For systems where the latter requirement is not met, such as for the vinyl radical, the gas phase acidity of a compound can sometimes be estimated by “bracketing” the reactivity of the carbanion. That is, by allowing the carbanion to react with increasingly stronger acids until one is found which undergoes proton transfer to the anion. For example, the vinylidene radical anion (eq. 8) has been shown to abstract a proton from methanol ($\Delta_{\text{acid}}G_{298}[\text{CH}_3\text{OH}] = 375.1 \pm 0.6 \text{ kcal mol}^{-1}$) but not from water ($\Delta_{\text{acid}}G_{298}[\text{H}_2\text{O}] = 383.9 \pm 0.3 \text{ kcal}$

mol⁻¹) thus bracketing the gas phase acidity of the vinyl radical as $\Delta_{\text{acid}}G_{298}[\text{CH}_2\text{CH}] = 378 \pm 3$ kcal mol⁻¹.¹²



More challenging, however, is the determination of the gas phase acidity of a system RH where R⁻ is unbound. DePuy and co-workers have developed a general method for determining the gas phase acidities of alkanes for which R⁻ is unbound.^{2,13} The methodology is illustrated for a particular example in Scheme 2. In this case, dimethyl diethylsilane reacts with hydroxide anions to form the trigonal bipyramidal silicon anion intermediate which decomposes by two competitive processes eliminating ethane and methane respectively. Both product channels require a build up of negative charge on the migrating alkyl group and thus the alkyl group better able to accommodate the charge migrates preferentially. Experimentally, loss of methane was found to be double that of ethane (Scheme 2), thus methane is a stronger acid than ethane (as predicted theoretically)¹⁴ and the ethyl anion (although unbound) is in theory a stronger gas phase base than the methyl anion. By using the $\Delta_{\text{acid}}G_{298}[\text{CH}_4] = 408.6 \pm 0.8$ kcal mol⁻¹ as a reference¹⁵ the gas phase acidity of ethane was determined to be $\Delta_{\text{acid}}G_{298}[\text{CH}_3\text{CH}_3] = 411.4$ kcal mol⁻¹.

Scheme 2



This method has been applied to a range of hydrocarbons and has generated many of the gas phase acidities listed in Table 1. These data can be employed to derive the electron affinities of hydrocarbon radicals. For example, using a C–H bond dissociation energy for ethane of $DH_{298}[\text{CH}_3\text{CH}_2\text{-H}] = 100.1$

kcal mol⁻¹, combined with $\Delta_{\text{acid}}H_{298}[\text{CH}_3\text{CH}_3] = 420.1$ kcal mol⁻¹ (derived from the $\Delta_{\text{acid}}G_{298}[\text{CH}_3\text{CH}_3]$), and $IE[\text{H}] = 313.6$ kcal mol⁻¹ gives an electron affinity of the ethyl radical of $EA[\text{CH}_3\text{CH}_2] \cong -6$ kcal mol⁻¹ (*cf.* Scheme 1). Such determinations establish the stability (or otherwise) of carbanions in the gas phase with respect to electron detachment.

While the DePuy method for measuring the relative gas phase acidities of hydrocarbon anions was effective in determining the thermochemical properties of such species it was Graul and Squires who first generated many of these anions using the decarboxylation and deformylation reactions outlined in eq. 2 and 3.^{5,16} These authors were able to demonstrate experimentally that some alkyl carbanions were stable in the gas phase, with a lifetime of at least 25 μs (a typical ion flight time in their selected ion flow tube). Furthermore, through precise measurement of the threshold energy (E_{T}) of the decarboxylation and deformylation reactions the heat of formation of the anion could be determined and thus $\Delta_{\text{acid}}H_{298}[\text{RH}]$ and $EA[\text{R}]$ could be derived. For example, the decarboxylation of the cyclopropane carboxylate anion was found to require $E_{\text{T}} = 59.5$ kcal mol⁻¹ which corresponds to the reaction enthalpy of eq. 9; $E_{\text{T}} = \Delta_{\text{f}}H_{298}[\text{c-C}_3\text{H}_5^-] + \Delta_{\text{f}}H_{298}[\text{CO}_2] - \Delta_{\text{f}}H_{298}[\text{c-C}_3\text{H}_5\text{CO}_2^-]$. Given these data, the heat of formation of the cyclopropyl anion, $\Delta_{\text{f}}H_{298}[\text{c-C}_3\text{H}_5^-]$, and thus the enthalpy of deprotonation of cyclopropane were derived, $\Delta_{\text{acid}}H_{298}[\text{c-C}_3\text{H}_6] = 408 \pm 5$ kcal mol⁻¹.



