FEATURE ARTICLE

Three Methods To Measure RH Bond Energies†

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We present a critical review of three different experimental methods used to measure bond energies: radical kinetics, gas-phase acidity cycles, and photoionization mass spectrometry. These experimental techniques are currently in use to measure the bond energies of a large number of molecules. We discuss the basic premises of each of these experiments and explicitly try to point out the strengths and weaknesses of each method. We directly compare each of these procedures using a set of about 30 important molecules. These three different techniques have only a few disagreements among them, the case of ethylene being the most serious. For the overwhelming number of studies, all measurements lead to bond energies within each other's error bars. We include tables of ionization potentials, electron affinities, and heats of formation for about 40 important organic and inorganic radicals. We also list bond energies for the parent molecules at 0 and 298 K.

All chemists need to know bond energies. The energy changes associated with making and breaking bonds between atoms in a molecule are important practical concepts used everywhere in chemistry. In addition to being useful to synthetic chemists and material scientists, bond energies are also very good tests for empirical and *ab initio* theories of electronic structure. Accurate energies are essential for atmospheric and combustion modeling.

Bond dissociation energies (BDEs) offer an interesting window through which to view stability of radicals. In contrast to closed-shell species, the bond energies of radicals can sometimes be surprising. To wit, both the C–H and O–H bonds in methanol are roughly 100 kcal/mol; in contrast, recent studies[1] reveal that the corresponding bond strengths of the methoxy radical or the hydroxymethyl radical are much less (21 and 29 kcal/mol). Likewise, the first C–H bond in benzene is approximately 110 kcal/mol, which contrasts[2,3] to the energy of the second C–H bonds leading to *o*-benzyne (78 kcal/mol), *m*-benzyne (97 kcal/mol), or *p*-benzyne (110 kcal/mol).

This is an essay which strives to compare and contrast three powerful methods for the experimental determination of polyatomic bond energies: radical kinetics, gas-phase acidity cycles, and photoionization mass spectrometry.

Many techniques have been used to measure a huge number of BDEs, and it is not our purpose to survey this massive field; some of the "standard reviews" are listed below.[4-6] Instead, we will discuss three approaches that are commonly used to determine the R–H bond energies of *gas-phase*[7] polyatomic molecules: (a) the study of radical kinetics, (b) the use of negative ion thermochemical cycles, and (c) photoionization mass spectrometric techniques. It is essential to stress the *complementarity* of these three experimental methods; they are all interrelated. Our goal in this essay is to dissect each method in order to describe how the measurements are carried out and what the limitations are and to demonstrate by direct comparison that all give the same bond energies.

What are these methods?

(*a*) *Radical Kinetics.* Studies of the kinetics of chemical equilibria, such as those involving the reaction of a halogen atom, X, with a substrate, RH, can provide very accurate thermochemical information on the radical, R, that is formed.

$$RH + X \rightleftharpoons R + XH \qquad (1)$$

By generating [X] or [R] under controlled conditions using laser or flash photolysis, one can determine the absolute rate constants k_1 and k_{-1} in time-resolved experiments using atomic fluorescence and/or photoionization mass spectrometric detection of the reactive intermediates. These rate constants fix the equilibrium constant, $K_{equi}(1)$, which permits one to determine $\Delta_{rxn}G(1)$, from which the enthalpy, $\Delta_{rxn}H(1)$, can be extracted.[8] If the heats of formation [$\Delta_fH°$(RH), $\Delta_fH°$(X), and $\Delta_fH°$(XH)] are known, $\Delta_{rxn}H(1)$ permits one to find $\Delta_fH°$(R) which fixes the bond energy, BDE(R–H). Under favorable conditions where the temperature dependences of k_1 and k_{-1} can be determined accurately, $\Delta_{rxn}H(1)$ can be derived directly from the differences in activation energies for the forward and reverse reactions, $\Delta_{rxn}H(1) = E_1$(measured) $- E_{-1}$(measured).

(*b*) *Negative Ion Cycles.* Ion chemistry can be used to deduce the gas-phase acidity of a target molecule, RH. The acidity,

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‡ David Gutman passed away in November 1993.

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$\Delta_{acid}H$, is the enthalpy for the proton abstraction reaction.

$$RH \rightarrow R^- + H^+ \quad (2)$$

This acidity is related to the bond dissociation energy and the electron affinity of the final radical by the following relationship:

$$\Delta_{acid}H(R\text{–}H) = BDE(R\text{–}H) + IP(H) - EA(R) \quad (3)$$

One uses negative ion photoelectron spectroscopy to measure the EA(R) of the radical and combines it with the $\Delta_{acid}H$(R–H) to extract values for BDE(R–H).

(*c*) *Photoionization Mass Spectrometry.* By photoionization mass spectrometry (PIMS), one can measure the appearance energy [E_{AP}(R–H)] of the dissociative process: AP(R^+,RH)

$$RH + h\nu_{AP} \rightarrow R^+ + H + e^- \quad (4)$$

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

$$E_{AP}(R^+,RH) = BDE(R\text{–}H) + IP(R) \quad (5)$$

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 BDE(R–H). Alternatively, if Δ_fH_0(RH) is known, E_{AP}(R^+,RH) provides one with the heat of formation of the cation; $\Delta_fH_0(R^+) = E_{AP}(R^+,RH) + \Delta_fH_0(RH) - \Delta_fH_0(H)$.

These three techniques are all gas-phase measurements which provide bond energies without having to deal with solvent effects. These methods can be used on a large number of species (hundreds) and have an accuracy between ±3 and ±0.2 kcal/mol.[9] Our goal here is to compare these three experiments with each other and to demonstrate by direct comparison that they achieve consistent results.

We will not attempt to survey the computational literature. It is very important to recognize that *ab initio* electronic structure calculations have developed to the point where they can provide significant assistance to the experimentalist. These elaborate computations require very large basis sets and careful attention to electron correlation and can only be applied to molecules with a few heavy atoms. When the target molecule is small enough for these techniques to be applied, bond energies can be computed to an accuracy of roughly ±2 kcal/mol.[10–16a,b]

Before we begin to discuss bond energies, it is important to define terms. This may seem pedantic, but not everyone means the same thing when referring to a BDE. Consider the dissociation of some polyatomic species (such as H_2O, NH_3, SiH_4, or $C_6H_5CH_2$–H):

$$RH \rightarrow R + H \quad (6)$$

At 0 K the energy for process 6 is called the dissociation energy and is written[17] as D_0(R–H). This is the energy difference of the appropriate species, each in its ground state (i.e., all fragments with $v'' = 0, J'' = 0$):

$$D_0(R\text{–}H) \equiv E_0(R) + E_0(H) - E_0(RH) \quad (7)$$

If one considers dissociation (6) at some temperature T other than 0 K, the proper function to consider is the enthalpy, H, since the dissociation breaks one molecule into two and produces pV work.

$$H = E + pV \cong E + RT \quad (8)$$

Thus dissociation at room temperature, where most experiments are done, is properly[18] a dissociation enthalpy (which is sometimes referred to as a bond enthalpy).

$$DH_{298}(R\text{–}H) \equiv \Delta_fH_{298}(R) + \Delta_fH_{298}(H) - \Delta_fH_{298}(RH) \quad (9)$$

In order to relate D_0(R–H) to DH_{298}(R–H), one makes use[19] of the integrated heat capacity.

$$DH_{298}(R\text{–}H) = D_0(R\text{–}H) + \int_0^{298} dT\,[C_p(R) + C_p(H) - C_p(RH)] \quad (10)$$

To dissociate R–H at temperature T, energy must be supplied to break the bond, but it flows into all accessible degrees of freedom of the products as well. The molecule RH with its translations, rotations, and vibrations at temperature, T, shatters to produce fragments with different masses, rotational constants, and vibrational frequencies. The dissociation products in (6), H and R, will also be described by a Maxwell–Boltzmann distribution. Equation 10 tells you that as $T \rightarrow 0$ K, $DH_T(R\text{–}H) \rightarrow D_0(R\text{–}H)$.

Experimental Probes of Bond Energies

A. Radical Kinetics. For nearly 50 years, studies of the kinetics of equilibria involving the reactions of halogen atoms (X = Cl, Br, I) with organic molecules R–H have been,[5,20–28] and continue to be, a rich source of thermochemical information on R–H bonds broken in reactions such as eq 1. Ideally, the forward and reverse reactions are isolated for direct study and rate constants (k_1 and k_{-1}) measured. If k_1 and k_{-1} can be measured accurately as a function of temperature, the Arrhenius activation energies (E_1 and E_{-1}) are established, and $\Delta_{rxn}H(1)$, obtained from $E_1 - E_{-1}$, for the midtemperature of the experiments is obtained directly. This is the **second law** method for obtaining $\Delta_{rxn}H$. If k_1 and k_{-1} can be determined at only a single temperature (or over a very limited temperature range), $\Delta_{rxn}H(1)$ can still be obtained. In this case, the more limited kinetic information provides $K_{equi}(1) = k_1/k_{-1}$ and hence $\Delta_{rxn}G(1)$ at one temperature. $\Delta_{rxn}G(1)$ may be combined with $\Delta_{rxn}S(1)$ at the same temperature to obtain $\Delta_{rxn}H(1)$. $\Delta_{rxn}S(1)$ is obtained from calculated entropies of reactants and products using partition functions. This latter procedure for obtaining $\Delta_{rxn}H(1)$ is referred to as the **third law** method. If R is a relatively small radical (≤15 atoms), its structure and vibrational frequencies are frequently known from experiment and/or *ab initio* calculations, permitting more accurate calculation of radical entropies (and hence of reaction entropies) than is obtained from experiment [from a knowledge of $\Delta_{rxn}G(1)$ and $\Delta_{rxn}H(1)$]. If this is the case, the third law method provides a somewhat more accurate radical heat of formation than does the second law method.

Experimentally determined values of $\Delta_{rxn}H(1)$ and/or $\Delta_{rxn}G(1)$ are for a characteristic temperature of the experiments and are "corrected" to 298 K using tabulated or calculated heat capacities.[18] $\Delta_{rxn}C_p(1)$ is usually so small that this correction rarely is over 0.2 kcal/mol. Hence, if the second law method is used, $\Delta_{rxn}H(1)$ is obtained essentially directly from experiment without the need for other data or for assumptions. Since $\Delta_fH°$(RH), $\Delta_fH°$(X), and $\Delta_fH°$(HX) are all known, $\Delta_fH°$(R) [and hence the BDE(R–H)] can be obtained from the experimental determination of $\Delta_{rxn}H(1)$.

Kinetic studies of equilibria other than those involving the hydrogen halides have also yielded thermochemical information on polyatomic free radicals, particularly studies of dissociation–recombination equilibria (see below). Due to space limitation we focus here on the family of studies involving the hydrogen halides.

In recent years, the development of flash-photolysis techniques combined with sensitive detection methods has permitted isolating both forward and reverse reactions of equilibria involving the reactions of halogen atoms with organic substrates, reactions 1 and −1. Atomic fluorescence has been most valuable for monitoring the kinetics of the forward X + R–H reactions[26,29–34] while photoionization mass spectrometry, which has been found to be extremely useful[35] as a sensitive detector of polyatomic free radicals, R, has been used to study R + HX reactions in time-resolved experiments under essentially isolated conditions.

