# The C−H Bond Energy of Benzene

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**Abstract:** A flowing afterglow/selected ion flow tube instrument has been used to measure the rates of reaction of amide ion with benzene and phenide ion with ammonia: $C_6H_6 + NH_2^- \rightleftharpoons C_6H_5^- + NH_3$. The ratio of these rate constants gives a free energy change: $\Delta_{\text{reaction}}G_{300} = -3.58 \pm 0.06$ kcal mol$^{-1}$. Use of the established gas-phase acidity of ammonia gives a value for $\Delta_{\text{acid}}G_{300}(C_6H_6)$ of 392.9 ± 0.4 kcal mol$^{-1}$. From the computed value for $\Delta_{\text{acid}}S_{300}(C_6H_6)$ of 29.6 ± 1.0 cal mol$^{-1}$ K$^{-1}$, the enthalpy change, $\Delta_{\text{acid}}H_{300}(C_6H_6) = 401.7 \pm 0.5$ kcal mol$^{-1}$, is derived. The enthalpy of deprotonation of benzene, the C−H bond dissociation energy, and the electron affinity of the phenyl radical are simply related to each other: $\Delta_{\text{acid}}H_{300}(C_6H_6) = DH_{300}(C_6H_5{-}H) + \text{IP(H)} - \text{EA}(C_6H_5)$. Since earlier photoelectron experiments have provided a value for the electron affinity for the phenyl radical, $\text{EA}(C_6H_5) = 25.3 \pm 0.1$ kcal mol$^{-1}$, the enthalpy of deprotonation can be used to extract a value for the C−H bond enthalpy of benzene at 300 K and the C−H bond energy at 0 K, $D_0$. These bond energies are used to compute the heats of formation of the phenyl radical at 0 and 300 K: $DH_{300}(C_6H_5{-}H) = 113.5 \pm 0.5$ kcal mol$^{-1}$, $\Delta_fH_{300}(C_6H_5) = 81.2 \pm 0.6$ kcal mol$^{-1}$; $D_0(C_6H_5{-}H) = 112.0 \pm 0.6$ kcal mol$^{-1}$, $\Delta_fH_0(C_6H_5) = 84.3 \pm 0.6$ kcal mol$^{-1}$.

## Introduction

Benzene is an important organic molecule and its thermochemistry has implications in many areas of chemistry. The phenyl radical is one of the most common aromatic radicals and is encountered frequently in many free-radical processes,[1] in atmospheric chemistry, and in combustion processes. The C−H bond energy of benzene is widely quoted[2] as lying in the 110−111 kcal mol$^{-1}$ range. But as has been strongly emphasized,[3] it is essential to know the heats of formation of simple radicals like $C_6H_5$ to an uncertainty of about ±1 kcal mol$^{-1}$ in order to assess properly the stability of diradicals.

We have used a combination of **gas-phase ion chemistry** and **negative ion photoelectron spectroscopy** to study the thermochemistry of benzene. The values of the enthalpy of deprotonation and C−H bond dissociation energy (BDE) of benzene determined in this study are slightly, but significantly, different from earlier values. The following quantities are determined: $\Delta_{\text{acid}}H_{300}(C_6H_6) = 401.7 \pm 0.5$ kcal mol$^{-1}$, $DH_{300}(C_6H_5{-}H) = 113.5 \pm 0.5$ kcal mol$^{-1}$, and $D_0(C_6H_5\text{-}H) = 112.0 \pm 0.6$ kcal mol$^{-1}$.

**A. Radical Chemistry of Benzene.** To begin we summarize some of the earlier studies of the C−H bond energy of benzene or, equivalently, the heat of formation of the phenyl radical.

In a comprehensive review of benzene published nearly 30 years ago,[4] Kerr tentatively recommended a C−H bond energy for $C_6H_6$ of 104 ± 2 kcal mol$^{-1}$. Some of the earlier studies included the pyrolysis[5] of iodobenzene (108 kcal mol$^{-1}$), the thermal decomposition[6] of bromobenzene (105.5 kcal mol$^{-1}$), and the abstraction reactions[7,8] of methyl radicals with benzene (102 kcal mol$^{-1}$). In later studies of hydrogen abstraction by $CF_3$ radicals[9,10] it was shown that radical "abstractions" of H atoms from the aromatic ring likely occur *via* addition to the aromatic ring to form a cyclohexadienyl radical followed by disproportionation. In a study of the kinetics of the reaction $CF_3 + C_6H_6 \rightleftharpoons HCF_3 + C_6H_5$, it was deduced that $\Delta_fH_{298}(C_6H_5) = 77.7 \pm 2.0$ kcal mol$^{-1}$ and $DH_{298}(C_6H_6) = 110.0 \pm 2.0$ kcal mol$^{-1}$. Recent "cavity ring down" photolysis experiments of $C_6H_5NO$ have studied the reaction of the phenyl radical with HBr and DBr.[11]

The reactions occurring in a mixture of iodobenzene and $I_2$ were studied in the gas phase[12] over the temperature range of 375−500 °C.

$$I_2 + M \rightleftharpoons 2I + M \tag{1}$$

$$C_6H_5I + I \rightleftharpoons C_6H_5 + I_2 \tag{2}$$

$$C_6H_5 + HI \rightleftharpoons C_6H_6 + I \tag{3}$$

A study of the kinetics of the conversion of $C_6H_5I$ led to Arrhenius parameters for $k_2$ (i.e., $A_2$ and $E_2$) and it was conjectured that $E_{-2} \simeq 0$. It was found that $\log k_2 = (11.36 \pm 0.06) - (28.4 \pm 0.2)/RT$ and $E_{-2}$ was set to (0 ± 1) kcal mol$^{-1}$. This treatment yielded $\Delta_fH_{298}(C_6H_5) = 80.0 \pm 1$ kcal mol$^{-1}$ and $DH_{298}(C_6H_6) = 112.3 \pm 1$ kcal mol$^{-1}$. However, these results are dependent on the precise value chosen for $\Delta_fH_{298}(C_6H_5I)$. Later workers have reconsidered the findings of

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Rodgers *et al.* with revised values of $\Delta_f H_{298}(C_6H_5I)$; this reanalysis[10] leads to $DH_{298}(C_6H_6) = 110.9 \pm 1.6$ kcal mol$^{-1}$.

The decomposition of $C_6H_5I$ to phenyl radical and atomic iodine in a shock tube has also been scrutinized. Earlier high temperature experiments[13] led to a value for $\Delta_f H_{300}(C_6H_5) = 335 \pm 8$ kJ mol$^{-1}$ (80.1 ± 1.9 kcal mol$^{-1}$). More recent shock tube studies of this same decomposition lead[14] to a value of $\Delta_f H_{1100}(C_6H_5) = 322.3$ kJ mol$^{-1}$ which was corrected to $\Delta_f H_{300}(C_6H_5) = 340.5 \pm 11$ kJ mol$^{-1}$ (81.4 ± 2.6 kcal mol$^{-1}$). A C−H bond enthalpy of benzene was extracted from this heat of formation: $DH_{300}(C_6H_5{-}H) = 475 \pm 11$ kJ mol$^{-1}$ (113.5 ± 2.6 kcal mol$^{-1}$).

Because the C−H BDE and the value for $\Delta_f H(C_6H_5)$ are directly linked, the bond energies of a large number of substituted benzenes ($C_6H_5X \rightarrow C_6H_5 + X$) are connected to the $C_6H_6$ BDE. As an example, the very low pressure pyrolysis (VLPP) of $C_6H_5X$ has been examined.[15] From the VLPP kinetic data and with the assumption that $\Delta_f H_{298}(C_6H_5) = 78$ kcal mol$^{-1}$, a set of [$C_6H_5{-}X$] bond strengths is reported.

| compd | $DH_{298}[C_6H_5{-}X]$/kcal mol$^{-1}$ |
|---|---|
| $C_6H_5{-}CH_3$ | 100 |
| $C_6H_5{-}H$ | 110 |
| $C_6H_5{-}I$ | 65 |
| $C_6H_5{-}NO$ | 51 |
| $C_6H_5{-}CF_3$ | 106 |
| $C_6H_5{-}Cl$ | 94 |
| $C_6H_5{-}OH$ | 110 |
| $C_6H_5{-}F$ | 124 |

In their comprehensive review of hydrocarbon bond energies,[2] McMillen and Golden noted that all of the chemical evidence points to a strong C−H bond in benzene in the range of 110 kcal mol$^{-1}$, and they recommended a value of $DH_{298}(C_6H_6) = 110.9 \pm 2$ kcal mol$^{-1}$.

**B. Photoionization Mass Spectroscopy of Benzene.** Photoionization mass spectrometry (PIMS) can also be used to measure bond energies. This procedure has recently been reviewed[16] and the discussion of PIMS studies of benzene will be summarized here. Photoionization mass spectrometry enables one to measure the appearance potential [$E_{AP}(C_6H_5^+,C_6H_6)$] of the dissociative process, AP($C_6H_5^+,C_6H_6$).

$$C_6H_6 + h\nu_{AP} \rightarrow C_6H_5^+ + H + e^- \qquad (4)$$

This threshold can be related to the ionization energy of the radical and the bond strength.

$$E_{AP}(C_6H_5^+,C_6H_6) = D_0(C_6H_5{-}H) + IP(C_6H_5) \qquad (5)$$

PIMS and photoelectron spectroscopy are complementary methods to study the ionization energies of radicals. If the threshold for (4) can be accurately found, then the combination of $E_{AP}$ and IP permits one to extract $D_0(C_6H_5{-}H)$. Alternatively, if $\Delta_f H_0(C_6H_6)$ is known, then $E_{AP}(C_6H_5^+,C_6H_6)$ provides one with the heat of formation of the cation; $\Delta_f H_0(C_6H_5^+) = E_{AP}(C_6H_5^+,C_6H_6) + \Delta_f H_0(C_6H_6) - \Delta_f H_0(H)$.