3.2 Thermochemistry of carbanions: electron affinity

For instances where a stable gas phase carbanion can be produced, negative ion photoelectron spectroscopy (NIPES) provides the most precise measure of electron affinity. The various experimental methods utilized in photoelectron spectroscopy have recently been reviewed.¹⁷ All of these techniques involve the removal of the excess electron from an anion by a photon as illustrated for the methyl anion in eq. 10. In most cases a fixed frequency laser ($h\nu$) is used to bring about electron detachment and the kinetic energies of the photoelectrons (eKE) are measured and related to the electron affinity by, $EA = h\nu - eKE$.



NIPES has been used to measure the electron binding energies of a range of carbanions usually to a precision of within 10 meV (0.23 kcal mol⁻¹). Ellison and co-workers have compiled a critically evaluated list of atomic and molecular electron affinities¹⁷ and an updated compendium is also located on the NIST database.¹⁰ Selected electron affinity values are listed in Table 1 with those determined by NIPES marked with an asterisk, while the remainder have been determined by the indirect methods described above (Scheme 1).

Table 1

4. The structure, stability and reactivity of carbanions.

Carbanions are an interesting group of anions with an incredible variation in physical properties depending on the bonding environment of the charged carbon. For example, the electron binding energies of carbon centred anions range from anions which are unbound with respect to electron detachment (e.g., $EA[\text{CH}_3\text{CH}_2\cdot] = -0.260$ eV), through to tightly bound anions such as acetylide, $EA[\text{HCC}\cdot] = 2.969$ eV. Similarly, the gas phase acidity of the conjugate hydrocarbon acids ranges from 347 – 411 kcal mol⁻¹. Representative examples covering the range of carbanion properties are discussed individually below.

4.1 Alkyl carbanions

From the examples listed in Table 1 one might surmise that saturated hydrocarbons are extremely weak gas phase acids while the corresponding radicals have low (or often negative) electron affinities. Both of these observations reflect the poor stability of the carbanions formed from saturated hydrocarbons and for some time it was believed that no such species could be generated in the gas phase. In 1978 however, Ellison, Engelking and Lineberger published the first observation of the CH_3^- anion in the gas phase.¹⁵ These authors obtained a photoelectron spectrum of CH_3^- which revealed a progression of peaks corresponding to excited vibrational states of the methyl radical (Figure 1a). The fundamental for this progression was determined to be 605 cm⁻¹, which corresponds

to the umbrella-like hydrogen-bending mode of the methyl radical. The vibrational progression observed in the photoelectron spectrum was fitted theoretically using pyramidal anion and planar neutral geometries. The fitted theoretical curves for anion and neutral potentials are illustrated in Figure 1b and show that inversion of the pyramidal anion requires some 460 cm^{-1} (or 1.3 kcal mol^{-1}). The geometrical description of a pyramidal methyl anion has since been strongly supported by electronic structure calculations.^{14,18,19}

Figure 1.

The experimental electron affinities listed in Table 1 indicate the stability of a range of alkyl carbanions with respect to electron detachment. Selected carbanion binding energies are plotted against increasing substitution of the carbanion centre in Figure 2. Interestingly, this figure reveals that although the methyl anion is bound, the primary ethyl anion is unbound with respect to electron detachment. This suggests that the addition of a methyl substituent to a carbanion centre results in *destabilization* of the anion. Whilst this observation may appear initially surprising, analogous alkoxide and alkylamide anions also exhibit this trend (Figure 2). Furthermore, all three anion-types demonstrate a near linear increase in anion stabilization with substitution at the β -position. This increase in stabilization is such that the neopentyl carbanion has been detected experimentally.⁵ Figure 2 suggests that the destabilizing inductive effects of α -substitution are counteracted by the stabilization gained from β -substitution. The latter has been attributed to hyperconjugation, which involves a stabilizing interaction between the non-bonding electron pair of the anion and an anti-bonding sigma orbital on the β -carbon (i.e., stabilization due to the resonance contributors $(\text{CH}_3)_3\text{C}-\text{CH}_2^- \leftrightarrow [(\text{CH}_3^-)(\text{CH}_3)_2\text{C}=\text{CH}_2]$). Such interactions are consistent with theoretical calculations of the structure of carbanions, which predict a truncated $\text{C}_\alpha-\text{C}_\beta$ bond and an elongated $\text{C}_\beta-\text{CH}_3$ bond antiperiplanar to the carbanion (Figure 3).¹⁹

Figures 2 & 3.