Prior to 1988, it was typically necessary to combine kinetic information on the forward reactions with assumed information

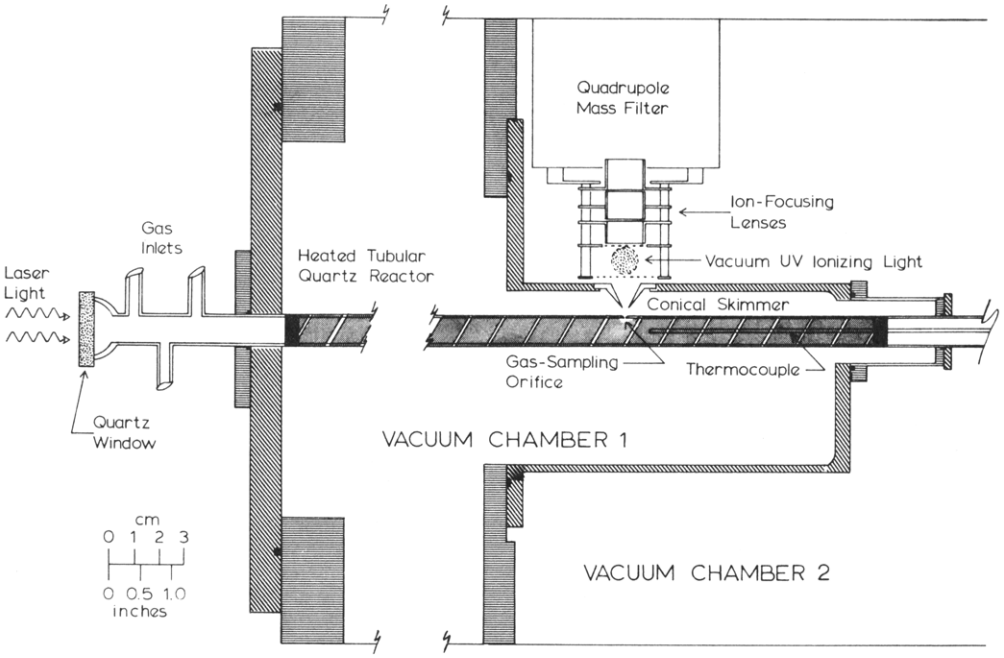


Figure 1. Drawing of heatable tubular reactor coupled to a photoionization mass spectrometer used to isolate and study reactions of polyatomic free radicals with hydrogen halides.[35]

on the reverse reactions to obtain the desired thermochemical information on reaction 1.[5,24,25] While there were many direct kinetic studies of X + R–H reactions reported, there were essentially none of the reverse reactions, (–1), due to the greater difficulty of isolating reactions of polyatomic free radicals for kinetic study. Typically, in these older thermochemical studies, the *measured* activation energies of the forward reactions were combined with *assumed* activation energies of the reverse reactions to obtain $\Delta_{rxn}H(1)$, $\Delta_{rxn}H(1) = E_1(\text{measured}) - E_{-1}(\text{assumed})$.[5,24] From general knowledge that R + HX reactions (involving HBr and HI) are very rapid processes and from observations that R + HI rate constants are larger than corresponding R + HBr rate constants, it became the practice to use the following assumed "generic" activation energies for R + HX reactions (which were presumed to be accurate to ±1 kcal/mol) to obtain $\Delta_{rxn}H(1)$ from the measured activation energies of X + R–H reactions: 2 ± 1 kcal/mol for all R + HBr reactions and 1 ± 1 kcal/mol for all R + HI reactions. Reviews of these earlier studies, discussions of the thermochemical calculations and the assumptions used, and tables of radical heats of formation are provided by O'Neal and Benson[24] and by McMillen and Golden.[5]

In the late 1980s, Gutman and co-workers developed a procedure to isolate R + HX reactions for direct kinetic study. It involved the use of a heatable tubular reactor coupled to a very sensitive photoionization mass spectrometer. These relatively recent experiments and the technique used to isolate and study R + HX reactions are described here. In these studies, it was discovered that virtually all the R + HBr and R + HI reactions investigated have negative activation energies, as low as –2 kcal/mol. Hence, new thermochemical calculations (since 1988) based on measured activation energies for the R + HX reactions have generally yielded higher radical heats of formation (and R–H bond energies). These revised values range from 1 to 4 kcal/mol higher than those that were obtained from prior studies of the same equilibria, when "generic" activation energies for R + HX reactions were used in thermochemical calculations.

The higher radical heats of formation (and R–H bond energies) now being obtained from thermochemical studies of reaction 1 are in complete accord with those obtained from studies of other equilibria involving neutral species, in particular studies of dissociation–recombination equilibria such as those involving several alkyl radicals which have been reviewed[36,37] by Tsang: R–H ⇌ R + H and R–CH_3 ⇌ R + CH_3. Former disparities between heats of formation derived from the two kinds of equilibria (i.e., X + RH and dissociation–recombination equilibria) which had cast doubts on the veracity of the results obtained from both kinds of studies have completely disappeared.[28,33]

The apparatus used by Gutman and co-workers[35] to study the kinetics of R + HX reactions is shown in Figure 1. Briefly, gas flowing through the heatable 1.05- or 2.20-cm-i.d. Pyrex (or quartz) tubular reactor contains the radical precursor, HX, in varying amounts and an inert carrier gas in large excess (>99% helium at a pressure of roughly 5 Torr). Homogeneous reaction is initiated by pulsed unfocused radiation (≅5 Hz) from an excimer laser (λ_0 = 193 or 248 nm) directed along the axis of the tubular reactor; this burst of laser light photolyzes the radical precursor to generate the reactive species, R. The flow velocity (3–5 m s^{-1}) is adequate to completely replace the gases in the reactor between laser pulses. Gas emerging from a small sampling orifice in the wall of the reactor is formed into a molecular beam and analyzed continuously using a photoionization mass spectrometer. The photoionizing light in the mass spectrometer is provided by simple high-intensity microwave-excited atomic resonance lamps.[38,39] By changing the gas flowing in the lamps, radiation of different ionizing energies is obtained in roughly 0.5-eV steps between 7 and 11.6 eV. By using an ionizing photon with energy between the ionization potential of the radical of interest and the fragment onset of the precursor molecule, specious signals are suppressed and the radical, R, is detected by the appearance of the ion R^+ with essentially no background. For example, a hydrogen resonance lamp (10.2 eV) is typically used to detect CH_3 radicals which have an ionization potential of 9.8 eV.

The technique is sensitive enough to permit the use of initial concentrations of polyatomic free radicals in the range 10^8–10^{11} radicals cm^{-3} in time-resolved kinetic experiments. Under these initial conditions, radical–radical recombination (a frequent competing process in kinetic studies involving polyatomic free radicals) has a negligible rate compared to that of the R + HX reaction under study. The reaction of interest is essentially isolated for direct study in these experiments typically under pseudo-first-order conditions.

The use of atomic resonance fluorescence to monitor the kinetics of atom–molecule reactions is well documented. Wine and co-workers[30,32,34] as well as Pilling and co-workers[29,31,33] have recently studied the kinetics of several Br + RH reactions. The results of such studies have been used in the thermochemical calculations of radical heats of formation given in Table 1. Both groups have extended the method to include monitoring Br formation in R +

TABLE 1: Second- and Third-Law Determinations of Radical Heats of Formation Based on Studies of the Kinetics of Br + RH ⇌ R + HBr Equilibria

radical	$\Delta_f H_{298}°$ (kcal/mol) second law	third law	recommended	DH_{298}(R–H)	ref
CH_3	34.8 ± 0.3	34.7 ± 0.6	34.8 ± 0.3	104.8 ± 0.3	40, 41, 182
CH_3CH_2	29.1 ± 0.4	29.2 ± 0.4	28.9 ± 0.4	101.1 ± 0.4	33
$CH(CH_3)_2$	21.3 ± 0.3	21.6 ± 0.5	21.5 ± 0.4	98.6 ± 0.4	33
$CH_3CHCH_2CH_3$	16.2 ± 0.7	16.1 ± 0.5	16.1 ± 0.5	98.2 ± 0.5	33
$C(CH_3)_3$	12.3 ± 0.4	12.3 ± 0.4	12.3 ± 0.4	96.5 ± 0.4	33
CH_2OH		−2.9 ± 1.0	−2.9 ± 1.0	97.2 ± 1.0	1, 44, 45, 183
CH_3CO	−2.5 ± 0.4	−2.4 ± 0.3	−2.4 ± 0.3	89.4 ± 0.3	184
SiH_3	48.0 ± 0.7	47.8 ± 0.6	47.9 ± 0.6	91.8 ± 0.5	29
SH	34.0 ± 0.7	34.4 ± 0.7	34.2 ± 0.7	91.2 ± 0.7	34
CH_3S	29.9 ± 0.4	29.7 ● 0.4	29.8 ± 0.4	87.4 ± 0.4	34

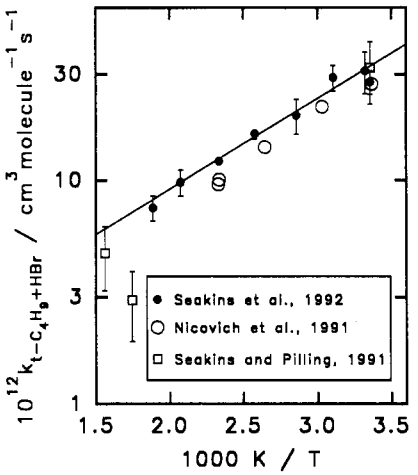


Figure 2. Arrhenius plot of t-C_4H_9 + HBr rate constants reported in three recent investigations. Rate constants below 500 K were obtained using conditions in which the t-C_4H_9 + HBr reaction proceeded to completion. Rate constants above 500 K obtained less directly, from studies of the relaxation of the reverse reaction (Br + i-C_4H_{10}) to equilibrium. Line on plot is fit of the rate constants of Seakins *et al.*[33] Other references are Seakins and Pilling[31] and Nicovich *et al.*[32]

HBr reactions and hence to obtain R + HBr rate constants as well as Br + RH constants. Agreement among the R + HBr rate constants is excellent for the different diagnostic methods used. For the case of the t-C_4H_9 radical, recently reported rate constants for the $C(CH_3)_3$ + HBr reaction are plotted in Figure 2. They include values obtained by monitoring Br atom production using atomic fluorescence by Nicovich *et al.*[32] and by Seakins and Pilling[31] and from monitoring the $C(CH_3)_3$ radical decay using photoionization mass spectrometry by Seakins *et al.*[33] The activation energy of the line through the data of Seakins *et al.* is −1.9 kcal/mol. Particular attention is drawn to the close agreement below 500 K (i.e., 1000 K/T from 2 to 3.5). The two t-C_4H_9 + HBr rate constants above 500 K were extracted from experiments in which the reaction did not go to completion but rather relaxed to an observable equilibrium which provides less accurate determinations of individual rate constants but direct determinations of $K_{rxn}(1)$. The existence of negative activation energies in selected exothermic R + HX reactions is now an established fact.

In the case of many of the X + RH equilibria studied (particularly involving bromine atoms), the reactions of interest are close to being thermoneutral. When this is the case, both the forward and reverse reactions are relatively fast and can be isolated for direct study, and absolute rate constants can be obtained for both reaction directions as a function of temperature. For a number of radicals, heats of formation were obtained from such studies with high accuracy using both the second law and third law methods. It should be pointed out that these two data-reduction methods are somewhat independent since the former uses only the *temperature dependencies* of the forward and reverse rate constants (E_1 − E_{-1}) to obtain $\Delta_{rxn}H(1)$ (ignoring the magnitudes of k_1 and k_{-1}) while the latter uses only the *magnitudes* of the two rate constants at a particular temperature to obtain $K_{rxn}(1)$ and $\Delta_{rxn}G(1)$. (In this case the temperature dependencies of k_1 and k_{-1} are ignored.) Results of both the second and the third law determinations of radical heats of formation from such kinetic data for reaction 1 (where both the forward and reverse reactions were isolated for study) are presented in Table 1. The close agreement between the two values of the radical heat of formation obtained from these two quite different properties of the measured rate constants (differences in $\Delta_f H°$ are typically under 0.3 kcal/mol) provides strong support for the stated accuracies of the heats of formation derived from these kinetic studies. (Stated 1σ accuracies of the radical heats of formation vary but are typically in the range 0.3–0.5 kcal/mol.)

The I + RH reactions are quite endothermic (typically $\Delta_{rxn}H(1)$ is 25–30 kcal/mol), making direct study essentially impossible to date. However, a considerable body of I + RH rate constants has been obtained from kinetic studies of complex iodination processes in which the rate of production or loss of stable species was monitored. These studies, reviewed and used by O'Neal and Benson and by McMillen and Golden in their evaluations of radical heats of formation and R–H bond energies, have resulted in many radical heats of formation (and R–H bond energies) which are too low by 2–4 kcal/mol, again due largely to the use of the assumed "generic" activation energy for R + HI reactions in the thermochemical calculations.