Let us consider the appearance potential first, $E_{AP}(C_6H_5^+,C_6H_6)$. Even though $C_6H_5^+$ is the lowest energy fragment formed upon photodissociative ionization of $C_6H_6$, the rate of decay is too small at the thermochemical threshold to be observed by conventional PIMS. This is an example of the kinetic shift expected for large molecules. Hence, one strategy is to determine the decay rate as a function of excess energy. By modeling this decay, using one or another form of unimolecular rate theory, one can infer a threshold energy. Photoelectron−photoion coincidence measurements are often used to measure decay rates as a function of time. However, in early forms of such experiments, the mass analyzers could not cleanly separate *m/z* 78 ($C_6H_6^+$) from *m/z* 77 ($C_6H_5^+$). Two alternative approaches have been employed that bear upon this problem.

Instead of $C_6H_6$, halobenzene targets have been used. This approach overcomes the mass separability problem and still enables one to determine $\Delta_f H_0(C_6H_5^+)$, if $\Delta_f H_0(C_6H_5X)$ is well-known. Some loss in accuracy does occur here, since $\Delta_f H_0(C_6H_6)$ is known to ±0.2 kcal mol$^{-1}$, whereas for example, $\Delta_f H_0(C_6H_5I)$ has an uncertainty of ±1.4 kcal mol$^{-1}$. A coincidence measurement was performed[17] on $C_6H_5I$, and it was inferred that $\Delta_f H_0(C_6H_5^+) = 270.8 \pm 1.4$ kcal mol$^{-1}$. Lifshitz and co-workers[18] have determined the decay rate at longer times (milliseconds as well as microseconds), utilizing a cylindrical ion trap to contain the ions. Modeling of their data by quasiequilibrium theory led to $\Delta_f H_0(C_6H_5^+) = 272.7 \pm 2.4$ kcal mol$^{-1}$. More recently, this group[19] has obtained a slightly higher value, 274.4 kcal mol$^{-1}$, from a modeling of the corresponding $C_6H_5Br$ system.

Recently[20] the mass separability problem in $C_6H_6$ has been solved by using a reflectron time-of-flight mass spectrometer which has superior resolution. The method of establishing the internal energy of $C_6H_6^+$ employed by Kuhlewind *et al.* also differed. They used two-photon ionization *via* a selected intermediate state to create $C_6H_6^+$ with very little excess energy and then (using another tunable laser) excited $C_6H_6^+$ to selected energies while examining the time-of-flight distribution of various ions. Their modeling of the rate constant for $C_6H_6^+ \rightarrow C_6H_5^+ + H$ by RRKM methods yielded $E_0 = 3.66$ eV for this reaction. With IP($C_6H_6$) = 9.245 9 ± 0.000 2 eV, the AP of $C_6H_5^+$ from $C_6H_6$ becomes 12.906 eV, or $\Delta_f H_0(C_6H_5^+) = 270.0$ kcal/mol. By using the same data but a "thermodynamic model" based on the Arrhenius equation,[21] a different value was obtained, $E_0 = 3.72$ eV. More recently,[22] additional data were gathered and analyzed by a variational transition state model that included radiative relaxation, and it was concluded that $E_0 = 3.88$ eV. The premise, however, was that $C_6H_5^+$ was formed in its excited triplet state ($^3B_1$) rather than in the ground $^1A_1$ state. If the excitation energy is estimated to be roughly 0.2 eV, then for the ground state, $E_0 \simeq 3.68$ eV. The use of $E_0 \simeq 3.68$ or 3.72 eV would imply an $E_{AP}(C_6H_5^+,C_6H_6)$ of 12.926 or 12.966 eV, and $\Delta_f H_0(C_6H_5^+) = 270.5$ or 271.4 kcal mol$^{-1}$, respectively, for an average value for $E_{AP}(C_6H_5^+)$ of 12.93 ± 0.04 eV or $\Delta_f H_0(C_6H_5^+) = 270.5 \pm 1.0$ kcal mol$^{-1}$.

An IP($C_6H_5$) of 8.1 ± 0.1 eV was measured[23] by PIMS, using pyrolysis of azobenzene as a source of phenyl radicals. More recently[24] $C_6H_5$ was prepared by the F + $C_6H_6$ reaction and the resultant He I photoelectron spectrum of the phenyl radical

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was studied. The lowest observed ionization band occurred at IP($C_6H_5$) = 8.32 ± 0.04 eV. However, *ab initio* calculations led the authors to conclude that the lowest electronic state of the cation ($^1A_1$) was not being observed but rather the excited $^3B_1$ state, which is favored by Franck–Condon overlap. They consequently estimated that the adiabatic IP($C_6H_5$), [$C_6H_5^+(\tilde{X}\ ^1A_1) \leftarrow C_6H_5(\tilde{X}^2A_1)$], is 8.0 ± 0.1 eV. If we accept their interpretation, the range of IP's (8.1 ± 0.1, 8.0 ± 0.1 eV) and the range of $E_{AP}$'s (12.93 ± 0.04, 13.01 ± 0.10 eV) lead to a range of bond energies $D_0(C_6H_5{-}H)$ from 110.4 to 115.6 kcal mol$^{-1}$.

**C. Negative Ion Chemistry of Benzene.** Our approach is to study the phenide ion to explore the thermochemistry of $C_6H_6$.[16] A flowing afterglow/selected ion flow tube (FA-SIFT) apparatus is used to scrutinize the proton transfer kinetics of amide ion with benzene.

$$C_6H_6 + NH_2^- \rightleftarrows C_6H_5^- + NH_3 \qquad (6)$$

We have measured the rate constants for the proton transfer reactions in (6), $k_6$ and $k_{-6}$, and used these values to extract the equilibrium constant, $K_{equi}(6) \equiv k_6/k_{-6}$ and the corresponding free energy change, $\Delta_{rxn}G_{300}(6) = -300R \ln K_{equi}(6)$. Since $\Delta_{rxn}G_{300}(6) = \Delta_{acid}G_{300}(C_6H_6) - \Delta_{acid}G_{300}(NH_3)$, the gas-phase acidity of ammonia[16,25,26] can be used to find the acidity of benzene, $\Delta_{acid}G_{300}(C_6H_6)$. Calculation of the corresponding entropy change, $\Delta_{acid}S_{300}(C_6H_6)$, enables the derivation of the enthalpy of deprotonation, $\Delta_{acid}H_{300}(C_6H_6)$, since $\Delta_{acid}G_{300}(C_6H_6) = \Delta_{acid}H_{300}(C_6H_6) - 300\ \Delta_{acid}S_{300}(C_6H_6)$.

Recall that the $\Delta_{acid}H$ of benzene is the enthalpy change associated with the heterolytic bond cleavage shown in eq 7.

$$C_6H_6 \rightarrow C_6H_5^- + H^+ \qquad \Delta_{acid}H_{300}(C_6H_6) \equiv \Delta_{rxn}H_{300} \qquad (7)$$

This value can be used to find the BDE at 300 K, $DH_{300}(C_6H_5{-}H)$, by completing the thermodynamic cycle:

$$\Delta_{acid}H_{300}(C_6H_6) = DH_{300}(C_6H_5{-}H) + IP_0(H) - EA_0(C_6H_5) - [\text{thermal correction}] \qquad (8)$$

The usefulness of cycle 8 has recently been discussed[16] and it was concluded that this approach is a reliable means to establish such bond enthalpies. The [thermal correction] term is always less than 0.3 kcal mol$^{-1}$ as might be expected[16] since it is an integral over similar functions with opposite signs.

$$[\text{thermal correction}] = \int_0^{300} dT[C_p(C_6H_5) + C_p(H) - C_p(C_6H_5^-) - C_p(H^+)] \qquad (9)$$

Consequently if we can evaluate the equilibrium constant in (6) and know the electron affinity of the phenyl radical, then we can use (8) to extract the bond enthalpy of benzene. Recent photodetachment studies[27] have established the electron affinity of the phenyl radical as EA($C_6H_5$) = 1.096 ± 0.006 eV (or 25.3 ± 0.1 kcal mol$^{-1}$).[28] The ionization potential of the hydrogen atom is also well-established,[29,30] IP(H) = 313.587 347 ± 0.000 001 kcal mol$^{-1}$.

## Experimental Section

All experiments were carried out with a tandem flowing afterglow-selected ion flow tube instrument (FA-SIFT) which has been described in detail previously.[31] Ions are prepared in a stream of helium buffer gas in a source flow tube by electron impact on a suitable neutral precursor or by reactions between primary reagent ions (such as $OH^-$, $NH_2^-$, etc.) and neutral reagents which are added downstream. At the end of the first flow tube, the helium and other neutrals are removed by using a roots pump, while the ions are sampled through a 2 mm orifice into a differentially pumped selection region where they are focused into a quadrupole mass filter via a series of electrostatic lenses. Tuning the quadrupole to transmit only ions of a certain *m/z* allows the ion of interest to be separated from all other ions. The mass-selected ions are injected into a second flow tube (reaction flow tube), where they are entrained in a helium buffer gas. We are able to vary the kinetic energy of the ions in the injection process; injecting the ions with excess kinetic energy (roughly 1–50 eV, lab) can collisionally activate them and lead to dissociation (CID). The ions in the reaction flow tube undergo multiple collisions with the helium and are rapidly thermalized to room temperature before being allowed to react with the neutral reagent. The ions are then sampled into the detection region where they are separated by a second quadrupole mass filter and counted with an electron multiplier. Reaction rate coefficients are measured by monitoring the reactant ion intensity as the neutral reagent is introduced at different distances along the reaction flow tube.