The cyclic saturated hydrocarbons cyclopropane and cubane are both more acidic than comparable secondary and tertiary acyclic systems such as *iso*-propane and *tert*-butane (Table 1). Indeed, the cyclopropyl and cubyl carbanions have both been detected in the gas phase.^{20,21} The gas phase acidity of cyclopropane, $\Delta_{\text{acid}}G_{298}[\text{c-C}_3\text{H}_6] = 408.2 \text{ kcal mol}^{-1}$ falls between the secondary protons of propane and the protons of ethylene, $\Delta_{\text{acid}}G_{298}[(\text{CH}_3)_2\text{CH-H}] = 411.4 \text{ kcal mol}^{-1}$ and $\Delta_{\text{acid}}G_{298}[\text{CH}_2\text{CH}_2] = 401.0 \text{ kcal mol}^{-1}$. This trend is consistent with increasing stabilization of the carbanion with increasing s-orbital character in the hybridization of the carbon. Kass has quantified this correlation by plotting the $^{13}\text{C-H}$ coupling constant (from nuclear magnetic resonance spectroscopy) against $\Delta_{\text{acid}}H_{298}[\text{RH}]$ for a range of simple saturated, unsaturated and cyclic hydrocarbons (Volume 1, "Strained Ring and Highly Basic Carbanions"). Increasing s-character in the hybridization of carbon can also explain the stability of the cubyl anion and is consistent with the well known stability of bridgehead anions in solution. Bridgehead carbons are constrained to a pyramidal geometry, which stabilizes a carbanion at this position but destabilizes the corresponding radical, which prefers a planar configuration (see CH_3^- discussion above). Stabilization of the anion and concomitant destabilization of the corresponding neutral results in a significant electron affinity, $EA[\text{cubyl radical}] = 0.5 \text{ eV}$.

While these relatively simple ideas of hyperconjugation and hybridization are instructive in a number of cases, they are by no means universal. Qualitative prediction of carbanion stability increases in complexity for systems where hybridization, substitution, strain energy, polarization and inductive effects may all contribute to stabilization and/or destabilization of the carbanion.

4.2 Allyl and benzyl anions.

Unsaturated hydrocarbons, which possess allylic or benzylic hydrogens are substantially more acidic than their saturated counterparts. For example, propene and toluene have gas phase acidities of $\Delta_{\text{acid}}G_{298}[\text{CH}_2\text{CHCH}_3] = 382.5 \text{ kcal mol}^{-1}$ and $\Delta_{\text{acid}}G_{298}[\text{PhCH}_3] = 372.1 \text{ kcal mol}^{-1}$ respectively (Table 1), and are therefore readily deprotonated by chemical ionization reagents such as HO^- and NH_2^- (*cf.* eq. 1). Deprotonation yields allyl and benzyl carbanions, which are resonance stabilized and thus stable with respect to electron detachment.

The photoelectron spectrum of the allyl anion has been measured and shows a pronounced progression in ν_7 of the allyl radical, which has a fundamental of 425 cm^{-1} and corresponds to the CCC

bending mode.^{22,23} The most intense peak observed in this spectrum corresponds to the $0 \leftarrow 0$ transition (i.e., the photoelectron transition from the ground vibrational state of the anion to the ground vibrational state of the neutral) which allows for an assignment of $EA[\text{CH}_2\text{CHCH}_2] = 0.481 \pm 0.008$ eV and suggests geometrical congruence between the anion and the neutral radical. Given that the structure of the neutral has been precisely determined from high resolution spectroscopy, the anion geometry may be optimized to obtain a best fit for the photoelectron data.²³ Unlike the pyramidal alkyl carbanions discussed above, the allyl anion is found to be planar with C_{2v} symmetry (Figure 4) as would be expected from the delocalization of the negative charge.

Figure 4.

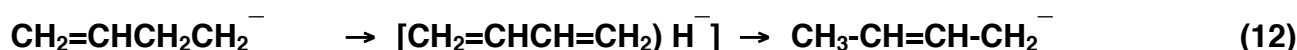
The photoelectron spectrum of the benzyl anion has also been measured providing an $EA[\text{PhCH}_2] = 0.912 \pm 0.006$ eV but given the complexities of this spectrum, little structural information regarding the structure of the anion has been derived. Electronic structure calculations suggest that there is a significant contraction of the Ph-CH₂ bond length in the benzyl anion compared to toluene which is indicative of delocalization of the charge onto the aromatic ring system.²⁴

In addition to the spectroscopy described above, DePuy and co-workers have developed a chemical method for the identification of allylic and benzylic anions in the gas phase by observing the rapid hydrogen-deuterium exchange reaction between such anions and D₂O.² For example, upon reaction with D₂O the *para*-xylyl anion exchanges all five of its benzylic hydrogens for deuterons leading to a mass shift of 5 Da whereas, in contrast, the isobaric ethyl benzene anion can exchange only two.