The kinetics of several R + HI reactions, including those of five alkyl[28] radicals, the silyl radical,[29] (SiH_3), and the hydroxymethyl radical[1] (CH_2OH), have recently been directly studied using the photoionization mass spectrometric technique. When the rate constants measured in these studies are combined with the old I + RH rate constants obtained indirectly, radical heats of formation (and R–H bond energies) are obtained which are in very good agreement with those now obtained in direct studies of Br + RH equilibria (and with dissociation–recombination equilibria).

A few studies have obtained radical thermochemistry from direct investigations of the kinetics of Cl + RH equilibria, in particular the near thermoneutral Cl + CH_4,[40,41] Cl + C_2H_4,[42,43] and Cl + CH_3OH systems.[44,45] Again, results are in very good agreement with those obtained from the Br atom and I atom equilibria and other methods as well, with the exception of the determination of the C_2H_3 heat of formation from the study of the Cl + C_2H_4 equilibrium which is in conflict with values obtained using other methods such as with negative ion cycles.[46] The forward Cl + C_2H_4 reaction is the elementary reaction involved in these three systems that was not studied directly,[41] i.e., not isolated for direct investigation. It was studied using a very-low-pressure well-stirred reactor in which Cl atom loss during the residence time in the reactor was monitored. Interpretation of these experiments is not completely straightforward since secondary reactions and heterogeneous effects can be important in the data interpretation.[47] There is a real need for a more direct kinetic study of the Cl + C_2H_4 reaction at elevated temperatures where the abstraction reaction can be observed without competition from the addition mechanism and under conditions where

secondary reactions are unimportant. It is to be hoped that such a study will resolve the one significant remaining disparity between the radical heats of formation obtained from kinetic studies of both the forward and reverse reactions involved in X + R–H equilibria and from other methods such as negative and positive ion cycles.

The thermochemistry of the CH_2OH radical has been studied using three different RH + X ⇌ R + XH equilibria. Dóbé *et al.*,[44,45] studying Cl + CH_3OH, obtained $\Delta_f H_{298}°(CH_2OH)$ = −2.0 ± 1.2 kcal/mol (second law) and −2.4 ± 1.2 kcal/mol (third law). Seetula and Gutman[1] obtained −2.9 ± 1.0 kcal/mol (Br + CH_3OH, third law; error limits have been revised upward), −2.1 ± 1.8 kcal/mol (I + CH_3OH, second law), and −2.7 ± 1.9 kcal/mol (I + CH_3OH, third law). The results are in close agreement. In their third law calculations Seetula and Gutman originally selected $S_{300}(CH_2OH)$ = 61.08 cal/(mol K) given by Tsang[48] and based upon free rotation about the C–O bond. There is now evidence that CH_2OH is in fact a hindered rotor. We recalculate $S_{298}(CH_2OH)$ = 58.71 cal/(mol K), using the most recently available information[49] on the structure, vibrational frequencies, and barrier to rotation of CH_2OH. Using this entropy for CH_2OH in the Br + CH_3OH, third law determination of Seetula and Gutman, we obtain $\Delta_f H_{298}°(CH_2OH)$ = −2.9 ± 1.0 kcal/mol, close to the third law result for the Cl + CH_3OH reaction, −2.4 ± 1.2 kcal/mol. From these latter values, we deduce DH_{298}(H–CH_2OH) = 97.2 ± 1.0 kcal/mol (Seetula and Gutman) and 97.7 ± 1.2 kcal/mol (Dóbé *et al.*), in basically good agreement with the AP/IP values of D_0(H–CH_2OH) = 94.55 ± 0.14 kcal/mol and DH_{298}(H–CH_2OH) = 96.15 ± 0.14 kcal/mol obtained from PIMS (see section C below).

B. Negative Ion Cycles. Rather than attempt the direct measurement of a bond energy, D_0(R–H), an alternative method is to embed the BDE in a negative ion thermochemical cycle. This cycle, eq 3, involves the acidity of RH[$\Delta_{acid}H$(R–H)], the electron affinity of R, [EA(R)], and the ionization potential[50] of H atom [IP(H)]. The strategy is to measure $\Delta_{acid}H$(R–H) and EA(R) and then invert (3) to extract the bond energy, BDE. Care is needed to do this. As eq 3 shows, any errors in $\Delta_{acid}H$(R–H) or EA(R) will propagate into BDE(R–H). Use of the acidity/EA cycle is only useful if $\Delta_{acid}H$(R–H) and EA(R) can be cleanly measured in separate experiments.

The energetics of deprotonation in eq 2 is formally described by expression 3. To be precise, one needs to pay attention to temperatures in eq 3. Gas-phase acidities are generally based on experiments carried out at 298 K while electron affinities and ionization potentials are 0 K measurements. Rather than eq 3, the proper relation[5,51] to connect the acidity to the bond dissociation energy and the electron affinity of the radical is

$$\Delta_{acid}H_{298}(\text{R–H}) = DH_{298}(\text{R–H}) + \text{IP}_0(\text{H}) - \text{EA}_0(\text{R}) - [\text{thermal correction}] \quad (11)$$

The thermal correction is simply the proper integrated heat capacities.

$$[\text{thermal correction}] = \int_0^{298} dT\,[C_p(\text{R}) - C_p(\text{R}^-) + C_p(\text{H}) - C_p(\text{H}^+)] \quad (12)$$

The correction in eq 12 is always smaller than 0.3 kcal/mol and most times is computed to be about 0.05 kcal/mol. This correction is commonly ignored;[51–53] consequently, it is standard procedure in (11) to simply equate $\Delta_{acid}H_{298}$(R–H) with {DH_{298}(R–H) + IP(H) − EA(R)}.

Expression 11 indicates that the acidity is a large number. If a typical bond enthalpy is about 100 kcal/mol and a common EA is roughly 1 eV, one uses the ionization energy of H atom (313 kcal/mol) to arrive at an approximate acidity, $\Delta_{acid}H$(R–H) ≅ 100 + 313 − 23 or 390 kcal/mol. For example some representative acidities (out of several hundred examples)[52] are as follows:

	molecule	$\Delta_{acid}H$ (kcal/mol)
↑	CH_4	416
less acidic	NH_3	404
	H_2O	391
more acidic	HF	371
↓	HI	314

In order to use expression 11 to compute DH_{298}(R–H), one needs separate measurements of (1) the acidity and (2) the electron affinity.

1. Gas-Phase Acidities. The acidity,[54] $\Delta_{acid}H$, is the enthalpy for the proton abstraction reaction, eq 2, and most often is measured in ICR spectrometers[55–57] or flowing afterglow devices.[58] We will discuss several ways to find $\Delta_{acid}H$(R–H): (a) thermochemically, (b) equilibrium measurements, (c) bracketing measurements, (d) photoion pair formation, and, most recently, (e) collision-induced dissociation (CID) of cluster ions. Another experimental approach to molecular acidities is high-pressure mass spectrometry, but we simply do not have space to cover this technique here.[59]

(a) For a set of molecules {H_2, HF, HCl, HBr, HI, H_2O, CH_2O, NH_3, and CH_4}, one knows the bond dissociation energies and electron affinities much more precisely[60–63] than any acidity measurements; some of these are collected together in part A of Table 2. Consequently, the acidities for these species are **computed** with eqs 11 and 12 using EA(R) and D_0(R–H). The halogen acids, HX, together with water and ammonia are useful anchoring compounds with which to reference other acidities.

(b) There are two **equilibrium** ways to find $\Delta_{acid}H$: temperature-dependent and temperature-independent measurements. Suppose one has an unknown acid, HU. A common measurement of $\Delta_{acid}H$(HU) is to study the proton-transfer reaction with reference acids, HA_1, HA_2, ... These are constant-temperature measurements which can yield $K_{equi}(13)$ at T = 298 K.

$$U^- + HA \rightleftharpoons HU + A^- \quad (13)$$

Now the equilibrium constant for (13) can be found from the ion–molecule rate constants or the concentrations. Flowing afterglow instruments usually report separate measurements of the rate constants, k_{13} and k_{-13}, while ICR spectrometers directly measure the equilibrium ratio, ([A^-][HU])/([U^-][HA]).

$$K_{13} = \frac{k_{13}}{k_{-13}} = \frac{[A^-][HU]}{[U^-][HA]} = e^{-\Delta G_{acid}/RT} \quad (14)$$

Let us see how a flowing afterglow device can provide ion chemistry that is of use in (14); we will consider the determination of the acidity of HC≡CH as an example.

Figure 3 is a schematic diagram of a tandem flowing afterglow/selected ion flow tube which can be used to study proton-transfer kinetics; the classical reviews of flowing afterglow technologies are listed below.[58,64,65] Consider an acidity measurement which connects the acidity of HCC–H to that of HF. From the definition (2), $\Delta_{rxn}G_{298}(15)$ is the difference [$\Delta_{acid}G_{298}$(HCCH) − $\Delta_{acid}G_{298}$(HF)].

$$F^- + HCCH \rightleftharpoons HF + HCC^- \quad (15)$$

The acidity of HCCH was studied[46] by using a SIFT device to measure both the (a) rate constant of proton abstraction (k_{15}) of F^- with HCCH and (b) rate constant of proton abstraction (k_{-15}) of HCC^- with HF. To do this, F^- was prepared in the ion source of the SIFT by electron bombardment of NF_3. Ions were extracted from the resultant plasma through the SIFT sampling orifice and the SIFT quadrupole used to select the F^- ions which were injected into the reaction flow tube. HCCH was added downstream *via* the fixed gas inlets, and the decay of F^- (at m/e 19) was monitored as a function of distance from the detection quadrupole mass filter. The buffer gas has a laminar flow through the afterglow in Figure 3, and this permits a simple determination of the ion–molecule kinetic rate constant.

TABLE 2: Molecular Acidities and Electron Affinities[a]