The $NH_2^-$ ion was generated by electron impact on ammonia. The phenide ion, $C_6H_5^-$, can be prepared by reaction of $NH_2^-$ with benzene; however, CID of $C_6H_5COCH_2^-$ (generated by reaction of $OH^-$ with acetophenone) produces a more intense and stable $C_6H_5^-$ signal. The nondissociated $C_6H_5COCH_2^-$ ion and the ketenyl ion (which is also formed in the CID process) do not react with $NH_3$ and do not interfere with the measurements reported in this paper.

The reaction of $NH_2^-$ and $C_6H_6$ is rapid and the measurement of $k_6$ is straightforward. However, the reverse reaction of $C_6H_5^-$ with $NH_3$ is relatively slow; amide ion is observed as the major product and only trace amounts of the cluster ion [$C_6H_5^- \cdot NH_3$] are detected. However, the measurement of $k_{-6}$ is complicated by the presence of small quantities of $H_2O$ which react rapidly with $C_6H_5^-$ by proton transfer. To minimize this problem, ultra-high-purity ammonia (99.9995%, <1 ppm $H_2O$) was used. The loss of $C_6H_5^-$ by residual water impurities was accounted for by monitoring the increase of $OH^-$ above the background level (≃5% of the total signal) when ammonia was added. This increase in $OH^-$ was equated to the $C_6H_5^-$ lost by reaction with water; this value was added to the observed $C_6H_5^-$ signal at each reaction distance to determine corrected values of $C_6H_5^-$ in the absence of water. The corrected values of $k_{-6}$ determined in this way were 10–27% smaller than the uncorrected values. These measurements indicated actual impurity levels of 200–500 ppm water (with the assumption that the $C_6H_5^- + H_2O$ reaction occurs at the ion–molecule collision rate). Traces of water in the calibrated volume system can contribute to this contamination. However, despite several flushings of the system with ammonia and the use of the system over several hours of rate measurements, the water impurity level was never reduced below 200 ppm. Regardless of the origin of the water contaminant,

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**Table 1.** Measured Rate Constants[a] for the Reaction

$$C_6H_6 + NH_2^- \rightleftharpoons C_6H_5^- + NH_3 \qquad (6)$$

| trial no. | $k_6$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | $k_{-6}$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | $K_{equi}(6)$ |
|---|---|---|---|
| 1 | 1.24 (±0.02) × $10^{-9}$ | 3.18 (±0.08) × $10^{-12}$ | 390 ± 12 |
| 2 | 1.23 (±0.01) × $10^{-9}$ | 3.15 (±0.15) × $10^{-12}$ | 390 ± 19 |
| 3 | 1.17 (±0.01) × $10^{-9}$ | 2.71 (±0.14) × $10^{-12}$ | 432 ± 23 |

[a] Flow tube kinetics carried out with 0.5 Torr of helium buffer gas at 300 ± 1 K; trials 1, 2, and 3 were carried out on three separate days. The error bars indicate one standard deviation of the mean of the measurements. Results for trial 1 are the average of six measurements, trial 2 is the average of three measurements, and in trial 3, $k_6$ averages five measurements while $k_{-6}$ results from three measurements.

the analysis procedure eliminates the effects of water impurities; we note, however, that use of the uncorrected $k_{-6}$ would change $\Delta_{acid}G_{300}(C_6H_6)$ by only 0.1 kcal mol$^{-1}$.

The measurements were made under conditions where mass discrimination of our quadrupole mass filter is minimized and the total ion signal remains approximately constant. The ion injection and dissociation processes can, in principle, produce vibrationally excited phenide ions, $(C_6H_5^-)^\dagger$, which might be more reactive and not efficiently relaxed by collisions with helium. To test for this possibility, roughly 2 mTorr of $CH_4$ was added to the reaction flow tube, immediately downstream of the venturi inlet. Under these conditions the phenide ions undergo more than 100 quenching collisions with methane before interacting with the ammonia reagent. The resulting rate coefficients for $C_6H_5^-$ + $NH_3$ were in agreement with those determined in the absence of $CH_4$, within experimental error. We conclude that there are no $(C_6H_5^-)^\dagger$ ions interfering with our kinetics.

The values of $k_6$ and $k_{-6}$ were determined on three separate days. Each value represents the average of at least three independent measurements carried out at 300 ± 1 K. Helium (99.995%) was purified by passage through a molecular sieve trap at 77 K. Benzene (spectrophotometric grade, >99.9%) was stored over activated molecular sieves for 1 week before use and then purified by several freeze−pump−thaw cycles.

## Results

**A. Gas-Phase Acidity of Benzene.** The values obtained for the reaction rates are shown in Table 1 along with the resulting value for $K_{equi}(6)$. By averaging these values $\bar{K}_{equi}(6)$ is determined to be 404. To assess the errors, we use "Student's t" method to find the deviation at the 95% confidence level.[32] The deviation is estimated to be $[t_{95\%}(S/N^{1/2})]$ where $S \equiv (N-1)^{-1/2}[\sum_{i=1}^{3}(K_{equi}(\text{trial } i) - \bar{K}_{equi})^2]^{1/2}$ and $N$ = number of trials, 3 in our case. The CRC handbook lists $t_{95\%}$ as 2.920 and we compute the standard deviation at a 95% confidence level as 40.4. Consequently we conclude $\bar{K}_{equi}(6) = 404 \pm 40$. This implies that $\Delta_{rxn}G_{300}(6) = -3.58 \pm 0.06$ kcal mol$^{-1}$. Because $\Delta_{rxn}G_{300}(6) = \Delta_{acid}G_{300}(C_6H_6) - \Delta_{acid}G_{300}(NH_3)$, the known acidity of ammonia[26] can be used to determine $\Delta_{acid}G_{300}(C_6H_6) = 392.9 \pm 0.4$ kcal mol$^{-1}$.

The enthalpy of deprotonation of benzene can be extracted from the gas-phase acidity term, $\Delta_{acid}G_{300}(C_6H_6)$, if we know $\Delta_{acid}S_{300}(C_6H_6)$.

$$\Delta_{acid}H_{300}(C_6H_6) = \Delta_{acid}G_{300}(C_6H_6) + 300\Delta_{acid}S_{300}(C_6H_6) \qquad (10)$$

The calculation of the entropy of deprotonation, $\Delta_{acid}S_{300}(C_6H_6)$, must be done carefully. Since the entropy of (7) is $[S_{300}(C_6H_5^-) + S_{300}(H^+) - S_{300}(C_6H_6)]$, we must find the entropy for benzene, phenide anion, and a proton. Equilibrium statistical mechanics can be employed to compute $\Delta_{acid}S_{300}(C_6H_6)$. These methods are generally applicable to molecules with no internal rotations at moderate temperatures; the present measurements have been carried out at 300 ± 1 K and both $C_6H_6$ and $C_6H_5^-$ are rigid molecules. The detailed formulae that are adopted here to calculate $S_{translation}$, $S_{rot}$, and $S_{vib}$ are discussed in the Appendix to this paper. These formulae require accurate rotational constants, $[A_0, B_0$, and $C_0]$, as well as the vibrational frequencies $\{\nu_i\}_{i=1,3n-6}$ for both benzene and phenide anion.

Benzene is a well-studied molecule. It is an oblate top with rotational constants[33] $B_0 = 0.189\,772\,9 \pm 0.000\,001\,5$ cm$^{-1}$ and $C_0 = 0.094\,857\,3 \pm 0.000\,001\,5$ cm$^{-1}$. An even more refined value for $B_0$ has been reported[34] as $0.189\,773\,89 \pm 0.000\,000\,03$ cm$^{-1}$. The current vibrational frequencies are best summarized by Dang-Nhu and Pliva.[33] With these molecular constants, expressions A2, A5, and A6 from the Appendix can be used to compute the entropy of benzene at 64.51 eu. This agrees well with the experimental value reported by Stull *et al.*,[35] 64.47 eu.

|  | exptl constants (eu) | RHF/6-31+G(d) *ab initio* constants (eu) |
|---|---|---|
| $S_{300}$(translation) | 39.0 | 39.01 |
| $S_{300}$(rotation) | 20.7 | 20.70 |
| $S_{300}$(vibration) | 4.8 | 4.82 |
| $S_{300}(C_6H_6)$ | 64.51 | 64.54 |

No experimental constants are available for the phenide ion, $C_6H_5^-$; we have approximated these by carrying out restricted Hartree−Fock, *ab initio* electronic structure calculations on this ion with the GAUSSIAN 92 suite of programs.[36] These RHF calculations used a 6-31+G(d) basis set to optimize the molecular geometry and to compute the harmonic vibrational frequencies. During the geometry optimization, the $C_6H_5^-$ ion was constrained to have $C_{2v}$ symmetry. Since computed values are being used for the geometry and vibrational frequencies of the phenide ion, we must calibrate the performance of the method by comparing the corresponding computational and the experimental values for benzene. We therefore also carried out RHF *ab initio* calculations on $C_6H_6$ using the 6-31+G(d) basis set.