4.3 Homoallyl and homobenzyl anions

There has been much debate concerning the stability of substituted ethyl anions, X-CH₂CH₂⁻. The gas phase acidity and electron affinity data recorded in Table 1 indicate that the homoallyl (CH₂=CH-CH₂CH₂⁻) and homobenzyl (Ph-CH₂CH₂⁻) anions are stable species. Such unusual stability has been attributed to anionic hyperconjugation (i.e., stabilization due to CH₂=CH-CH₂CH₂⁻ ↔ [(CH₂=CH⁻)CH₂=CH₂] resonance contributions), and to inductive effects.²⁵ If β-ethyl anions are energized

however, they may rearrange to more stable isomers. For example, when the homoallyl anion is formed by the collision induced decarboxylation process shown in eq. 11, evidence based on appearance energy measurements⁵ and gas phase acidity bracketing²⁶ indicate that the product carbanion is not the homoallyl anion, $\Delta_{\text{acid}}H_{298}[\text{CH}_2=\text{CHCH}_2\text{CH}_2^-] = 412 \text{ kcal mol}^{-1}$, but deprotonated 2-butene, $\Delta_{\text{acid}}H_{298}[\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2^-] = 393 \text{ kcal mol}^{-1}$.^{13,26} This suggests that decarboxylation leads to rearrangement of the homoallyl anion, presumably by the mechanism shown in eq. 12.



Such experimental limitations mean that very few β -substituted ethyl anions ($\text{X}-\text{CH}_2\text{CH}_2^-$) have been experimentally identified in the gas phase. Only a handful of such anions, including $\text{X} = \text{CN}$, CF_3 and CH_3CO , have been shown to be stable with respect to electron detachment, rearrangement and elimination (i.e. $\text{X}-\text{CH}_2\text{CH}_2^- \rightarrow \text{X}^- + \text{CH}_2\text{CH}_2$) reactions.^{5,27} Noest and Nibbering have shown that the related β -substituted ethyl anions $^- \text{CH}_2\text{C}(\text{CH}_3)_2-\text{CHO}$ and $^- \text{CH}_2\text{C}(\text{CH}_3)_2-\text{NO}$ are also surprisingly stable with both species readily exchanging methyl hydrogens for deuteriums in the presence of D_2O .²⁸

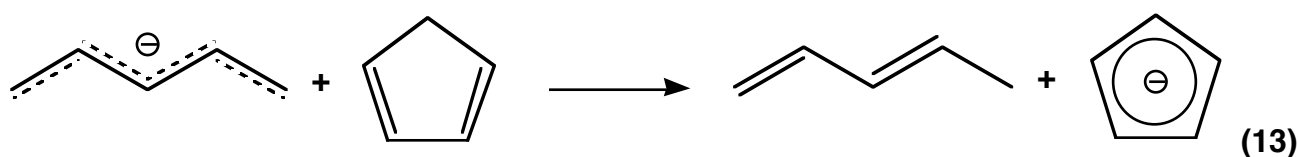
4.4 The vinyl and phenyl anions

Both ethylene and benzene can be deprotonated by reaction with NH_2^- in the gas phase (*cf.* eq. 1) to form vinyl and phenyl anions respectively. Consequently, ammonia has been employed as a reference for measuring the precise gas phase acidities of both compounds via proton transfer kinetics (*cf.* eq. 7). The vinyl and phenyl anions show significant stability with respect to electron detachment ($EA[\text{CH}_2\text{CH}^\bullet] = 0.667 \pm 0.024 \text{ eV}$ and $EA[\text{C}_6\text{H}_5^\bullet] = 1.096 \pm 0.006 \text{ eV}$)^{12,24} which is largely attributed to the sp^2 hybridization of the carbanion centre.

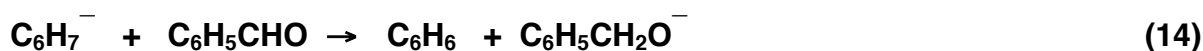
4.5 Cyclopentadiene and Cyclohexadiene

The cyclopentadienyl anion is an important ligand in numerous organometallic complexes: most famously in ferrocene. In the gas phase, the C_5H_5^- anion can be formed by deprotonation of cyclopentadiene and the electron affinity of the cyclopentadienyl radical, $EA[\text{C}_5\text{H}_5^\bullet] = 1.786 \pm 0.020$

eV, has been measured by photoelectron spectroscopy.²⁹ The electron affinity of the radical, combined with the measured C–H homolytic bond dissociation energy of cyclopentadiene provides a gas phase acidity of $\Delta_{\text{acid}}G_{298}[\text{C}_5\text{H}_6] = 347.7 \pm 2.0 \text{ kcal mol}^{-1}$, via the negative ion thermochemical cycle shown in Scheme 1. The stability of C_5H_5^- with respect to the corresponding neutral ($\text{C}_5\text{H}_5^\bullet$) and protonated forms (C_5H_6) can be attributed to the aromatic stabilization of the carbanion which satisfies the Hückel $(4n + 2)\pi$ electron rule. Using the gas phase acidities of cyclopentadiene and pentadiene, a reaction enthalpy for eq. 13 of $\Delta_{\text{rxn}}H_{298} \cong 16 \text{ kcal mol}^{-1}$ can be determined, which represents an estimate for the aromatic stabilization energy in the cyclopentadienyl anion.