molecule (RH)	$\Delta_{acid}H_{298}$(R–H)	electron affinity (R)	DH_{298}(R–H)	D_0(R–H)	ref
	Part A: $\Delta_{acid}H$(RH) is computed from EA(R) and D_0(RH)				
H_2	400.401 ± 0.002	17.3921 ± 0.0004	104.206 ± 0.001	103.266 ± 0.001	62, 91
HF	371.5 ± 0.2	78.4333 ± 0.0001	136.4 ± 0.2	135.4 ± 0.2	62, 67
HCl	333.4 ± 0.03	83.311 ± 0.001	103.15 ± 0.03	102.24 ± 0.03	62, 185
HBr	323.57 ± 0.05	77.5662 ± 0.0001	87.54 ± 0.05	86.64 ± 0.05	62, 185
HI	314.36 ± 0.07	70.545 ± 0.023	71.32 ± 0.06	70.42 ± 0.06	62, 185
H_2O	390.74 ± 0.05	42.1471 ± 0.0005	119.30 ± 0.05	118.08 ± 0.3	62, 186
CH_2O	394.4 ± 0.2	7.2 ± 0.1	88.04 ± 0.16	86.57 ± 0.16	187
NH_3	404.0 ± 0.4	17.8 ± 0.1	108.2 ± 0.3	106.7 ± 0.3	188, 189
CH_4	416.7 ± 0.7	1.8 ± 0.7	104.9 ± 0.1	103.3 ± 0.1	190–192
	Part B: D_0(RH) is determined by EA(R) and $\Delta_{acid}H$(RH)				
HCN	351.4 ± 0.5	89.1 ± 0.1	126.3 ± 1.5	124.8 ± 0.4	143, 193
H_2S	351.1 ± 2.0	53.43 ± 0.05	90.7 ± 2.0	89.8 ± 2.0	114, 194
H_2Se	350.5 ± 4.6	51.0 ± 0.7	87.9 ± 4.7	86.4 ± 4.7	195, 196
PH_3	370.8 ± 2.0	29.3 ± 0.2	86.5 ± 2.0	85.0 ± 2.1	114, 197
AsH_3	357.7 ± 2.0	29.3 ± 0.7	73.4 ± 2.1	72.0 ± 2.1	198, 199
SiH_4	372.2 ± 2.0	32.4 ± 0.3	91.1 ± 2.1	89.6 ± 2.0	114, 200
GeH_4	355.9 ± 3.6	≤40.1 ± 0.9	≤82.5 ± 3.7	≤81.0 ± 3.7	201
HCCH	378.0 ± 0.6	68.5 ± 0.2	133.1 ± 0.7	131.5 ± 0.7	202
CH_2CH_2	409.4 ± 0.6	15.4 ± 0.6	111.2 ± 0.8	109.7 ± 0.8	46
C_6H_6	399.8 ± 0.7	25.3 ± 0.1	111.2 ± 0.8	109.8 ± 0.8	203–205
CH_2CHCH_2–H	390.8 ± 2.1	10.9 ± 0.2	88.2 ± 2.1	86.7 ± 2.1	206–208
$C_6H_5CH_2$–H	380.8 ± 2.0	21.0 ± 0.1	88.2 ± 2.1	86.8 ± 2.1	114, 205
H–CH_2CHO	365.8 ± 2.2	42.08 ± 0.01	94.3 ± 2.2	92.8 ± 2.2	94, 114
CH_3CO–H	391.1 ± 2.1	9.8 ± 0.9	87.2 ± 2.3	85.7 ± 2.3	115, 116
CH_2CO	364.7 ± 2.0	54.2 ± 0.5	105.3 ± 2.1	103.9 ± 2.1	70
CH_3O–H	381.6 ± 0.7	36.2 ± 0.5	104.2 ± 0.9	103.0 ± 0.9	78, 209
CH_3CH_2O–H	378.6 ± 0.8	39.5 ± 0.2	104.6 ± 0.8	103.1 ± 0.9	46
CH_3S–H	356.9 ± 2.2	43.1 ± 0.3	86.4 ± 2.2	84.9 ± 2.2	114, 210
H–CH_2SH	394 ± 3	$HSCH_2^-$ has never been photodetached			118
CH_3CN	372.9 ± 2.1	35.6 ± 0.3	94.8 ± 2.1	93.3 ± 2.1	114, 120
CH_3NC	380.0 ± 2.0	24.4 ± 0.6	91.0 ± 2.1	89.5 ± 2.1	121, 131
HCOO–H	345 ± 2	$HCOO^-$ has never been photodetached			211
H–COOH	$^-$COOH acidity could not be determined				119
CH_3COO–H	342 ± 3	CH_3COO^- has never been photodetached			212
H–CH_2COOH	368 ± 3	$HOOCCH_2^-$ has never been photodetached			213
H–CH_2OH	$HOCH_2^-$ has never been prepared				
CH_3CH_3	$CH_3CH_2^-$ has never been prepared				
$(CH_3)_2CH_2$	$(CH_3)_2CH^-$ has never been prepared				
$(CH_3)_3CH$	$(CH_3)_3C^-$ has never been prepared				

[a] All values are in kcal/mol; see text for further details.

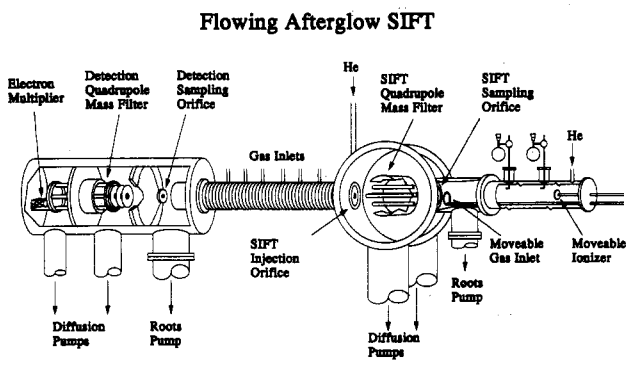


Figure 3. Schematic diagram of a flowing afterglow SIFT apparatus.

The resulting bimolecular rate constants were found to be $k_{15} = (1.0 \pm 0.3) \times 10^{-12}$ cm^3 s^{-1} and $k_{-15} = (1.3 \pm 0.2) \times 10^{-9}$ cm^3 s^{-1}. The ratio of these rate constants is the equilibrium constant, $K_{equil}(15) = k_{15}/k_{-15}$ or 0.0008 ± 0.0003. The equilibrium constant yields the free energy, $\Delta_{rxn}G_{298}(15) = 4.2 \pm 0.2$ kcal/mol. The free energy change for (15) can be expressed in terms of the gas-phase acidities: $\Delta_{rxn}G_{298}(15) = \Delta_{acid}G_{298}(HCCH) - \Delta_{acid}G_{298}(HF)$. So if the acidity of HF can be established as an anchor, $K_{equil}(15)$ will yield the acidity of HCCH, $\Delta_{acid}G_{298}(HCCH)$.

As mentioned earlier in section 1a, the gas-phase acidity of HF has been established by using the precise values of $DH_{298}(HF)$, IP(H), and EA(F) in eq 11. $D_0(HF)$ is known[66] to be 135.4 ± 0.2 kcal/mol, and the electron affinity[67] of fluorine atom is EA(F) = 3.401 190 ± 0.000 004 eV; consequently, $\Delta_{acid}H_0(HF) = 370.6 \pm 0.2$ kcal/mol. If the appropriate heat capacity corrections are applied, one finds $\Delta_{acid}H_{298}(HF) = 371.5 \pm 0.2$ kcal/mol (see Table 2); entropies of F^-, H^+, and HF lead to $\Delta_{acid}S_{298}(HF) = 19.30 \pm 0.01$ cal/(mol K) so eq 11 produces $\Delta_{acid}G_{298}(HF) = 365.8 \pm 0.2$ kcal/mol. Consequently, we see that $\Delta_{rxn}G_{298}(15) = 4.2 \pm 0.2$ kcal/mol implies that $\Delta_{acid}G_{298}(HCC–H) = 370.0 \pm 0.3$ kcal/mol. We desire $\Delta_{acid}H_{298}(HCC–H)$ so we have a final entropic correction to make; we need $\Delta_{acid}S_{298}(HCC–H)$. This is found[68] to be $\Delta_{acid}S_{298}(HCC–H) = 26.8$ cal/(mol K), and finally[69] we are led to $\Delta_{acid}H_{298}(HCC–H) = 370.0 \pm 0.3 + (298)(0.0268) = 378.0 \pm 0.6$ kcal/mol.

The case of acetylene is an unusually favorable one since the acidity can be tied *directly* to HF, one of the firmly established points of the acidity scale (top of Table 2). What happens if the target acid cannot be tied to such a point? Consider the ketene molecule, CH_2CO. When treated (eq 16) with a variety of bases in a flowing afterglow, the acidity of ketene was found[70] to be greater than CH_3CN (373 kcal/mol) and less than CH_3NO_2 (356 kcal/mol).

$$CH_2CO + NH_2^- \rightarrow HCCO^- + NH_3 \quad \text{(fast)} \quad (16a)$$

$$CH_2CO + CH_3O^- \rightarrow HCCO^- + CH_3OH \quad \text{(fast)} \quad (16b)$$

$$CH_2CO + CH_2CN^- \rightarrow HCCO^- + CH_3CN \quad \text{(fast)} \quad (16c)$$

$$CH_2CO + CH_3COCH_2^- \rightleftharpoons HCCO^- + CH_3COCH_3 \quad \text{(equil)} \quad (16d)$$

$$CH_2CO + CH_2CHO^- \rightleftharpoons HCCO^- + CH_3CHO \quad \text{(equil)} \quad (16e)$$

$$CH_2CO + CF_3CH_2O^- \rightarrow HCCO^- + CF_3CH_2OH \quad \text{(slow)} \quad (16f)$$

$$CH_2CO + CH_2NO_2^- \rightarrow HCCO^- + CH_3NO_2 \quad \text{(no rxn)} \quad (16g)$$

The equilibrium (16e) was studied in detail. Measurement of the proton-transfer rates (k_{16e} and k_{-16e}) leads to $K_{equil}(16e) = 6.8$, which corresponds to $\Delta_{rxn}G_{298}(16e) = -1.1 \pm 0.2$ kcal/mol. Now $\Delta_{rxn}G_{298}(16e) = [\Delta_{acid}G(CH_2CO) - \Delta_{acid}G(H\text{–}CH_2CHO)]$ so[71] $\Delta_{acid}G(CH_2CO) = 357.9 \pm 2.2$ kcal/mol. To extract the enthalpy, one has to compute $\Delta_{acid}S(CH_2CO)$ and finds[72] a value of 23.6 ± 2.2 cal/(mol K). Consequently, the acidity we seek, $\Delta_{acid}H(CH_2CO)$, is 364.8 ± 2.1 kcal/mol.

A word about uncertainties. Generally the weak link in this procedure is the necessary appeal to a ladder of "known" acidities. You will almost always find that the acidity of the target acid, HU, is known with respect to other acids on the acidity scale[73] to an uncertainty of about ± 0.2 kcal/mol. In order to account for errors in anchoring the *entire* acidity scale, one generally has to include an additional ±2 kcal/mol to the error bar. Converting $\Delta_{acid}G$ to $\Delta_{acid}H$ implies an additional uncertainty ($T\delta(\Delta S)$) of ±0.6 kcal/mol. Consequently, the final uncertainty in a typical acidity measurement[74] swells to $\pm\{0.2^2 + 2^2 + 0.6^2\}^{1/2}$ or ±2.1 kcal/mol.[75] Unless great care is taken to tie the unknown acid, HU, to one of the primary anchors, the resulting acidity $\Delta_{acid}H(HU)$ is generally uncertain to roughly ±2 or ±3 kcal/mol.

Another difficulty in acidity measurements is the *availability* of handy reference compounds. In order to make equilibrium measurements as in eq 13, you must relate the unknown ion, U^-, to a reference acid, HA. The acidity of HA and HU have to be within about 5 kcal/mol of each other, and this is not always easy to arrange. There is a useful chart of acidities published by Bartmess[76] which shows that the acidity scale is rather sparse from H_2O (391 kcal/mol) to NH_3 (404 kcal/mol) and CH_4 (416 kcal/mol).

An alternative to the single point (third law) method described above in (13) is to study the *temperature dependence* of the equilibrium (second law) in a pulsed electron beam mass spectrometer.[77] This technique has not been applied as frequently as the *constant-temperature* kinetic measurements in a flowing afterglow or an ICR. Consider the study of the acidity of methanol.[78]

$$HO^- + CH_3OH \rightleftharpoons H_2O + CH_3O^- \quad (17)$$

While varying the temperature over the range 298–700 K, the equilibrium constant (18) was measured.

$$K_{equil}(T) = \frac{[CH_3O^-][H_2O]}{[HO^-][CH_3OH]} \quad (18)$$

Since $K_{equil}(T)$ and $\Delta_{rxn}G(17)$ are related, one can use

$$\ln K_{equil}(T) = \frac{-\Delta_{rxn}H}{RT} + \frac{\Delta_{rxn}S}{R} \quad (19)$$

So a plot of $\ln K_{equil}(T)$ vs T^{-1} provides a straight line with $[\Delta_{rxn}S/R]$ as the intercept and $[-\Delta_{rxn}H/R]$ as the slope. Since $\Delta_{rxn}H$ is directly related to $\delta\Delta_{acid}H$, $\Delta_{acid}H(H_2O)$ fixes the acidity of methanol, $\Delta_{acid}H(CH_3O\text{–}H)$.

(c) There are a number of cases when two-way equilibrium measurements are just not possible. Then all one can do is to **bracket** the acidity. Consider the acidity of methylenimine, CH_2NH. One[79,80] can measure k_{20}, but since CH_2NH is not an available reagent, k_{-20} cannot be found.

$$CH_2N^- + HA \rightleftharpoons CH_2NH + A^- \quad (20)$$

In such cases, all that can be done is to bracket the unknown ion, U^-.