The computed geometry for the phenide ion directly influences the rotational entropy, *via* the rotational constants in (A5), while the vibrational frequencies are important for the vibrational entropy, (A6). For closed-shell, neutral species Hartree−Fock calculations with modest-sized basis sets have been shown to reproduce[37] molecular structures to within ±0.01 Å.

However, accurate vibrational frequencies are more difficult to compute. It is well-known that one must empirically scale the *ab initio* harmonic frequencies to achieve accurate results.[37] This scaling factor naturally depends upon not only the basis set used but also what group of molecules is used for comparison and whether or not the comparisons are made with only harmonic frequencies or with all fundamentals. For comparison to measured frequencies of polyatomic molecules, it is found that the computed frequencies from 6-31G(d) calculations have an average percent deviation of 13.9%. If the comparison is

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(33) Dang-Nhu, M.; Pliva, J. *J. Mol. Spectrosc.* **1989**, *138*, 423.

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(36) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Gill, P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Baker, J.; Martin, R. L.; Pople, J. A., *Gaussian 92*, Revision A; Gaussian, Inc.: Pittsburgh, PA, 1992.

(37) Hehre, W. J.; Radom, L.; Schleyer, P. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 226−261.

**Table 2.** Comparison between the Measured Properties of Benzene and Those Calculated by an *ab Initio* Hartree–Fock Model

| spectroscopic constants for benzene | *ab initio* HF/6-31+G(d) computations |
|---|---|
| exptl[61,65] geometry<br>$r_0$(CC) = 1.397 Å<br>$r_0$(CH) = 1.084 Å<br>exptl[33] rotational constants/$cm^{-1}$<br>($C_6H_6$ is an oblate top, $\kappa$ = 1.0)<br>$B_0$ = 0.189 772 9 ± 0.000 001 5<br>$C_0$ = 0.094 857 3 ± 0.000 001 5 | calcd geometry<br>$r_0$(CC) = 1.388 Å<br>$r_0$(CH) = 1.076 Å<br>calcd rotational constants/$cm^{-1}$<br>($C_6H_6$ constrained as an oblate top, $\kappa$ = 1.0)<br>$B_0$ = 0.192<br>$C_0$ = 0.096 |

| vib[33] freq for benzene, $\nu$/$cm^{-1}$ | | | harmonic freq for HF/6-31+G(d) computations, $\omega$/$cm^{-1}$ | |
|---|---|---|---|---|
| mode | approx motion | exptl freq | raw $\omega$ | $\omega$ scaled by 89.3% |
| $a_{1g}$ $\nu_2$ | CH stretch | 3073.94 | 3389 | 3026 |
| $b_{1u}$ $\nu_{13}$ | CH stretch | 3057 | 3349 | 2991 |
| $e_{2g}$ $\nu_7$ | CH stretch | 3056.7 | 3360 | 3000 |
| $e_{1u}$ $\nu_{20}$ | CH stretch | 3047.908 | 3378 | 3016 |
| $e_{2g}$ $\nu_8$ | ring stretch | 1609.518 | 1786 | 1595 |
| $e_{1u}$ $\nu_{19}$ | ring defor + stretch | 1483.985 | 1645 | 1469 |
| $a_{2g}$ $\nu_3$ | CH bend | 1350 | 1507 | 1345 |
| $b_{2u}$ $\nu_{14}$ | ring stretch | 1309.8 | 1354 | 1209 |
| $e_{2g}$ $\nu_9$ | CH bend | 1177.776 | 1292 | 1153 |
| $b_{2u}$ $\nu_{15}$ | CH bend | 1148.5 | 1202 | 1073 |
| $e_{1u}$ $\nu_{18}$ | CH bend | 1038.267 | 1137 | 1015 |
| $b_{1u}$ $\nu_{12}$ | ring deformation | 1010 | 1097 | 979 |
| $a_{1g}$ $\nu_1$ | ring stretch | 993.063 | 1076 | 961 |
| $b_{2g}$ $\nu_5$ | CH bend | 990 | 1142 | 1020 |
| $e_{2u}$ $\nu_{17}$ | CH bend | 967 | 1109 | 990 |
| $e_{1g}$ $\nu_{10}$ | CH bend | 846 | 961 | 858 |
| $b_{2g}$ $\nu_4$ | ring deformation | 707 | 775 | 695 |
| $a_{2u}$ $\nu_{11}$ | CH bend | 673.9732 | 761 | 679 |
| $e_{2g}$ $\nu_6$ | ring deformation | 608.13 | 664 | 593 |
| $e_{2u}$ $\nu_{16}$ | ring deformation | 398 | 451 | 403 |

limited to harmonic frequencies, then the average deviation is 12.8%. If one limits the comparison further to polyatomic hydrides for which complete harmonic analysis has been carried out on the experimental data, then the percent deviation for computations in a 6-31G(d) basis set is 10.6% on the measured frequencies and 7.8% on the harmonic frequencies. Two studies have recommended scaling factors of 88.4% (based on 83 different polyatomics)[38] and 87.4% (resulting from a comparison of 36 different polyatomics).[39] The most recent study of Hartree–Fock harmonic frequencies[40] recommends 89.29% as the proper scaling factor for harmonic frequencies derived from a HF calculation in a 6-31G(d) basis.

We have chosen to adopt a scaling factor of 89.29% to use with our Hartree–Fock/6-31+G(d) calculations; the results for benzene are shown in Table 2. Note that the geometry of $C_6H_6$ is computed accurately; both the CC and CH bond lengths are estimated to be too long by only 0.01 Å. The calculated rotational constants are in error by 0.003 ($B_0$) and 0.001 $cm^{-1}$ ($C_0$). Table 2 compares the experimental vibrational frequencies of $C_6H_6$ with the "raw" *ab initio* harmonic frequencies and those scaled by the conventional factor, 89.29%. Most of the scaled frequencies closely approximate the experimental values, but some are in error by 5% or 6%.

Use of the *ab initio* molecular constants for $C_6H_6$ from Table 2 (with 89.29% scaling) leads to very good values for the entropy. The computed value of $S_{300}$(total) = 64.54 cal $mol^{-1}$ $K^{-1}$ is in close agreement with the statistical mechanical result based on the experimental spectroscopic constants (64.51 cal $mol^{-1}$ $K^{-1}$) or the literature value (64.47 cal $mol^{-1}$ $K^{-1}$). Given the good match between experiment and the Hartree–Fock result for benzene, we feel confident in using the calculated values for the phenide ion, especially since the anion is localized on a single C atom in an orbital perpendicular to the $\pi$ electron system.

The results of the 6-31+G(d) RHF *ab initio* electronic structure calculations on the $C_6H_5^-$ ion are listed in Table 3. The molecular constants (rotational constants, $A_0$, $B_0$, and $C_0$, and the harmonic vibrational frequencies, $\{\omega_i\}$, scaled by 89.3%) in eqs A2, A5, and A6 give the following:

| entropy of phenide anion | *ab initio* constants (eu) |
|---|---|
| $S_{300}$(translation) | 38.97 |
| $S_{300}$(rotation) | 24.20 |
| $S_{300}$(vibration) | 4.93 |
| $S_{300}(C_6H_5^-)$ | 68.10 |

This computed value for $S_{300}(C_6H_5^-)$ of 68.1 cal $mol^{-1}$ $K^{-1}$ seems reasonable. An isoelectronic species that has been well studied[35] is pyridine; the entropy of pyridine has been measured to be $S_{298}(C_5H_5N)$ = 67.8 cal $mol^{-1}$ $K^{-1}$.

Combining the values for $S_{300}(C_6H_6)$, $S_{300}(C_6H_5^-)$, and $S_{300}(H^+)$ gives an entropy of deprotonation, $\Delta_{acid}S_{300}(C_6H_6)$, of 29.76 cal $mol^{-1}$ $K^{-1}$. The error bars associated with this entropy will depend on the accuracy of the factor used to scale the harmonic frequencies of the $C_6H_5^-$ ion. Based on the comparison of the Hartree–Fock harmonic frequencies of benzene with the experimental values (Table 2), we believe that an uncertainty of ±5% in this factor is a conservative estimate. Consequently, a scaling factor of 89% ± 5% is adopted for the vibrational frequencies of the $C_6H_5^-$ ion. This leads to a computed entropy of deprotonation of $\Delta_{acid}S_{300}(C_6H_6)$ = 29.6 ± 1.3 cal $mol^{-1}$ $K^{-1}$. This value for the entropy is within 0.1 eu of the approximate value that eq A9 would predict; $\Delta_{acid}S_{300}(C_6H_6) \simeq 29.5$ cal $mol^{-1}$ $K^{-1}$. Of the various terms in (A9), the dominant one is

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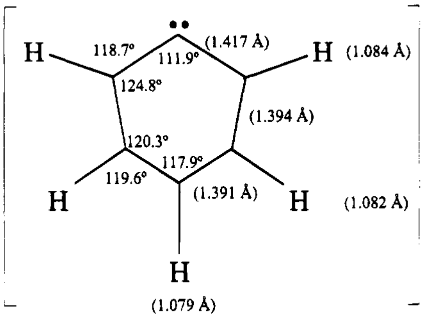
(38) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem.* **1981**, *15*, 269.