In contrast to eq. 13, the analogous reaction between the pentadienyl anion and cyclohexadiene is essentially thermoneutral due to the absence of aromatic stabilization in the cyclohexadienyl anion. Interestingly, DePuy and co-workers have demonstrated that the cyclohexadienyl anion acts as an efficient gas phase reducing agent by transferring a hydride anion and thus forming aromatically stabilized benzene (e.g., eq. 14).³⁰



4.6 Acetylide and polyacetylide anions.

Acetylene is one of the most acidic hydrocarbons listed in Table 1 and thus the acetylide anion is readily produced via deprotonation of acetylene with almost any basic anion (*cf.* eq. 1). The stability of the carbanion is attributed to the significant s-character ($\cong 50\%$) of the charge bearing sp-hybridized carbon. The photoelectron spectrum of the acetylide anion was recorded by Ervin and Lineberger and provides a precise measure of the electron affinity of the acetylide radical, $EA[\text{HCC}] = 2.969 \pm 0.006 \text{ eV}$.³¹ This electron affinity is by far the largest reported in Table 1 and reflects the incredible stability of the acetylide anion with respect to the acetylide radical. Hotbands identified in the photoelectron spectrum of HC_2^- have been assigned to the HCC bending and CC stretching fundamentals of the

anion, $\nu_2 = 505 \pm 20 \text{ cm}^{-1}$ and $\nu_3 = 1800 \pm 20 \text{ cm}^{-1}$ respectively. These values are lower than the corresponding fundamentals in acetylene (612 cm^{-1} and 1974 cm^{-1} respectively)¹⁰ and are in good agreement with the *ab initio* calculations of Botschwina that predict a linear geometry for the acetylide anion with equilibrium bond lengths of $R_e(\text{C-C}) = 1.2463 \text{ \AA}$ and $R_e(\text{C-H}) = 1.0696 \text{ \AA}$.³²

Polyacetylide anions, HC_n^- where n is even, can also be generated in the gas phase, usually by electrical discharge in an acetylene rich environment. The HC_4^- , HC_6^- and HC_8^- carbanions have been prepared in this way and their photoelectron spectra recorded. The electron binding energy of these species increase with increasing carbon chain length up to almost 4 eV.³³ The HC_n^- carbanions represent some of the most tightly bound anions identified thus far and have even been shown to have stable excited electronic states below the electron detachment threshold.³⁴ Perhaps not surprisingly, HC_n^- carbanions for which n is odd have proven difficult to generate in acetylene discharges. Bowie and co-workers have devised a gas phase synthesis that targets such species and have successfully prepared HC_3^- , HC_5^- and HC_7^- using substituted polyacetylene precursors such as those in eq. 15.³⁵



Several long chain neutral cumulenes of the form, HC_n , have been identified in interstellar and circumstellar gas clouds via radioastronomy. Given the large electron affinities of such species, it has been proposed that the analogous HC_n^- carbanions might also be formed in these environments either via electron attachment or by hydrogen addition to carbon chain anions (eq. 16).³⁶ The latter reaction has been observed by Bierbaum and co-workers in a flowing afterglow apparatus for carbon chain carbanions, C_n^- where $n \geq 7$.³⁷



References

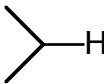
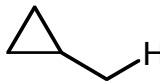
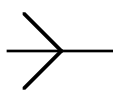

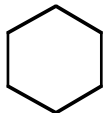


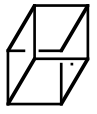
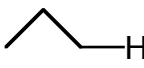
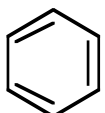
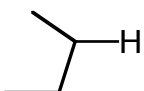
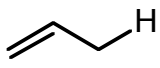
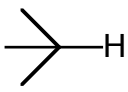
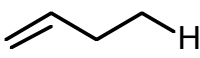
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Table 1. The gas phase acidities of a representative group of hydrocarbons are listed below along with the electron affinities of the corresponding free radicals. These thermochemical properties have been determined using the various experimental methodologies described in Section 2. The absolute uncertainties in the $\Delta_{\text{acid}}G_{298}$ values listed are typically ± 2 kcal mol⁻¹, although the relative gas phase acidity scale is of much greater precision. Similarly, most of the electron affinities listed here are derived via Scheme 1 and thus have an associated uncertainty of at least ± 0.1 eV. The values marked with an asterisk (*) indicate electron affinities which have been precisely measured via negative ion photoelectron spectroscopy (NIPES) with uncertainties of *ca.* ± 0.01 eV.