As a specific example,[46] consider the vinylidene anion, H_2CC^-. If one prepares the H_2CC^- ion in a SIFT, one rapidly sees that

$$H_2CC^- + H_2O \not\rightarrow H_2CCH + HO^- \quad (21a)$$

$$H_2CC^- + CH_3OH \rightarrow H_2CCH + CH_3O^- \quad (21b)$$

the acidity is somewhere between water and methanol. The facts are that the vinylidene anion does not react with water. With the detection limits of the flowing afterglow, this implies $k_{21a} \leq 4 \times 10^{-12}$ cm^3/s. The fastest that the reverse reaction could go is at the collision rate (if one had samples of the H_2CCH radical to measure it); $k_{-21a} \simeq 1.4 \times 10^{-9}$ cm^3/s. So $K_{21a} \leq 0.003$ and $\Delta G_{21a} \geq 3.5$ kcal/mol. From the acidity of water, this implies $\Delta_{acid}G(H_2CC\text{–}H) \leq 380.4 \pm 0.3$ kcal/mol. In the case of methanol, H_2CC^- reacts very rapidly to produce CH_3O^-; $k_{21b} = 1.20 \times 10^{-9}$ cm^3/s and k_{-21b} could not be measured. Consequently $\Delta_{acid}G(H_2CC\text{–}H)$ is greater than that of methanol,[81] so $\Delta_{acid}G(H_2CC\text{–}H) \geq 375.1 \pm 0.6$ kcal/mol.

What is the bottom line? $\Delta_{acid}G(H_2CC\text{–}H)$ is estimated by splitting the difference between water and methanol; $\Delta_{acid}G(H_2CC\text{–}H) = 377.6 \pm 3.1$ kcal/mol. If we estimate that $\Delta_{acid}S(H_2CC\text{–}H) \simeq S_{298}(H^+) = 26 \pm 4$ cal/(mol K), one finally computes the acidity of the vinyl radical,[82] $\Delta_{acid}H(H_2CC\text{–}H) = 385 \pm 3$ kcal/mol.

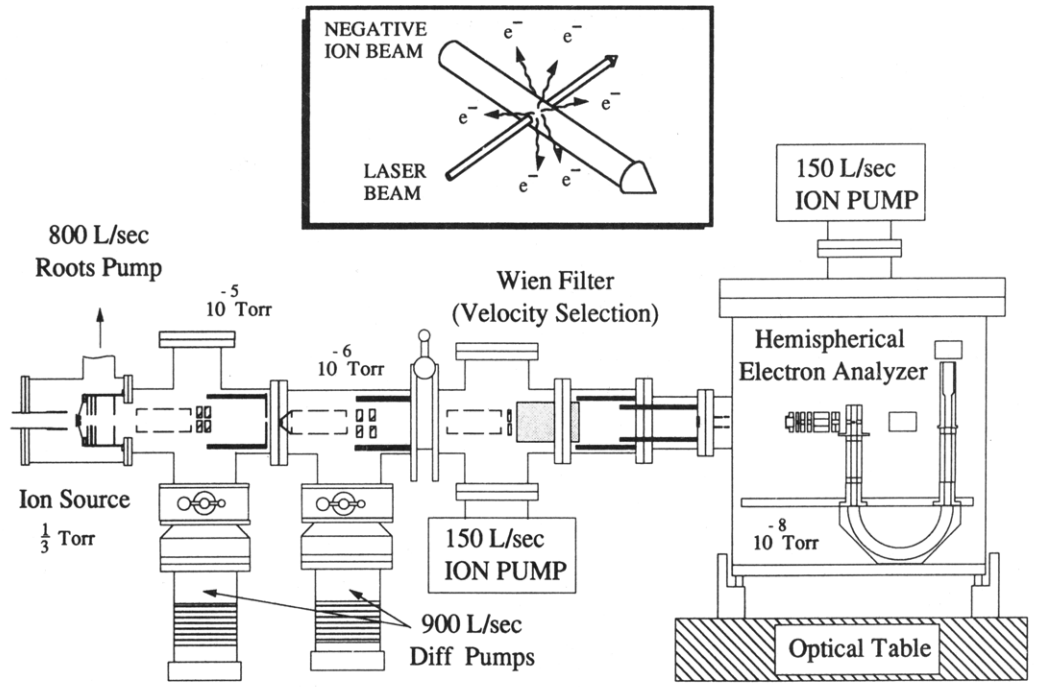
(d) One usually regards photoionization as the creation of a positive ion–electron pair upon interaction of sufficiently energetic photons with gaseous molecules. However, ionization can also occur without the formation of an electron, by production of a positive ion–negative ion pair. **Photoion-pair formation** can occur below the normal ionization threshold of the molecule.

$$RH + h\nu_{thresh} \rightarrow R^- + H^+ \quad (22)$$

Consider a diatomic molecule, MX. One can readily show that the ion-pair process may occur below IP(MX) if EA(X) exceeds $D_0(MX^+)$. Photoion-pair formation can occur by dissociation or predissociation. In the former, an electronic transition takes place between the ground state and the ion-pair state. The latter has (by definition) a long-range attractive force. In the absence of additional attractive covalent forces, the equilibrium separation of the ion-pair state will usually occur at much longer internuclear distances than in the ground state. Consequently, the Franck–Condon factors will not be favorable. Predissociation involves curve crossing. The initial photoabsorption can occur to a quasi-bound state whose geometry is close to that of the ground state, allowing for favorable Franck–Condon factors. This quasi-bound state is crossed by an ion-pair state, and predissociation to ion-pairs occurs, just as predissociation into neutrals can proceed. When the process of ion-pair formation is predissociative, one can anticipate a structured photoion yield curve, whereas direct dissociation, usually accessing the repulsive limb of the potential curve, will be structureless. Most experimentally observed cases of photoion-pair formation are predissociative.

About 40 examples of photoion-pair formation are known. This field has been the topic of a recent review article.[83] Here, we note that several examples relate to gas-phase acidity determinations, e.g., H_2, HF, H_2O, H_2S, HCN, and C_2H_2. In all of these cases, the threshold for photoion-pair formation *is* the gas-phase acidity; a few of these are listed in Table 3. These thresholds are just the gas-phase acidities at 0 K; consequently, $\Delta_{acid}H_0(RH)$ and $\Delta_{acid}H_{298}(RH)$ are tabulated for comparison to Table 2, and the agreement is good.

(e) Recent progress in mass spectroscopy[84] has demonstrated the fact that **collision-induced dissociation** of proton bound dimer



Negative Ion Photoelectron Spectrometer

Figure 4. Schematic diagram of a negative ion photoelectron spectrometer.

TABLE 3: Photoion-Pair Thresholds: RH + $h\nu \rightarrow R^- + H^+$

molecule	ion pair threshold/eV	$\Delta_{acid}H_0$(RH)/ kcal mol^{-1}	$\Delta_{acid}H_{298}$(RH)/ kcal mol^{-1}
HF	16.039 ± 0.021	369.9 ± 0.5	370.8 ± 0.5
H_2O	16.87 ± 0.03	389.0 ± 0.7	390.2 ± 0.7
HCN	15.18 ± 0.02	350.1 ± 0.5	351.4 ± 0.5
HCCH	16.335 ± 0.02	376.7 ± 0.5	378.1 ± 0.5

ions, $[U{\cdot}HA]^-$, reflects the relative acidities of the product acids. The ratio of product CID ions, U^-/A^-, reflects only the difference in acidity, $\Delta_{acid}G$(HU) and $\Delta_{acid}G$(HA).

$$[U{\cdot}HA]^- + CID \xrightarrow{k_{HA}} U^- + HA \qquad [U{\cdot}HA]^- + CID \xrightarrow{k_{HU}} A^- + HU \tag{23}$$

If HA and HU are similar species with *comparable* acidities, then the thresholds for dissociation to U^- or A^- will be quite similar. Under such conditions,[85,86] it is claimed that

$$\ln\left(\frac{k_{HA}}{k_{HU}}\right) = \ln\left(\frac{[U^-]}{[A^-]}\right) = \frac{\delta\Delta_{acid}G}{RT} \tag{24}$$

Such a CID approach may become an important avenue to secure thermochemical parameters for ultratrace samples, or molecules with high molecular weights (such as proteins and nucleic acids), or substances which are unavailable in a pure state.

As an example, the relative acidities of CH_3CH_2OH and its isotopomers (CH_3CD_2OH, CD_3CH_2OH, and CD_3CD_2OH) were scrutinized[87] by CID studies of the cluster ions such as $[CH_3CH_2O^-{\cdot}HOCD_2CD_3]$. When the dimer ion is subjected to CID, more $CH_3CH_2O^-$ is formed than $CD_3CD_2O^-$, reflecting the greater exothermicity toward the d_0 product ion, $C_2H_5O^-$.

$$(<50\%)\ C_2H_5OH + C_2D_5O^- \leftarrow [C_2H_5O^-{\cdot}HOC_2D_5] \rightarrow (>50\%)\ C_2H_5O^- + C_2D_5OH \tag{25}$$

Adoption of the ICR acidity of ethanol permitted the results of the CID process (25) to be analyzed and to convert the relative ethanol acidities to absolute values: $\Delta_{acid}H(CH_3CD_2O{-}H)$ = 377.85 ± 0.15 kcal/mol, $\Delta_{acid}H(CD_3CH_2O{-}H)$ = 377.70 ± 0.15 kcal/mol, and $\Delta_{acid}H(CD_3CD_2O{-}H)$ = 378.00 ± 0.15 kcal/mol. Notice that these CID *relative* acidities are found to within less than ±0.5 kcal/mol. Error bars this small are only possible when the components of the proton bound dimer, $[U{\cdot}HA]^-$, have similar acidities, $\Delta_{acid}G(HA) \simeq \Delta_{acid}G(HU)$.

2. Electron Affinities. In a separate experiment, the electron affinity of radical R has to be measured. Just as in the case of the acidity measurements, this is a gas-phase measurement; the EA(R) is just the energy required to detach an electron.

$$R^- + h\nu \rightarrow R + e^- \tag{26}$$

There are several ways to utilize (26) to measure EA(R). A very precise method[88-90] is to scan the photon energy, $h\nu$, to find the threshold for photodetachment ($h\nu_{thresh}$) which is the threshold for photodestruction of the ions. Thus, the electron affinity of the H atom has been measured by observation of the photodestruction threshold[91] for H^- at 6082.99 ± 0.15 cm^{-1}, corresponding to EA(H) = 0.754 195 ± 0.000 019 eV; the threshold for D^- was found to be 6086.2 ± 0.6 cm^{-1}, implying that EA(D) = 0.754 593 ● 0.000 074 eV. When this can be carried out on a polyatomic molecule, very precise electron affinities can be determined. As an example,[92-94] the threshold for the detachment $CH_2CHO^- \rightarrow CH_2CHO$ is measured to be ν_{thresh} = $14\,718^{+2}_{-5}$ cm^{-1} or EA(CH_2CHO) = 42.08 ± 0.01 kcal/mol.