(39) Hout, R. F.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234.

(40) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

**Table 3.** Properties of the $C_6H_5^-$ Ion As Calculated by an *ab Initio* Hartree−Fock Model with a 6-31+G(d) Basis Set

Optimized Geometry



Rotational Constants

| | GHz | cm$^{-1}$ |
|---|---|---|
| $A_0$ | 5.907 | 0.197 |
| $B_0$ | 5.867 | 0.196 |
| $C_0$ | 2.943 | 0.098 |

$$\kappa \equiv \frac{2B - (A + C)}{(A - C)} = 0.973$$

Harmonic Frequencies

| mode | | freq/cm$^{-1}$ | scaled (89.3%) freq/cm$^{-1}$ |
|---|---|---|---|
| $a_1$ | $\omega_1$ | 3316 | 2961 |
| $b_2$ | $\omega_2$ | 3278 | 2927 |
| $a_1$ | $\omega_3$ | 3270 | 2920 |
| $b_2$ | $\omega_4$ | 3232 | 2886 |
| $a_1$ | $\omega_5$ | 3231 | 2885 |
| $a_1$ | $\omega_6$ | 1714 | 1531 |
| $b_2$ | $\omega_7$ | 1713 | 1530 |
| $a_1$ | $\omega_8$ | 1595 | 1424 |
| $b_2$ | $\omega_9$ | 1552 | 1386 |
| $b_2$ | $\omega_{10}$ | 1449 | 1293 |
| $a_1$ | $\omega_{11}$ | 1290 | 1152 |
| $b_2$ | $\omega_{12}$ | 1285 | 1148 |
| $b_2$ | $\omega_{13}$ | 1215 | 1085 |
| $a_1$ | $\omega_{14}$ | 1131 | 1010 |
| $b_2$ | $\omega_{15}$ | 1127 | 1007 |
| $b_1$ | $\omega_{16}$ | 1080 | 964 |
| $a_2$ | $\omega_{17}$ | 1078 | 962 |
| $a_1$ | $\omega_{18}$ | 1077 | 962 |
| $a_1$ | $\omega_{19}$ | 1033 | 922 |
| $b_1$ | $\omega_{20}$ | 956 | 854 |
| $a_2$ | $\omega_{21}$ | 947 | 846 |
| $b_1$ | $\omega_{22}$ | 776 | 693 |
| $b_1$ | $\omega_{23}$ | 750 | 670 |
| $b_2$ | $\omega_{24}$ | 675 | 603 |
| $a_1$ | $\omega_{25}$ | 644 | 575 |
| $b_1$ | $\omega_{26}$ | 440 | 392 |
| $a_2$ | $\omega_{27}$ | 426 | 380 |

controlled by the change in the symmetry between the acid, $\sigma(C_6H_6)$, and the anion, $\sigma(C_6H_5^-)$: $R \ln|12/2| = 3.6$ cal mol$^{-1}$ K$^{-1}$.

Use of $\Delta_{acid}S_{300}(C_6H_6) = 29.6 \pm 1.0$ cal mol$^{-1}$ K$^{-1}$ with $\Delta_{acid}G_{300}(C_6H_6) = 392.9 \pm 0.4$ kcal mol$^{-1}$ leads to a value of the enthalpy of deprotonation of benzene; we find $\Delta_{acid}H_{300}(C_6H_6) = 401.7 \pm 0.5$ kcal mol$^{-1}$.

**B. The Bond Energy of Benzene.** Expressions 8 and 9 can now be used to extract the C−H bond enthalpy of benzene. From (9) the [thermal correction] is determined to be −0.1 kcal mol$^{-1}$ with estimated error limits of ±0.1 kcal mol$^{-1}$. Combining this with $\Delta_{acid}H_{300}(C_6H_6)$, the measured electron affinity of the phenyl radical,[27] and the ionization potential of hydrogen atom[29] gives the C−H bond enthalpy: $DH_{300}(C_6H_5{-}H) = 113.5 \pm 0.5$ kcal mol$^{-1}$. To determine the C−H bond energy at 0 K, $D_0(C_6H_5{-}H)$, an appropriate heat capacity correction is required,[16]

$$DH_{300}(C_6H_5{-}H) = D_0(C_6H_5{-}H) + \int_0^{300} dT[C_p(C_6H_5) + C_p(H) - C_p(C_6H_6)] \quad (11)$$

which is estimated to be 1.4 ± 0.2 kcal mol$^{-1}$. This leads to $D_0(C_6H_5{-}H) = 112.0 \pm 0.6$ kcal mol$^{-1}$.

The bond energy of benzene can be used to determine the heat of formation of the phenyl radical, $\Delta_fH_{300}(C_6H_5)$.

$$C_6H_6 \rightarrow C_6H_5 + H \qquad DH_{300}(C_6H_6) \equiv \Delta_fH_{300}(C_6H_5) + \Delta_fH_{300}(H) - \Delta_fH_{300}(C_6H_6) \quad (12)$$

The experimental $\Delta_fH$ value for benzene at room temperature is tabulated[41] as $\Delta_fH_{298} = 19.7 \pm 0.2$ kcal mol$^{-1}$. The heat of formation for $C_6H_6$ at 0 K can be estimated if one knows the heat capacities of benzene, C atom, and $H_2$.

$$\Delta_fH_{298}(C_6H_6) = \Delta_fH_0(C_6H_6) + \int_0^{298} dT[C_p(C_6H_6) - 6C_p(C) - 3C_p(H_2)] \quad (13)$$

In (13) the integral over the heat capacities is evaluated as [+3.407 − 7.578] = −4.2 kcal mol$^{-1}$. This leads to proper values for the heat of formation of benzene, $\Delta_fH_0(C_6H_6) = 23.9 \pm 0.3$ kcal mol$^{-1}$ and $\Delta_fH_{300}(C_6H_6) = 19.7 \pm 0.3$ kcal mol$^{-1}$. Consequently using (12), the C−H bond energies lead to the phenyl radical heats of formation at 300 and 0 K: $\Delta_fH_{300}(C_6H_5) = 81.2 \pm 0.6$ kcal mol$^{-1}$ and $\Delta_fH_0(C_6H_5) = 84.3 \pm 0.6$ kcal mol$^{-1}$.

## Discussion

**A. Comparisons.** The present value of the enthalpy of deprotonation of benzene, 401.7 ± 0.5 kcal mol$^{-1}$, differs somewhat from earlier values. Lias *et al.*[42] have summarized most of the earlier gas-phase ion chemistry involving benzene and have recommended the following values: $\Delta_{acid}G_{298}(C_6H_6) = 390.9 \pm 2$ kcal mol$^{-1}$ and $\Delta_{acid}S_{298}(C_6H_6) = 28.5 \pm 2$ cal mol$^{-1}$ K$^{-1}$. These parameters lead to $\Delta_{acid}H_{300}(C_6H_6) = 399.5 \pm 2.1$ kcal mol$^{-1}$ and, consequently, the value from the present study (401.7 ± 0.5 kcal mol$^{-1}$) is just within the error bars. Meot-Ner and Sieck[43] have used high-temperature mass spectrometry to study the equilibrium between phenide ion and water: $C_6H_6 + OH^- \rightleftharpoons C_6H_5^- + H_2O$. From a van't Hoff plot, they deduced the enthalpy of deprotonation of benzene at 600 K: $\Delta_{acid}H_{600}(C_6H_6) = 400.7 \pm 0.8$ kcal mol$^{-1}$. An attempt[16] to carry out the heat capacity corrections to deduce the acidity at 298 K led to an extrapolated value of $\Delta_{acid}H_{298}(C_6H_6)$ equal to 399.8 ± 0.7 kcal mol$^{-1}$ (footnote no. 205 in Berkowitz *et al.*).

The present value, $\Delta_{acid}H_{300}(C_6H_6) = 401.7 \pm 0.5$ kcal mol$^{-1}$, is compatible with all other measurements of this quantity. The high-temperature studies of Meot-Ner and Sieck are carefully done but extrapolation from 600 to 298 K is difficult. We have measured the relative acidity of benzene in a flow tube at 300 K and chosen ammonia as our reference point to anchor the

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(41) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemistry of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986. It is recommended that $\Delta_fH_{298}(C_6H_6) = 19.7 \pm 0.2$ kcal mol$^{-1}$ and a value of $\Delta_fH_0(C_6H_6) = 23.9 \pm 0.3$ kcal mol$^{-1}$ is adopted.

(42) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17 (Suppl. 1)*, 1. All data taken from the NIST Negative Ion Energetics Database, Version 3.00, NIST Standard Reference Database 19B, October 1993.

(43) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Phys. Chem.* **1986**, *90*, 6687.

acidity. The gas-phase acidity of ammonia is well-established.[25,26] Since the equilibrium studies tie the acidity of $C_6H_6$ to $NH_3$ at 300 K, we believe that 392.9 ± 0.4 kcal mol$^{-1}$ is the most accurate value for $\Delta_{acid}G_{300}(C_6H_6)$ now available. In order to extract the enthalpy of deprotonation from $\Delta_{acid}G_{300}$, a value for the entropy was used which is derived from accurate spectroscopic constants of benzene and reasonable constants computed for the phenide ion, $\Delta_{acid}S_{300}(C_6H_6) = 29.6 \pm 1.0$ cal mol$^{-1}$ K$^{-1}$. As shown in the Appendix, this value for the entropy can be accurately approximated by a formula, (A9), which is dominated by the lowering of the symmetry of benzene ($D_{6h}$) to phenide anion ($C_{2v}$). This approximation leads to $\Delta_{acid}S_{300}(C_6H_6) \simeq 29.5$ cal mol$^{-1}$ K$^{-1}$. With the entropy of 29.6 ± 1.0 cal mol$^{-1}$ K$^{-1}$, the value $\Delta_{acid}H_{300}(C_6H_6) = 401.7 \pm 0.5$ kcal mol$^{-1}$ is derived.