Hydrocarbon	$\Delta_{\text{acid}}G_{298}[\text{RH}]$ kcal mol ⁻¹	$EA[\text{R}]$ eV	Hydrocarbon	$\Delta_{\text{acid}}G_{298}[\text{RH}]$ kcal mol ⁻¹	$EA[\text{R}]$ eV
	411.4	-0.321		402.1	0.147
CH ₃ CH ₃	411.4	-0.260	CH ₂ =CH ₂	401.0	0.667*
CH ₄	408.6	0.080*		400.1	0.230
	408.4	-0.317		398.0	N/A
	408.2	0.397	Ph-CH ₂ -CH ₂ -H	397.7	0.343
	407.4	-0.195		396.5	0.5
	407.2	-0.074		392.9	1.096*
	407.1	-0.121		382.5	0.481*
	405.7	-0.156	Ph-CH ₂ -H	372.1	0.912*
	404.0	0.082	HC≡CH	369.8	2.969*

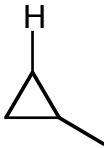
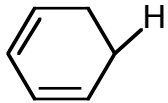
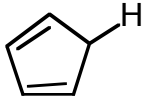
	403.3	0.373		365.8	0.71
				347.2	1.786*

Figure Captions:

Figure 1. (a) The photoelectron spectrum of the methyl anion showing the ground state transition from anion to neutral (2_0^0) which corresponds to the electron affinity of the methyl radical. The spectrum also shows the progression of excited vibrational states of the methyl radical in ν_2 as well as the first excited vibrational state of the anion in ν_2 (2_1^0), which appears as a hotband. (b) Computed potential energy curves for the methyl anion and neutral methyl radical. The anion is shown to have a barrier to inversion whereas no significant barrier could be fitted to the neutral potential. These data suggest that the ground state geometries of the anion and neutral are pyramidal and planar respectively. Figures are reproduced from Ellison *et al.*¹⁵ with the permission of the American Chemical Society.

Figure 2. The electron affinity of carbon, nitrogen and oxygen centred radicals RX [where X = C, N, O] plotted against the anion substituents R [where R = H, CH₃, CH₃CH₂, (CH₃)₂CH, (CH₃)₃C]. All data points are taken from Graul and Squires and references cited therein.⁵

Figure 3. The structure of the neopentyl anion calculated at the RB3LYP/6-311++G(2d,p) level of theory. These data are taken from Sauers.¹⁹

Figure 4. (a) The structure of the allyl anion derived by Wenthold *et al.* from the photoelectron spectrum of the anion²³ and the known geometry of the neutral allyl radical (b).