Alternatively,[95,96] one can find EA(R) by irradiating with a fixed frequency laser, $h\nu_0$, and measuring the kinetic energies of the scattered photoelectrons. Figure 4 is a schematic view of this experiment. Ions are extracted from a source at about $^1/_3$ Torr, formed into a beam, velocity-selected with a Wien filter, and delivered to a vacuum chamber maintained below 10^{-8} Torr. In this chamber ions are irradiated with a CW argon ion laser operating at a single frequency. Typically, ν_0 is 488.0 nm (2.540 eV) or 351.1 nm (3.531 eV); consequently, it is a limitation of this CW laser experiment that high EA species (EA ≥ 3.5 eV) cannot be studied. In Figure 4, the scattered photoelectrons are energy analyzed with a hemispherical electrostatic analyzer. As an example of negative ion photoelectron spectroscopy,[97] irradiation of a mass-selected ion beam of CH_2N^- ions with a 488-nm Ar II laser permits the determination of EA(CH_2N). The kinetic energy of photoelectrons belonging to the (0,0) transition is 2.030 ± 0.006 eV; since the laser photon energy is 2.540 eV, the binding energy of the electron is 0.510 ± 0.006 eV. This is

TABLE 4: Photoionization Appearance Potentials and Radical Ionization Potentials

molecule	AP[R^+←(RH)]/eV	IP(R)/eV	D_0(R–H)/kcal mol^{-1}	ref
HF	H^+ = 19.42 ± 0.01	13.5984	134.8 ± 0.2	138
H–CN	H^+ = 19.00 ± 0.01	13.5984	124.6 ± 0.2	140
HO–H	OH^+ = 18.115 ± 0.008	13.0170 ± 0.0002	117.6 ± 0.2	214, 215
H_2N–H	NH_2^+ = 15.768 ± 0.004	11.14 ± 0.01	106.7 ± 0.3	188, 216
HN–H	NH^+ = 17.440 ± 0.005	13.49 ± 0.01	91.0 ± 0.5	188, 217
H_3C–H	CH_3^+ = 14.320 ± 0.004	9.843 ± 0.002	103.2 ± 0.1	190, 191
H_2C–H	CH_2^+ = 15.09 ± 0.03	10.396 ± 0.003	108.2 ± 0.7	191, 218
C_2H_5–H	$\Delta_f H_0°(C_2H_5^+)$ = 218.8 ± 0.5 kcal/mol	8.117 ± 0.008	99.5 ± 0.5	144, 145
C_2H_3–H	$C_2H_3^+$ = 13.22 ± 0.02	≤8.59 ± 0.3	≥106.8	155, 219
	$\Delta_f H_0°(C_2H_3^+) = 256^{+1}_{-2}$ kcal/mol	$8.25^{+0.20}_{-0.05}$	$111.8^{+1.1}_{-4.6}$	154, 156
$HOCH_2$–H	CH_2OH^+ = 11.649 ± 0.003	7.553 ± 0.006	94.46 ± 0.15	136, 146
H–CO_2H	$^+$COOH = 12.30 ± 0.02	≤8.48 ± 0.012	≥88	172, 174
		(8.20)	(94.5)	
$HSCH_2$–H	CH_2SH^+ = 11.611 ± 0.005	7.536 ± 0.003	93.97 ± 0.14	147, 149
H–CHO	HCO^+ = 11.92 ± 0.01	8.14 ± 0.04	87.2 ± 0.9	220, 221
H–CHS	HCS^+ = 11.533 ± 0.021	≤7.499 ± 0.005	≥93.0 ± 0.5	222
		(7.412 ± 0.007)	(94.0 ± 1.2)	
H–C_6H_5	$C_6H_5^+$ = 12.93 ± 0.04	8.1 ± 0.1	110.5 – 115.6	160, 163
	= 13.01 ± 0.10	8.0 ± 0.1		158, 164
	= 13.13 ± 0.05 ($^3C_6H_5^+$ ← C_6H_6)	8.32 ± 0.04 ($^3C_6H_5^+$ ← C_6H_5)	110.9 ± 1.5	162
$C_6H_5CH_2$–H	$C_6H_5CH_2^+$ = 11.17 ± 0.10	7.2487 ± 0.0006	90.4 ± 2.3	165, 167, 168, 223
	$\Delta_f H_0°(C_6H_5CH_2^+)$ = 219.6 ± 1.2		86.6 ± 1.2	166
H_2P–H	PH_2^+ = 13.40 ± 0.02	9.824 ± 0.002	82.46 ± 0.46	224
HP–H	$PH^+(PH_3)$ = 12.492 ± 0.005	10.149 ± 0.008	74.8 ± 0.5	224, 225
H_2As–H	AsH_2^+ = 12.69 ± 0.01	9.443 ± 0.007	74.9 ± 0.2	226
HAs–H	$AsH^+(AsH_3)$ = 11.295 ± 0.005	9.641 ± 0.008	66.5 ± 0.3	226
HSe–H	SeH^+ = 13.266 ± 0.007	9.845 ± 0.003	78.89 ± 0.18	227
Se–H	$Se^+(H_2Se)$ = 11.916 ± 0.006	9.7525	74.27 ± 0.23	50, 227
H_3Si–H	SiH_3^+ ≤ 12.086 ± 0.020	$8.135^{+0.005}_{-0.002}$	≤91.1 ± 0.5	228, 229
H_2Si–H	$SiH_2^+(SiH_4)$ = 11.54 ± 0.01	9.15 ± 0.02	≥67.3 ± 0.5	137, 228
HSi–H			75.6 ± 1.4	137
Si–H			68.7 ± 0.7	137
H_3Ge–H	GeH_3^+ ≤ 11.657 ± 0.01	≤7.94_8 ± 0.005	≤85.5	230
			(82 ± 2)	
B_2H_5–H	$B_2H_5^+$ ≤ 11.40 ± 0.05	(≥6.94_5)	≤102.7	231
B_2H_4–H	$B_2H_4^+(H_2)$ ≤ 11.41_5 ± 0.04	9.70 ± 0.02	≅40.1	232
Si_2H_5–H	$Si_2H_5^+$ ≤ 11.59 ± 0.02	7.60 ± 0.05	<92.0	233, 234
	(11.41 ± 0.03)		(87.9 ± 1.3)	
Si_2H_4–H	$Si_2H_4^+(Si_2H_6)$ ≤ 10.04 ± 0.02	8.09 ± 0.03	(60.4 ± 1.5)	233
N_2H_3–H	$N_2H_3^+$ = 11.11_2 ± 0.01_0	7.61 ± 0.01	80.8 ± 0.3	227, 235
N_2H_2–H			43.8 ± 1.1	235

the "raw" electron affinity which often must be corrected for the fact that the spectrometer cannot resolve individual rotational transitions or spin–orbit states. After small rotational corrections, EA(CH_2N) = 0.511 ± 0.008 eV or 11.8 ± 0.2 kcal/mol. With the proper assignment of the (0,0) band in the spectrum, it is a common finding that nearly all modern photodetachment studies measure the electron affinity to an uncertainty of ±0.03 eV (±0.7 kcal/mol) or better.

In addition to simple ions, larger clustered ions have also been successfully[98–101] photodetached. Recent developments[102–105] with pulsed lasers have led to photodetachment machines that use excimer lasers as the light source. Instead of conventional electrostatic analyzers, the photodetached electrons are detected by time-of-flight spectrometers. These pulsed lasers have energies up to 6.4 eV and permit the study of high electron affinity species. Excellent reviews of molecular electron affinities have been published.[106,107]

We now present a partial survey of the acidity/EA technique. Table 2 collects about 30 representative molecules for which the acidities, electron affinities, and bond enthalpies are available. The species in part A have their acidities **computed** from known EA(R) and D_0(R–H) values; those in part B use the measured EA(R) and $\Delta_{acid}H_{298}$(R–H) to *determine* the BDE(R–H). In addition to hydrogen sulfide, arsine, phosphine, and silane which we need for comparison with PIMS and radical kinetics studies, we list a number of important organic species. Acetylene and ethylene are the two simplest sp-hybridized (HCCH) and sp^2-hybridized (CH_2CH_2) hydrocarbons. Benzene is the standard of aromaticity while the allylic species (derived from CH_2=CH–CH_3) and benzylic species (derived from $C_6H_5CH_3$) are two of the most fundamental conjugated systems. Formaldehyde (CH_2O), acetaldehyde (CH_3CHO), and ketene (CH_2CO) are three of the most important carbonyl systems. The only measured[108] acidity for CH_2O is $\Delta_{acid}H$(H–CHO) = 402 ± 5 kcal/mol, but this value is now known to be slightly off. From the extensive, thorough studies of the photochemistry of formaldehyde,[109] the bond energy is now established while the EA(HCO) is measured[110] by photoelectron spectroscopy. The acidity computed *via* eq 11 is $\Delta_{acid}H$(H–CHO) = 394.4 ± 0.3 kcal/mol. Methanol and ethanol are two of the simplest alcohols while hydrogen sulfide and thiomethanol are elementary mercaptans. Both isomeric nitriles (CH_3CN, CH_3NC) have been scrutinized. The isomeric sulfur ions ($HSCH_2^-$, CH_3S^-) have both been prepared but not completely studied yet; no one has ever observed the $HOCH_2^-$ ion. Likewise, all efforts to generate the simple alkyl anions ($C_2H_5^-$, $C_3H_7^-$, and $C_4H_9^-$) have failed; so it is not possible to compare acidity/EA measured alkyl C–H bonds with Tables 1 and 4.

For the special case of CH_2CH_2, the bond energy resulting from the acidity/EA cycle, $D_0(CH_2CH–H)$ = 109.7 ± 0.8 kcal/mol, is *higher* than the kinetically determined energy of 104–105 kcal/mol although it is compatible with the AP/IP measurements. These AP/IP studies have their own difficulties as described below in section C. The higher value in Table 2 results from measurements of EA(CH_2CH) and $\Delta_{acid}H(CH_2CH–H)$. The experimental EA has been investigated on two different photoelectron spectrometers, and three isotopically substituted vinyl anions were studied. All lead to a consistent (0,0) assignment, EA(CH_2CH) = 0.67 ± 0.02 eV. But if the EA of 0.67 eV was "lowered" by 5 kcal/mol, the acidity would lead to a BDE(CH_2CH_2) of 105 kcal/mol. Consequently, a BDE (CH_2CH_2) of 105 kcal/mol might imply an EA(CH_2CH) of

TABLE 5: Recommended R–H Bond Energies and Radical (R) Heats of Formation (kcal mol^{-1})

molecule (RH)	$\Delta_f H_{298}°$(R)	DH_{298}(R–H)	$\Delta_f H_0°$ (R)	D_0(R–H)	ref
H_2	52.103 ± 0.001	104.206 ± 0.001	51.633 ± 0.001	103.266 ± 0.001	62
HF	18.97 ± 0.07	136.4 ± 0.2	18.47 ± 0.07	135.4 ± 0.2	236
HCl	28.992 ± 0.002	103.15 ± 0.03	28.590 ± 0.002	102.24 ± 0.03	237
HBr	26.74 ± 0.03	87.54 ± 0.05	28.18 ± 0.03	86.64 ± 0.05	238
HI	25.52 ± 0.01	71.32 ± 0.06	25.61 ± 0.01	70.42 ± 0.06	239
H_2O	9.40 ± 0.05	119.30 ± 0.05	9.34 ± 0.05	118.08 ± 0.05	240
H_2CO	9.96 ± 0.20	88.04 ± 0.16	9.88 ± 0.20	86.57 ± 0.16	241
NH_3	45.1 ± 0.3	108.2 ± 0.3	45.8 ± 0.3	106.7 ± 0.3	242
CH_4	35.0 ± 0.1	104.9 ± 0.1	35.8 ± 0.1	103.3 ± 0.1	243
HCN	105.5 ± 1.1	126.1 ± 0.4	104.8 ± 1.1	124.8 ± 0.4	244
H_2S	34.18 ± 0.68	91.2 ± 0.7	34.07 ± 0.72	89.9 ± 0.7	245
H_2Se	34.6 ± 0.5	80.05 ± 0.18	34.9 ± 0.5	78.89 ± 0.18	246
H_2Te	37.9 ± 1.2	66.2 ± 1.2	38.3 ± 1.2	65.1 ± 1.2	247
PH_3	33.1 ± 0.6	83.9 ± 0.5	34.0 ± 0.6	82.46 ± 0.46	248
AsH_3	40.1 ± 0.3	76.3 ± 0.2	41.0 ± 0.3	74.9 ± 0.2	249
SbH_3	51.5 ± 0.6	68.9 ± 0.5	52.5 ± 0.6	67.5 ± 0.5	250
SiH_4	47.9 ± 0.6	91.7 ± 0.5	49.4 ± 0.9	90.4 ± 0.8	251
GeH_4	53 ± 2	83.4 ± 2	54.7 ± 2	82 ± 2	252
H_2CS	71.8 ± 2.0	95.5 ± 1.2	71.7 ± 2.0	94.0 ± 1.2	253
HCCH	135.1 ± 0.7	132.8 ± 0.7	134.1 ± 0.7	131.3 ± 0.7	254
H_2CCH_2	71.6 ± 0.8	111.2 ± 0.8	72.6 ± 0.8	109.7 ± 0.8	255
C_6H_6	78.9 ± 0.8	111.2 ± 0.8	81.6 ± 0.8	109.8 ± 0.8	256
CH_2CHCH_2–H	40.8 ± 2.1	88.2 ± 2.1	43.5 ± 2.1	86.7 ± 2.1	257
$C_6H_5CH_2$–H	48.4 ± 1.5	88.5 ± 1.5	53.0 ± 1.5	87.2 ± 1.5	258
H–CH_2CHO	2.5 ± 2.2	94.3 ± 2.2	4.0 ± 2.2	92.8 ● 2.2	259
CH_3CO–H	–2.4 ± 0.3	89.4 ± 0.3	–0.9 ± 0.3	87.9 ± 0.3	260
CH_2CO	41.9 ± 2.0	105.3 ± 2.1	41.6 ± 2.1	103.9 ± 2.1	261
H–CH_2OH	–4.08 ± 0.8	96.06 ± 0.15	–2.59 ± 0.22	94.46 ± 0.15	262
CH_3O–H	4.1 ± 0.9	104.2 ± 0.9	5.9 ± 0.9	103.0 ± 0.9	263
CH_3CH_2O–H	–3.7 ± 0.8	104.6 ± 0.8	–0.4 ± 0.9	103.1 ± 0.9	264
CH_3S–H	29.8 ± 0.4	87.4 ± 0.5	31.4 ± 0.5	86.1 ± 0.5	265
H–CH_2SH	36.3 ± 2.0	93.9 ± 2.0	37.8 ± 2.0	92.4 ± 2.0	149
CH_3CN	58.1 ± 2.7	94.8 ± 2.1	58.7 ± 2.7	93.3 ± 2.1	266
CH_3NC	78.0 ± 2.7	91.0 ± 2.1	78.5 ± 2.7	89.5 ± 2.1	267
H–COOH	>–53.2	>89.5	>–52.4	>88	268
	(–47.3)	(95.4)	(–46.5)	(93.9)	269
CH_3CH_2–H	28.9 ± 0.4	101.1 ± 0.4	31.5 ± 0.5	99.5 ± 0.5	270
$(CH_3)_2CH$–H	21.5 ± 0.4	98.6 ± 0.4	25.6 ± 0.5	97.1 ± 0.4	271
$CH_3CH_2CH(CH_3)$–H	16.1 ± 0.5	98.2 ± 0.5	21.9 ± 0.6	96.7 ± 0.5	272
$(CH_3)_3C$–H	12.3 ± 0.4	96.5 ± 0.4	18.1 ± 0.6	95.0 ± 0.6	273