The recommended bond energies from this negative ion study, $DH_{300}(C_6H_5-H) = 113.5 \pm 0.5$ and $D_0(C_6H_5-H) = 112.0 \pm 0.6$ kcal mol$^{-1}$, are slightly higher than those in current use. We believe that these bond energies are the most accurate ones now available and that they are compatible with most earlier kinetic experiments and PIMS results. As mentioned in the Introduction, radical kinetics studies find values for the bond enthalpy over a range of 102 to 112 kcal mol$^{-1}$. The current, accepted[2] value for the C−H bond energy is $DH_{298}(C_6H_5-H) = 110.9 \pm 2$ kcal mol$^{-1}$ and these error bars just barely overlap 113.5 ± 0.5 kcal mol$^{-1}$. PIMS studies also lead to a set of values for the bond energy. From the range of photoion appearance energies and ionization potentials of the phenyl radical, the deduced value of the C−H bond energy, $D_0(C_6H_5-H)$, varies from 110 to 116 kcal mol$^{-1}$.

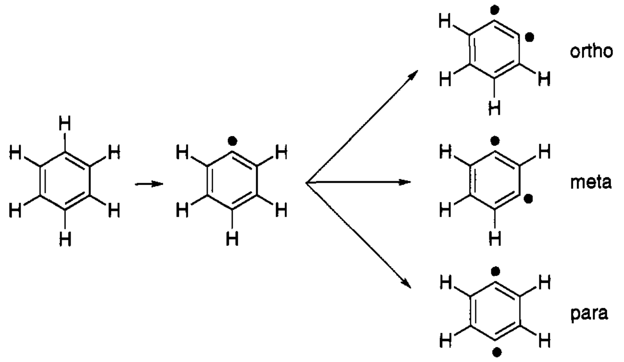
**B. Thermochemical Implications.** The availability of a C−H bond energy of benzene with an uncertainty of less than 1 kcal mol$^{-1}$ permits us to make some interesting comparisons. Consider the following bond energies to carbon atoms that are nominally sp$^2$; experimental values for all compounds but benzene are taken from Table 5 of Berkowitz *et al.*[16] Note that these species show quite a range of C−H bond energies (from 34 to 112 kcal mol$^{-1}$). It is also clear that benzene has a stronger bond (112 kcal mol$^{-1}$) than ethylene (110 kcal mol$^{-1}$); this 2 kcal mol$^{-1}$ difference may reflect the ability of a vinyl radical to relax its geometry while the structure of the phenyl radical is constrained by the ring.[44]

| molecule | $D_0$/kcal mol$^{-1}$ |
|---|---|
| $CH_3 \rightarrow H + CH_2$ | 108.6 ± 0.6 |
| $CH_2O \rightarrow H + HCO$ | 86.57 ± 0.16 |
| $CH_2S \rightarrow H + HCS$ | 94.0 ± 1.2 |
| $CH_3CHO \rightarrow H + CH_3CO$ | 87.9 ± 0.3 |
| $HCOOH \rightarrow H + COOH$ | ≃94 |
| $H_2C{=}CH_2 \rightarrow H + HC{=}CH_2$ | 109.7 ± 0.8 |
| $H_2C{=}CH \rightarrow H + HC{\equiv}CH$ | 33.6 ± 0.8 |
| $H_2C{=}C \rightarrow H + HC{\equiv}C$ | 83.9 ± 4.2 |
| $H_2C{=}CO \rightarrow H + HCCO$ | 103.9 ± 2.1 |
| $C_6H_6 \rightarrow H + C_6H_5$ | 112.0 ± 0.6 |

The new values for the gas-phase acidity and C−H bond energy of benzene determined in this study are sufficiently different from other values used previously that a discussion is warranted. A re-analysis of some of the relevant thermochemical data in the literature that are dependent upon the acidity and C−H bond energy of benzene is provided below.

To begin with, it is useful to consider the idea of a "non-interacting" diradical. It is common for one to assume[45] that the bond energies of a molecule are largely independent[46] and to use BDE values to estimate the heat of formation of a diradical. Consider the case of dehydrobenzene ("benzyne"). Removal of two H atoms from benzene can produce three isomeric benzynes, *ortho, meta,* and *para* (see Scheme 1). The coupling between the radical centers in each isomer is likely to be different and this may lead to different heats of formation for each species. A naive view of these benzynes might suggest that there is *no* interaction between the radical centers. In this instance, the energy required to remove the first hydrogen atom from benzene will be the same as the energy required to remove any subsequent hydrogen atom from the phenyl radical.

**Scheme 1**



$$C_6H_6 \rightarrow C_6H_5 + H \rightarrow C_6H_4 + 2H \qquad (14)$$

If the bond energies are identical, then one can find the heat of formation of a "non-interacting" benzyne, $\Delta_fH(C_6H_4)$. And, of course, this implies that all the benzynes have the same energy: $\Delta_fH(C_6H_4) \equiv \Delta_fH(o\text{-}C_6H_4) = \Delta_fH(m\text{-}C_6H_4) = \Delta_fH(p\text{-}C_6H_4)$. The energetics implied by (14) are:

$$2BDE(C_6H_6) \equiv \Delta_fH(C_6H_4) + 2\Delta_fH(H) - \Delta_fH(C_6H_6) \qquad (15)$$

Use of the bond energies from this work, $DH_{300}(C_6H_5-H) = 113.5 \pm 0.5$ and $D_0(C_6H_5-H) = 112.0 \pm 0.6$ kcal mol$^{-1}$, and

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(44) Petersson, G. A.; Borden, W. T., 1994. Our experimental finding about benzene's bond energy is consistent with two recent *ab initio* electronic structure studies of $C_6H_6$. These results were communicated to us by Professors Petersson and Borden. The CBS-Q method was used by Ochterski, Petersson, and Montgomery [*J. Chem. Phys.*, submitted for publication] to calculate a dissociation energy for benzene, $D_0(C_6H_5-H) = 113.1 \pm 1.3$ kcal mol$^{-1}$. This was significantly higher than earlier estimates (110.9 ± 2 kcal mol$^{-1}$) but in agreement with the current finding, $D_0(C_6H_5-H) = 112.0 \pm 0.6$ kcal mol$^{-1}$. This CBS-Q method is similar in concept to their recently published CBS-QCI/APNO method [*J. Chem. Phys.* **1994**, *101*, 5900], but it is much less computationally demanding, permitting applications to benzene and the phenyl radical. The components of the CBS-Q calculation are a single-point MP2 calculation with a large basis set [6-311++G(2df,2p)] at the MP2/6-31G$^\dagger$ optimized geometry, a correction for higher-order electron correlation by adding MP4(SDQ) and QCISD(T) contributions obtained with much smaller basis sets [6-31+G$^{\dagger\dagger}$ and 6-31+G$^\dagger$ respectively], and an extrapolation to the complete basis set (CBS) limit. It is found [*J. Chem. Phys.* **1991**, *94*, 6081] that the CBS method gives an RMS deviation from experiment for the 55 dissociation energies in Pople's G2 test set of 1 kcal mol$^{-1}$. In the last two months, *ab initio* CASSCF and CASPT2N/6-31G* electronic structure calculations of the bond energies of ethylene and benzene have been completed by D. Hrovat and W. T. Borden. They find that $D_e(C_6H_5-H) > D_e(C_2H_3-H)$ by 1.0 or 0.6 kcal mol$^{-1}$ at these two levels of theory. Add to this the 0.7 kcal mol$^{-1}$ greater ZPE decrease on breaking a C−H bond in ethylene (RHF vibrational analyses), and the $D_0$ values differ by 1.7 kcal mol$^{-1}$ at CASSCF and 1.3 kcal mol$^{-1}$ at CASPT2N. These calculations indicate that benzene has the stronger C−H bond by 1−2 kcal mol$^{-1}$, about half of which comes from the ZPE correction. When the bond angles at the phenyl or vinyl radical centers are constrained to have the same values as those in the hydrocarbons, the purely electronic difference between the C−H BDEs is reduced to 0.3 kcal mol$^{-1}$ at the CASSCF level and −0.3 kcal mol$^{-1}$ at CASPT2N. Consequently geometry relaxation on C−H bond breaking lowers the C−H BDE of $CH_2{=}CH_2$ by 0.7−0.9 kcal mol$^{-1}$ more than it lowers the C−H BDE of $C_6H_6$.

(45) Blush, J. A.; Clauberg, H.; Kohn, D. W.; Minsek, D. W.; Zhang, X.; Chen, P. *Acc. Chem. Res.* **1992**, *25*, 385. This account provides a brief review of the thermochemistry and spectroscopy of diradicals.

(46) Carter, E. A.; Goddard, W. A., III *J. Phys. Chem.* **1986**, *90*, 998.

the appropriate benzene heats of formation[41] permits the computation *via* (15) of the "bond additivity heats of formation" for benzyne at 300 and 0 K. The resulting values are $\Delta_fH_{300}(C_6H_4) = 142.6 \pm 0.8$ kcal mol$^{-1}$ and $\Delta_fH_0(C_6H_4) = 144.7 \pm 0.8$ kcal mol$^{-1}$.