Figure 1a

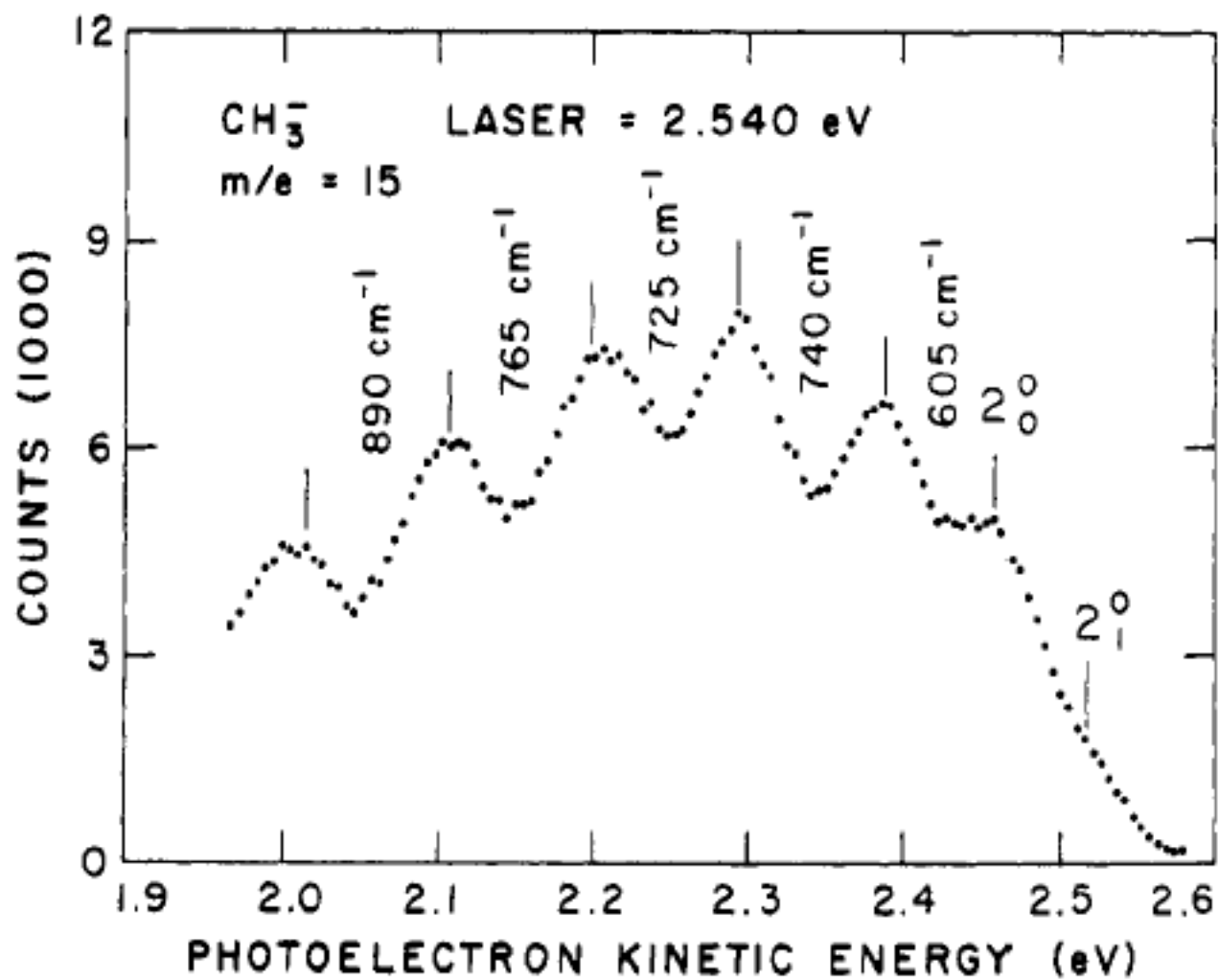


Figure 1b

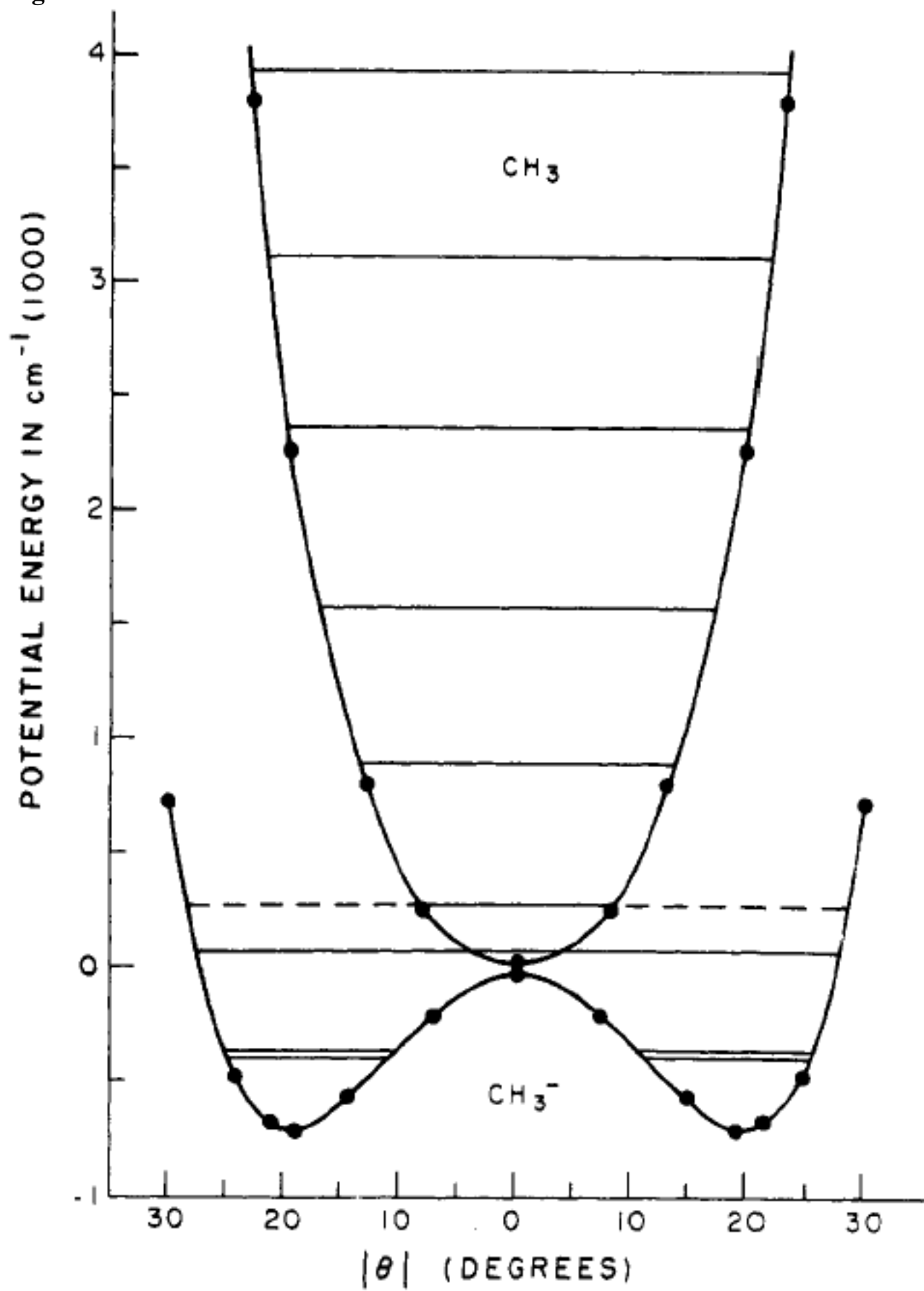