roughly 0.45 eV. This was checked by searching for charge transfer to O_2 since EA(O_2) is[111] 0.451 ± 0.007 eV; the CH_2CH^- should charge transfer to O_2 in a flow tube if the EA of vinyl radical is approximately 0.45 eV. When CH_2CH^- was added to excess O_2 in an afterglow, no charge transfer to oxygen was observed.

How about the acidity of ethylene? In separate experiments, the acidity of ethylene was determined by proton-transfer studies with amide ion, NH_2^-.

$$NH_2^- + CH_2CH_2 \rightleftharpoons NH_3 + CH_2CH^- \qquad (27)$$

Both rate constants were measured [$k_{27} = (2.7 \pm 1.0) \times 10^{-13}$ cm^3 s^{-1} and $k_{-27} = (5.5 \pm 0.9) \times 10^{-10}$ cm^3 s^{-1}]. The exceedingly slow rate, k_{27}, was independently checked by calibration with an internal HCCH standard; this cross check leads to $k_{27} = 2.6 \times 10^{-13}$ cm^3 s^{-1}, in good agreement with the directly determined k_{27}. The rate constants give $\Delta_{rxn}G(27) = 4.5 \pm 0.2$ kcal/mol. Now the gas-phase acidity of ammonia anchors ethylene since $\Delta_{rxn}G(27) = \Delta_{acid}G(CH_2CH_2) - \Delta_{acid}G(NH_3)$, but $\Delta_{acid}G(NH_3)$ is known from PIMS studies and the EA(NH_2). All of these negative ion studies suggest that a CH bond energy of 104–105 kcal/mol is incompatible with the measured EA(CH_2CH) and $\Delta_{acid}G(CH_2CH_2)$.

Two remarks are in order as to the **accuracy** and **range** of acidity/EA measurement of BDEs. Generally, bond energies found by this approach are reliable to roughly ±2 or ±3 kcal/mol, and the major reason for this is the use of a ladder of reference acids. In a few cases such as HCCH and CH_2CH_2 (see Table 2), one can control the uncertainties to less than 1 kcal/mol, but this is not always possible. However, the range of the acidity/EA cycle is impressive. There are over 2500 negative ions that have been prepared and studied. In a great number of cases,[52] the acidity is reported by ICR studies as well as by flowing afterglow and variable-temperature mass spectrometry. It is almost always the case that these different mass spectrometric measurements (ICR, flow tube studies, and high-temperature mass spectrometry) find the same value, within their respective uncertainties.

The "chemical" control of the target ions is an important feature of the acidity/EA cycle. By manipulating the structure[112] of the target ion, one can fix the R–H bond that is to be studied. Negative ions are straightforward to work with since they can be prepared by sensible ion chemistry[113] and are not prone to rearrangements like carbonium ions.

An example of this control is shown by acetaldehyde; there are now two types of protons to account for. How can one measure the bond energy of each of the these two different C–H bonds?

$$H\text{–}CH_2CHO \rightarrow CH_2CHO^- + H^+ \qquad (28a)$$

$$CH_3CO\text{–}H \rightarrow CH_3CO^- + H^+ \qquad (28b)$$

The acetaldehyde enolate ion (CH_2CHO^-) is the easiest to prepare by removal of the more acidic methyl proton. ICR studies[114]

$$HO^- + CH_3CHO \rightarrow H_2O + CH_2CHO^- \qquad (29a)$$

report $\Delta_{acid}H$(H–CH_2CHO) = 365.8 ± 2.2 kcal/mol while threshold photodetachment studies[94] find EA(CH_2CHO) = 1.8248 ± 0.0006 eV. These findings lead to the bond energies, DH_{298}(H–CH_2CHO) = 94.3 ± 2.2 kcal/mol and D_0(H–CH_2CHO) = 92.8 ± 2.2 kcal/mol. In contrast, the more reactive acyl anion, CH_3CO^-, is not so easy to prepare and has

to be forced by a fluorodesilylation reaction.

$$F^- + (CH_3)_3Si{-}COCH_3 \rightarrow FSi(CH_3)_3 + CH_3CO^- \quad (29b)$$

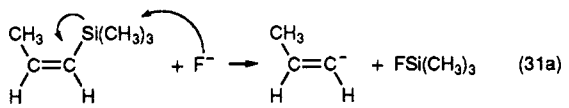
In this way the acidity of the acyl proton in acetaldehyde (28b) has been studied. At 298 K, the acidity has been measured in a flowing afterglow,[115] $\Delta_{acid}H(CH_3CO{-}H)$ = 391.1 ± 2.1 kcal/mol. Likewise, the electron affinity is reported[116] as EA(CH_3CO) = 0.423 ± 0.037 eV; consequently, use of eq 11 determines the bond energy, $DH_{298}(CH_3CO{-}H)$ = 87.2 ± 2.3 kcal/mol. With a heat capacity correction, the bond energy becomes $D_0(CH_3CO{-}H)$ = 85.7 ± 2.3 kcal/mol.

Some other pairs of isomeric ions that have been synthesized are deprotonated acetic acid[117] ($HOOCCH_2^-$, CH_3COO^-), deprotonated thiomethanol[118] ($HSCH_2^-$, CH_3S^-), deprotonated formic acid[119] ($HOOC^-$, $HCOO^-$), and the isomeric nitriles[80,114,120,121] (CH_2NC^-, CH_2CN^-). As Table 2 shows, only the nitriles have been completely studied.

As a demonstration of the exquisite chemical control that negative ion techniques offer, we turn to propene. There are four different C–H bonds in $CH_2{=}CH{-}CH_3$ to consider: the methyl C–H and three distinct vinyl C–H bonds. As Table 2, shows, study of the allylic ion has furnished $D_0(CH_2CHCH_2{-}H)$ = 86.7 ± 2.1 kcal/mol. Since the methyl C–H is the most acidic site, the $CH_2CHCH_2^-$ ion is readily formed by an appropriate base.

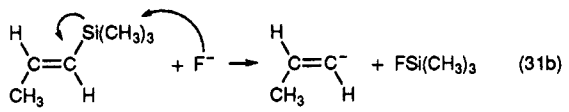
$$HO^- + H{-}CH_2CHCH_2 \rightleftharpoons H_2O + CH_2CHCH_2^- \quad (30)$$

Using technology based on the fluorodesilylation of substituted trimethylsilanes,[122] it has been possible to synthesize two *stereoisomeric* 1-propenyl anions.[123]



(31a)

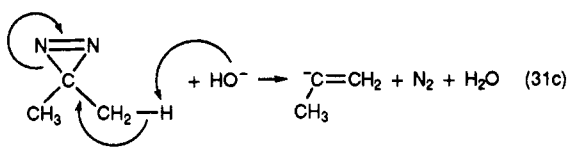
(*Z*)-1-propenyl carbanion



(31b)

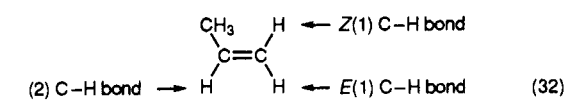
(*E*)-1-propenyl carbanion

Flowing afterglow studies have clearly demonstrated that these stereoisomeric carbanions (31a and 31b) are configurationally stable because they exhibit different chemistry. Finally, the 2-propenyl anion can be prepared by use of an ingenious synthetic route based on diazirines pioneered by Kass.[124]



(31c)

Treatment of an appropriate diazirine with OH^- generates the 2-propenyl carbanion. Since the three isomeric propenyl ions have been prepared (31), it will be possible to complete the acidity/EA cycle and measure the bond dissociation energies of three different vinyl C–H bonds (32).



(32)

Such measurements will provide heats of formation of the (*Z*)-1-propenyl radical, the (*E*)-1-propenyl radical, and the 2-propenyl radicals. All are isomers of the allyl radical, CH_2CHCH_2. The stereospecific radicals, (*Z*)-1-propenyl and (*E*)-1-propenyl, are likely to be configurationally stable, but this remains to be proven.

Finally, a very general route to carbene radical ions needs to be explicitly noted. Ion–molecule reactions[125] with O^- generate the anions of diradicals. Species such as CX_2^-, CH_2C^-, $C_6H_4^-$, $CHCN^-$, and $CH_2COCH_2^-$ have been reported (X = halogen). As a result, an avenue is open to the thermochemical properties of the corresponding[82,126–133] diradicals: CX_2, CH_2C, C_6H_4, CHCN, and CH_2COCH_2.

$$O^- + H_2CX_2 \rightarrow H_2O + CX_2^- \quad (33a)$$

$$O^- + H_2CCH_2 \rightarrow H_2O + CH_2C^- \quad (33b)$$

$$O^- + C_6H_6 \rightarrow H_2O + C_6H_4^- \quad (33c)$$

$$O^- + H_3CC{\equiv}N \rightarrow H_2O + HCCN^- \quad (33d)$$

$$O^- + CH_3COCH_3 \rightarrow H_2O + CH_2COCH_2^- \text{ and } CH_3COCH^- \quad (33e)$$

C. Photoionization Mass Spectrometry. *1. Introduction.* As mentioned earlier (eq 4), this approach depends upon the determination of (a) an accurate onset energy for the appearance of R^+, together with (b) an independent (and usually much more difficult) measurement of the adiabatic ionization potential of the radical, IP(R). This appearance potential/ionization potential method (AP/IP) has several advantages: (i) Detection of a charged species, R^+, is usually much more sensitive than that of neutral species. (ii) In most cases, selection rules or correlation rules do not prevent the observation of the lowest-energy fragment. (iii) Experience has shown that the onset of fragmentation can be observed even at energies where the He I photoelectron spectrum does not indicate states of the parent ion. This so-called Franck–Condon gap region is evidently filled in, to some extent, by autoionization processes. (iv) If the adiabatic ionization potential of R is accurately known, then the AP of R^+ provides a rigorous upper limit to $\Delta_fH°(R^+)$, $\Delta_fH°(R)$, and $D_0(R{-}H)$. (v) Both the AP and IP experiments can, in principle, be performed with the same apparatus. Photoion-pair formation is also investigated with this type of instrument. The disadvantages of this method are the following: (i) The AP of R^+ provides a rigorous upper limit, but is it the true thermochemical onset? When one considers the reverse of fragmentation, i.e., an ion–molecule reaction, it is obvious that there exists a long-range ($1/r^4$) attractive potential and, in most cases, a short-range valence attraction. If these attractive potentials are separated by a substantial repulsive barrier, then the first sign of fragmentation may be accompanied by excess internal energy or excess kinetic energy. Usually, this is not the case. (ii) If the ionization process $R \rightarrow R^+$ involves a large change in molecular geometry, the Franck–Condon factors (i.e., vibrational progression in the cation) may be extensive. In such a case, the (0,0) transition may be difficult to observe or to distinguish from a hot band. (iii) If the desired fragmentation process is not the lowest-energy fragmentation, then it may be retarded in energy (kinetic shift), due to competition from the lower-energy process in their respective unimolecular decay modes. (iv) For large molecules, unimolecular decay may be very slow, even if the desired fragmentation process is the lowest-energy one. On the usual experimental time scale of several microseconds, a significant, or even serious, kinetic shift may be manifest. Thus, for $C_6H_5^+$ from benzene this shift is about 1 eV and tends to increase for larger polyaromatic hydrocarbons. For C_{58}^+ from C_{60}, it may be[134] tens of volts! The above comments apply to the determination of bond energies in general, not just to $D_0(R{-}H)$.