What do experiments tell us about "real" benzynes? The interaction or coupling of the radical pair ($\sigma_l$, $\sigma_r$) of electrons in $o$-$C_6H_4$ has been studied by many clever spectroscopic methods. The ionization potential of benzyne has been measured,[47] IP($o$-$C_6H_4$) = 9.03 ± 0.05 eV, and the matrix isolation infrared spectrum has been scrutinized.[48] Likewise, negative ion photoelectron spectroscopy of the [$o$-$C_6H_4$]$^-$ ion has been used[49] to measure the electron affinity of benzyne, EA($o$-$C_6H_4$) = 0.560 ± 0.010 eV, and to find the singlet−triplet splitting: $\Delta E_{ST} = 38.0 \pm 0.7$ kcal mol$^{-1}$.

Careful FTMS studies[50] have been used to find the acidity of phenyl ($\Delta_{acid}H_{298}(C_6H_5) = 380.5 \pm 1.9$ kcal mol$^{-1}$) and a revised value[51] of the heat of formation of $o$-benzyne ($\Delta_fH_{298}(o\text{-}C_6H_4) = 105$ kcal mol$^{-1}$). Guo and Grabowski recently reported[52] measurements of the gas-phase acidity of the phenyl radical by means of proton transfer bracketing experiments with the $o$-benzyne negative ion, $o$-$C_6H_4^-$. From their $\Delta_{acid}H_{298}(C_6H_5) = 379 \pm 5$ kcal mol$^{-1}$ and the known[53] electron affinity of $o$-benzyne, EA($o$-$C_6H_4$) = 12.9 ± 0.2 kcal mol$^{-1}$, they derived a heat of formation for neutral $o$-benzyne of 105 ± 5 kcal mol$^{-1}$ using

$$\Delta_fH(o\text{-}C_6H_4) = \Delta_{acid}H(C_6H_5) + \mathrm{EA}(C_6H_5) + \Delta_fH(C_6H_5) - \Delta_fH(H^+) \quad (16)$$

For this determination a value for the heat of formation of the phenyl radical of 78.6 kcal mol$^{-1}$ was employed. Use of the present value for $\Delta_fH_{300}(C_6H_5)$ of 81.2 kcal mol$^{-1}$ gives a new estimate for $\Delta_fH_{300}(o\text{-}C_6H_4)$ of 108 ± 5 kcal mol$^{-1}$. This is dramatically different from the value for the "non-interacting" benzyne given above, $\Delta_fH(C_6H_4) = 142.6 \pm 0.8$ kcal mol$^{-1}$. This implies that the radical sites *do* interact and that there are energetic consequences.

Recent studies at Purdue[54] have sought accurate heats of formation for all three benzyne isomers from measurements of the halide ion dissociation energies of isomeric halophenide anions: $C_6H_4X^- \rightarrow C_6H_4 + X^-$. The fragmentation of the halophenide ions was monitored and $E_{AP}(X^-, C_6H_4X^-)$ was reported. These CID measurements of the appearance energy of the halide ion provide the bond enthalpies, $DH_{298}(C_6H_4{-}X^-)$. Thus the heat of formation for $o$-benzyne was extracted from the measured dissociation enthalpy of $o$-chlorophenide anion, $DH_{298}(o\text{-}C_6H_4{-}Cl^-)$, and the measured value for the positional acidities and heat of formation of chlorobenzene according to expressions 17a−d.

$$DH_{298}(o\text{-}C_6H_4{-}Cl^-) = \Delta_fH_{298}(o\text{-}C_6H_4) + \Delta_fH_{298}(Cl^-) - \Delta_fH_{298}(o\text{-}C_6H_4{-}Cl^-) \quad (17a)$$

$$\Delta_{acid}H_{298}(o\text{-}C_6H_4Cl{-}H) = \Delta_fH_{298}(o\text{-}C_6H_4{-}Cl^-) + \Delta_fH_{298}(H^+) - \Delta_fH_{298}(C_6H_5Cl) \quad (17b)$$

$$\Delta_{acid}H_{298}(HCl) = \Delta_fH_{298}(Cl^-) + \Delta_fH_{298}(H^+) - \Delta_fH_{298}(HCl) \quad (17c)$$

These expressions can be combined to yield an expression for $\Delta_fH_{298}$(benzyne).

$$\Delta_fH_{298}(o\text{-}C_6H_4) = DH_{298}(o\text{-}C_6H_4{-}Cl^-) + \Delta_{acid}H_{298}(o\text{-}C_6H_4Cl{-}H) + \Delta_fH_{298}(C_6H_5Cl) - \Delta_{acid}H_{298}(HCl) - \Delta_fH_{298}(HCl) \quad (17d)$$

The enthalpy of deprotonation of chlorobenzene in the *ortho* position was determined by a bracketing procedure to be 388 ± 2 kcal mol$^{-1}$. Combining this with the CID results and other thermochemical data from the literature gave $\Delta_fH_{298}(o\text{-}C_6H_4) = 106.6 \pm 3.0$ kcal mol$^{-1}$, a value in good agreement with the revised value derived from the results of Guo and Grabowski.[52] The corresponding acidities for the *meta* and *para* positions were obtained by the silane cleavage method[55,56] to be 391.1 ± 2.0 and 393.9 ± 2.0 kcal mol$^{-1}$, respectively. The silane cleavage method requires calibration with silylated derivatives of compounds having known gas-phase acidities. For the chlorobenzene experiments, benzene was used as one of the reference compounds, and the value $\Delta_{acid}H_{298}(C_6H_6) = 399.8 \pm 0.8$ kcal mol$^{-1}$ was employed in the calibration.[54]

The new value for the acidity of benzene obtained in the present study leads to small changes in the absolute heats of formation for $m$- and $p$-benzyne, while the revised C−H bond energy of benzene has a major impact on how we interpret the benzyne thermochemistry. Re-analysis of the experimental data using the new value for the acidity of benzene recommended in the present work gives revised $\Delta_{acid}H$ values for the *meta* and *para* positions of chlorobenzene of 391.0 ± 1.9 and 394.4 ± 1.3 kcal mol$^{-1}$, respectively, where the smaller uncertainties reflect the more accurately known acidity of the benzene reference and a more rigorous propagation of error in the silane cleavage data. Use of these revised values in conjunction with eq 17 gives $\Delta_fH_{298}(m\text{-}C_6H_4) = 121.9 \pm 3.1$ kcal mol$^{-1}$ and $\Delta_fH_{298}(p\text{-}C_6H_4) = 137.8 \pm 2.9$ kcal mol$^{-1}$.

Thus, the actual heats of formation of $o$-, $m$- and $p$-benzyne are lower than the bond energy additivity estimate by 36, 21, and 5 kcal mol$^{-1}$, respectively, indicating the substantial interaction between the two radical sites. The origins of these effects have been discussed in detail previously;[57−59] their magnitudes are somewhat amplified by the change in the benzene C−H bond energy. A complementary perspective is obtained by computing the actual magnitudes of the *ortho*, *meta*, and *para* C−H bond energies in the phenyl radical from expression 18.

$$DH(o\text{-},m\text{-},p\text{-}C_6H_4{-}H) = \Delta_fH(o\text{-},m\text{-},p\text{-}C_6H_4) + \Delta_fH(H) - \Delta_fH(C_6H_5) \quad (18)$$

The resulting 298 K bond enthalpies are $DH_{298}(o\text{-}C_6H_4{-}H)$ =

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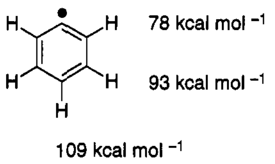
77.5 ± 3.1 kcal mol$^{-1}$, $DH_{298}(m\text{-}C_6H_4\text{-}H)$ = 92.8 ± 3.2 kcal mol$^{-1}$, and $DH_{298}(p\text{-}C_6H_4\text{-}H)$ = 108.7 ± 3.0 kcal mol$^{-1}$.



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## Appendix: Symmetry and Rotational Entropy

Benzene is a symmetric molecule and symmetry plays an important role in fixing the entropy of ionization. Let us see how this works using ammonia as a simple example.

$$NH_3 \rightarrow NH_2^- + H^+ \tag{A1}$$

In this case, $NH_3$ is a species with 3-fold symmetry that deprotonates to an anion with 2-fold symmetry. How does one use statistical methods to compute the entropy change for this process: $\Delta_{acid}S_{300}(NH_3) = S_{300}(NH_2^-) + S_{300}(H^+) - S_{300}(NH_3)$?

For moderate temperatures (such as 300 K where flow tube experiments are done) when equilibrium statistical mechanics can be applied, the entropy can be computed.[60] The translational entropy of a mole of gas with mass $M$ at a pressure $p$ of 1 013 250 dyn cm$^{-2}$ with temperature $T$ is given by (A2). Here $h$ is the Planck constant, $k_B$ the Boltzmann constant, $N_0$ Avogadro's number, and $R$ the gas constant.

$$S_{\text{translation}} = \frac{5}{2}RT + \frac{3}{2}R\ln(M) + R\ln\left(\left(\frac{2\pi}{N_0}\right)^{3/2}\frac{k_B^{5/2}}{h^3}\right) + \frac{5}{2}R - R\ln(p) \tag{A2}$$

This expression requires only the mass of the molecule and a translational temperature. Application of (A2) to the proton leads to a value for the translational entropy at 300 K of $S_{300}(H^+)$ = 26.0 cal mol$^{-1}$ K$^{-1}$.