Figure 2.

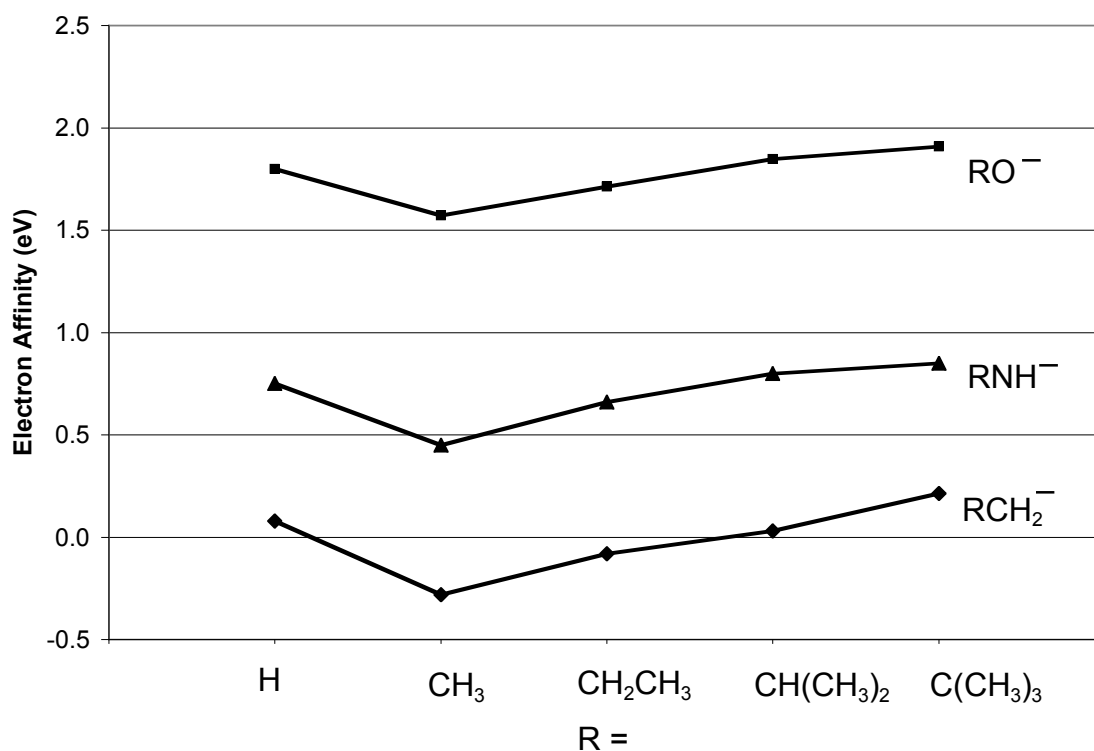


Figure 3.

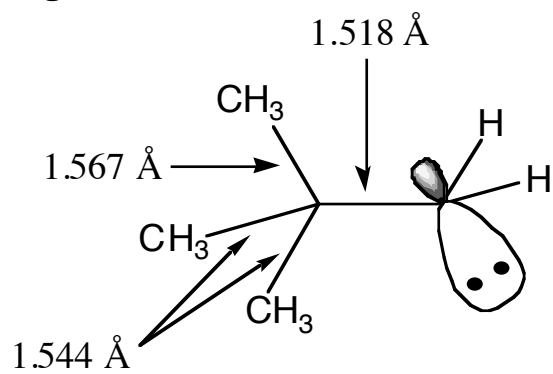


Figure 4.