For internal degrees of freedom such as rotations or vibrations, the entropy is computed from the appropriate partition function, $Q_{int}$.

$$S_{\text{internal}} = RT\frac{d[\ln(Q_{int})]}{dT} + R\ln(Q_{int}) \tag{A3}$$

The key ingredient in (A3) is the partition function, $Q_{int}$, the sum over all distinguishable, accessible, molecular states.

First consider the rotational states, $Q_{rot}$. For a simple diatomic with a rotational constant $B_0$ (in cm$^{-1}$) the rotational partition function is $(k_BT)/\sigma B_0)$. For a rigid, nonlinear molecule with rotational constants $A_0$, $B_0$, and $C_0$, the polyatomic partition function can be accurately approximated[60] as:

$$Q_{rot} = \frac{1}{\sigma}\sqrt{\frac{\pi(k_BT)^3}{A_0B_0C_0}} \tag{A4}$$

In these simple expressions, $\sigma$ is the symmetry number; see Table 140 of Herzberg.[60] The symmetry number, $\sigma$, is equal to the number of indistinguishable positions into which the molecule can be turned by rigid rotations. For $NH_3$, $\sigma$ is 3 whereas for $NH_2^-$, $\sigma$ is 2. The rotational entropy becomes:

$$S_{rot} = \frac{3}{2}R + \frac{R}{2}\ln\left|\frac{\pi(k_BT)^3}{ABC}\right| - R\ln(\sigma) \tag{A5}$$

To employ (A5) we require $A_0$, $B_0$, $C_0$, and $\sigma$ for $NH_3$ and $NH_2^-$; these values are available.

| | ammonia[61] | amide anion[62] |
|---|---|---|
| $A_0$/cm$^{-1}$ | 9.444 3 | 22.75 |
| $B_0$/cm$^{-1}$ | 6.196 | 13.11 |
| $C_0$/cm$^{-1}$ | 6.196 | 8.34 |
| $\sigma$ | 3 | 2 |

In the case of the $(3n - 6)$ vibrations, one assumes that the frequencies $\nu_i$ (with degeneracies $g_i$) are separable and finds:

$$S_{vib} = -R\sum_{i=1}^{3n-6} g_i \ln(1 - e^{-\nu_i/k_BT}) + R\sum_{i=1}^{3n-6} g_i\left(\frac{\nu_i}{k_BT}\right)\left(\frac{1}{e^{\nu_i/k_BT} - 1}\right) \tag{A6}$$

The vibrational entropy requires experimental vibrational frequencies (in cm$^{-1}$) which are experimentally known for both $NH_3$ and $NH_2^-$.

| | ammonia[61] | amide anion[63] |
|---|---|---|
| $\nu_1$ | 3336.2 | 3121.9 |
| $\nu_2$ | 932.5 | 1463.0 |
| $\nu_3$ | 3443.6 | 3190.3 |
| $\nu_4$ | 3443.6 | |
| $\nu_5$ | 1626.1 | |
| $\nu_6$ | 1626.1 | |

Application of eqs A2, A5, and A6 to $NH_3$ and $NH_2^-$ yields the following results (in cal mol$^{-1}$ K$^{-1}$ or entropy units, eu).

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[60] Herzberg, G. H. *Molecular Spectra and Molecular Structure: Infrared and Raman Spectra of Polyatomic Molecules*; D. Van Nostrand: Princeton, NJ, 1945; Vol. II, see Chapter V.

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| | $NH_3$ | $NH_2^-$ |
|---|---|---|
| $S_{300}$(translation) | 34.5 | 34.3 |
| $S_{300}$(rotation) | 11.6 | 10.9 |
| $S_{300}$(vibration) | 0.1 | 0.0 |

Summing the entropies leads to the entropy of ionization, $\Delta_{acid}S_{300}(NH_3) = S_{300}(NH_2^-) + S_{300}(H^+) - S_{300}(NH_3)$, which is 45.2 + 26.0 − 46.2 or 25.1 cal mol$^{-1}$ K$^{-1}$.

Note that the translational and rotational contributions to the entropy are much more important than vibrational components. Suppose that we ignore both the vibrational (eq A6) and translational contributions (eq A2) to the entropy of ionization. Thus we examine $\Delta_{acid}S_{300}(NH_3) \simeq S_{300}(NH_2^-)_R + S_{300}(H^+) - S_{300}(NH_3)_R$ which can be written with the help of (A5) as:

$$\Delta_{acid}S_{300}(NH_3) \simeq \frac{R}{2}\ln\left|\frac{A_0B_0C_0(NH_3)}{A_0B_0C_0(NH_2^-)}\right| + R\ln\left|\frac{\sigma(NH_3)}{\sigma(NH_2^-)}\right| + S_{300}(H^+) \tag{A7}$$

If we evaluate (A7) by assuming that the rotational constants are roughly equal, $(A_0B_0C_0)_{NH_3} \simeq (A_0B_0C_0)_{NH_2^-}$, we estimate $\Delta_{acid}S_{300}(NH_3) \simeq 26.9$ cal mol$^{-1}$ K$^{-1}$ which is in error by roughly 1.8 cal mol$^{-1}$ K$^{-1}$. However, if the proper rotational constants are included in the evaluation of (A7), this expression gives $\Delta_{acid}S_{300}(NH_3) \simeq 25.4$ cal mol$^{-1}$ K$^{-1}$ which compares favorably with the exact value of 25.1 cal mol$^{-1}$ K$^{-1}$.

Finally, if we only exclude vibrations (eq A6) from the entropy calculation, we can find a superior estimate of the entropy of ionization. Use of (A2) with (A7) gives:

$$\Delta_{acid}S_{300}(NH_3) \simeq \frac{3}{2}R\ln\left|\frac{M(NH_2^-)}{M(NH_3)}\right| + \frac{R}{2}\ln\left|\frac{A_0B_0C_0(NH_3)}{A_0B_0C_0(NH_2^-)}\right| + R\ln\left|\frac{\sigma(NH_3)}{\sigma(NH_2^-)}\right| + S_{300}(H^+) \tag{A8}$$

Expression A8 is quite useful; evaluation for the case of ammonia leads to an estimate, $\Delta_{acid}S_{300}(NH_3) \simeq 25.2$ cal mol$^{-1}$ K$^{-1}$, that is within 0.1 eu of the exact value of 25.1 eu.

Expression A8 can be generalized for the ionization of a nonlinear, rigid polyatomic molecule: $AH \rightarrow A^- + H^+$. If the mass of anion $A^-$ is written as $M(A^-)$ with rotational constants $A_0B_0C_0(A^-)$ and symmetry number $\sigma(A^-)$, an approximation to the entropy of ionization analogous to (A8) can be given which only omits the small vibrational contribution, (A6).

$$\Delta_{acid}S_{300}^{nonlinear}(AH) \simeq \frac{3}{2}R\ln\left|\frac{M(A^-)}{M(AH)}\right| + \frac{R}{2}\ln\left|\frac{A_0B_0C_0(AH)}{A_0B_0C_0(A^-)}\right| + R\ln\left|\frac{\sigma(AH)}{\sigma(A^-)}\right| + S_{300}(H^+) \tag{A9}$$

Note that the mass units ($M$), amu or kg, do not matter since only a ratio is involved; likewise the rotational constants can be used in cm$^{-1}$, or GHz, or MHz. Sometimes the rotational energy levels are computed[30] in terms of the moments of inertia, $I_a$ given in units of (amu Å$^2$) or (g cm$^2$), rather than with the rotational constant, $A_0$. Since the two are reciprocally related, $A_0 \equiv h/(8\pi^2 cI_a)$, we need only to invert the logarithm to find the approximation, (A10).

$$\Delta_{acid}S_{300}^{nonlinear}(AH) \simeq \frac{3}{2}R\ln\left|\frac{M(A^-)}{M(AH)}\right| + \frac{R}{2}\ln\left|\frac{I_aI_bI_c(A^-)}{I_aI_bI_c(AH)}\right| + R\ln\left|\frac{\sigma(AH)}{\sigma(A^-)}\right| + S_{300}(H^+) \tag{A10}$$

Finally we can cast (A9) into the proper form to handle the ionization of a linear species such as $HCN \rightarrow CN^- + H^+$ or $HCCH \rightarrow HCC^- + H^+$. In this case there is only one rotational constant for AH, $B_0$, and (A9) becomes (A11).

$$\Delta_{acid}S_{300}^{linear}(AH) \simeq \frac{3}{2}R\ln\left|\frac{M(A^-)}{M(AH)}\right| + R\ln\left|\frac{B_0(AH)}{B_0(A^-)}\right| + R\ln\left|\frac{\sigma(AH)}{\sigma(A^-)}\right| + S_{300}(H^+) \tag{A11}$$

Use of (A11) for HC≡CH is an instructive example. With the rotational constants and vibrational frequencies for acetylene,[61] and the ethynyl anion,[64] HC≡C$^-$ (tabulated in footnote 68 in the review of Berkowitz *et al.*[16]), we estimate $\Delta_{acid}S_{300}^{linear}(HCCH) \simeq 27.0$ cal mol$^{-1}$ K$^{-1}$. This is close to the correct value of 26.9 eu arrived at through use of (A2), (A5), and (A6).

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