2. Experimental Procedures. Photoionization mass spectrometry has been practiced for about 3 decades and is by now quite standard. Basically, one requires a broad-banded source of vacuum-ultraviolet (VUV) radiation, a dispersive device (typically a VUV monochromator), a vacuum vessel where the selected wavelengths traverse the target gas sample, and the usual

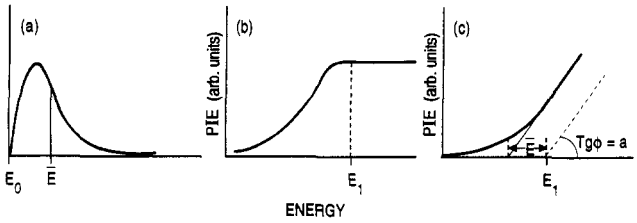


Figure 5. Folding of a thermal energy distribution with a 0 K photoion yield curve: (a) shape of the thermal energy distribution; (b) convolution of this distribution with a step function; (c) convolution with a linear function. Here, E_1 is the true threshold, while $\bar{E}$ is the average thermal energy.[135]

ion optics for introduction of ions to a mass analyzer, with subsequent detection. It is also necessary to monitor simultaneously the intensity of the vacuum-UV radiation, in order to construct a normalized photoion yield curve, i.e., normalized ion intensity as a function of photon energy, $h\nu$. Nowadays, the light source may be (a) capillary discharge in H_2, He, or Ar; (b) synchrotron radiation, or (c) a vacuum-UV laser. The mass analyzer may be of magnetic or quadrupole type or (especially useful with a pulsed light source) a time-of-flight instrument. There are advantages and disadvantages to each of these instruments, but such a discussion is beyond the scope of this review.

In the measurement of appearance potentials, the onset of fragmentation is not abrupt. Typically, there is a more-or-less linear increase in the fragment photoion yield just above threshold, with an exponential tail to still lower energies, attributable to a Boltzmann distribution of internal thermal energy in the initial gas sample.

It has been shown[135] that, if the inherent fragment photoion yield curve is linear (i.e., if a hypothetical experiment of 0 K gives rise to a sudden linear ascent), then the effect of a Boltzmann distribution of target internal energy is to shift the linear function to lower energy by precisely the internal (vibrational plus rotational) energy and to add an exponential tail to still lower energy (see Figure 5). Consequently, to recover the 0 K threshold from the experimental photoion yield curve, one extrapolates the linear portion to the background level and then adds to the photon energy at this extrapolated value the average internal energy. For small molecules investigated at room temperature, this correction is usually <0.1 eV and is typically about 0.04 eV. Sometimes, the approach to threshold is more gradual. This may be due to a "tight" transition state preceding the unimolecular decay, competition from a lower-energy fragmentation, or traversal of a potential barrier. However, if the process involves a simple bond rupture ($RH \rightarrow R^+ + H$), and if this is the lowest-energy fragmentation process, such pathology is less likely (but note the case of $C_2H_4 \rightarrow C_2H_3^+ + H$, below). Another problem that must be recognized is the site of bond cleavage, e.g., HCOOH $\rightarrow$ ($^+$COOH or $HCOO^+$) + H, $CH_3OH \rightarrow$ ($^+CH_2OH$ or CH_3O^+) + H, and $CH_3SH \rightarrow$ ($^+CH_2SH$ or CH_3S^+) + H. In these cases, the appropriate process (which corresponds to the least endothermic fragmentation) has been proven by selective deuterium substitution.

A more general approach would be to establish the functional form of the internal energy distribution function (see Figure 5a) and to deconvolute from the experimental data this distribution function. Since the deconvolution process may be ambiguous and is quite sensitive to the quality of the data, a convolution procedure may be preferable. Here, one assumes a functional form of the fragment photoion yield at 0 K (called the kernel function) and convolutes it with the internal energy distribution function. Various kernel functions can be assumed, and the resulting convoluted functions can be compared with experiment. The convoluted function which has the smallest deviation from experiment (judged by an objective least-squares criterion) yields the best 0 K threshold. This procedure has recently been implemented to determine the AP(CH_2OH^+,CH_3OH).[136]

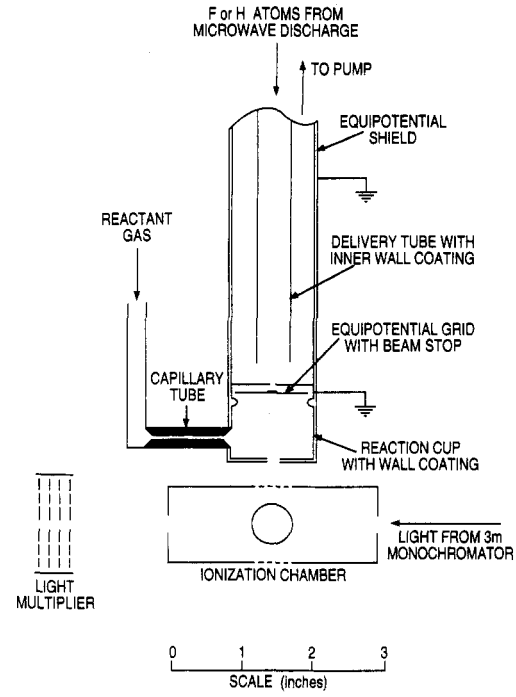


Figure 6. Schematic diagram of the generating tube for preparing transient species *in situ*.

The more difficult experiment involves the determination of the adiabatic ionization potential of the radical, IP(R). In the generation of a transient species, one usually loses at least 1 order of magnitude in partial pressure of sample compared to the case of a stable species. There may also be some additional background, attributable to the method of generation. Various methods have been used, depending upon the most facile technique appropriate to a particular species. These include pyrolysis, photolysis, electrical discharge, and chemical abstraction reactions. The latter processes, involving the reaction of H or F atoms with an appropriate reagent, have proven to be particularly effective: RH + F $\rightarrow$ R + HF.

A schematic diagram of this method for generating transient species *in situ* is shown in Figure 6. Here, the effect of temperature may cause "hot bands" to appear. The influence of rotational hot bands is generally not severe, because rotational energies are small, and selection rules limit the changes in angular momentum. Vibrational hot bands can cause difficulties when a significant change in geometry occurs between the radical and its ground-state cation. This circumstance gives rise to an extended Franck–Condon region, where the (0,0) transition may be weak and comparable to a (1,0) hot band. A more extensive discussion, and a list of species prepared by various means, appears elsewhere.[137]

3. Examples of Experimental Results. a. Early Success Stories with Redundancy. About 20 years ago, a discrepancy arose regarding D_0(HF). A solution was provided by a measurement[138] determining the AP of H^+ from HF. In this case, there was no need to determine the IP of the fragment. From the observed threshold (19.42 ± 0.01 eV) and the internal energy correction (0.025 eV) and IP(H) = 13.5984 eV, one uses eq 5 to obtain D_0(HF) = 5.85 ± 0.01 eV. An independent experiment yielded D_0(DF) = 5.91_2 ± 0.005 eV, consistent with zero-point energy differences. Subsequently, Di Lonardo and Douglas[139] obtained D_0(HF) = 5.869 ± 0.007 eV from the onset of predissociation. Photoion-pair formation is also prominent in this system. It manifests itself as sharp, predissociative structure. The threshold for $H^+ + F^-$ from HF is ≥773 Å (or ≤16.039 eV). If we take 3.401 190 ± 0.000 004 eV as the electron affinity[67] of F, and the aforementioned IP(H), one obtains D_0(HF) ≤ 5.84 eV. The lower value here is due to the fact that internal thermal energy has not been taken into account.

Another potential case incorporating redundancy was that of HCN. The threshold for formation of $H^+ + CN$ (corrected for internal energy) was found[140] to be 19.00 ± 0.01 eV, and hence D_0(H–CN) = 5.40 ± 0.01 eV.[141] The threshold for photoion-pair formation ($H^+ + CN^-$) was observed to be 15.18 ± 0.02 eV. At that time, the electron affinity of CN was not well known, and hence this measurement was used to deduce EA(CN) = 3.82 ± 0.02 eV. Since that time, EA(CN) has been studied[142] by optogalvanic spectroscopy and reported to be 3.821 ± 0.004 eV. More recently,[143] photodetachment studies have clearly shown that the correct EA(CN) is 3.862 ± 0.004 eV, slightly above these earlier values. Unpublished work from our laboratory indicates that H_2O and H_2S undergo photoion-pair formation ($H^+ + OH^-$, $H^+ + SH^-$), with thresholds consistent with currently available knowledge on D_0(H–OH), D_0(H–SH) and EA(OH), EA(SH).

b. Other Successful Applications of the AP/IP Method to D_0(R–H). D_0(H–C_2H_5). The AP of $C_2H_5^+$ from C_2H_6 has some ambiguity, possibly due to the contribution of a weak photoion-pair process ($C_2H_6 \rightarrow C_2H_5^+ + H^-$). However, thermodynamics offers other alternatives. It is only important that one establishes $\Delta_f H°(C_2H_5^+)$, and the photolysis of ethyl iodide was used to accomplish this.

$$C_2H_5I + h\nu_{AP} \rightarrow C_2H_5^+ + I + e^- \qquad (34)$$

Rosenstock *et al.*[144] summarized earlier studies of ethyl halides and incorporated their own photoion–photoelectron coincidence study of C_2H_5I to arrive at the threshold for $C_2H_5^+$ appearance of 10.52 ± 0.01 eV; use of standard heats of formation of ethyl iodide and I atom leads to $\Delta_f H_0°(C_2H_5^+)$ = 218.8 ± 0.5 kcal/mol. Ruscic *et al.*[145] prepared C_2H_5 by the reaction of F + C_2H_6. The photoion yield curve yields IP(C_2H_5) = 8.117 ± 0.008 eV. Thus, $\Delta_f H_0°(C_2H_5) = \Delta_f H_0°(C_2H_5^+) - IP(C_2H_5)$ = 31.6 ± 0.5 kcal/mol. The heats of formation of C_2H_6 ($\Delta_f H_0°$ = −16.3 ± 0.1 kcal/mol) and H ($\Delta_f H_0°$ = 51.634 kcal/mol) are well established. Thus, D_0(H–C_2H_5) = 99.5 ± 0.5 kcal/mol.

D_0(H–CH_2OH). The AP of CH_2OH from CH_3OH has recently been redetermined[136] using higher-quality data and a fitting procedure which removed the effect of internal thermal energy. The value obtained was 11.649 ± 0.003 eV. This is the lowest-energy fragment and hence should experience a negligible kinetic shift. It has also been established that the structure is CH_2OH^+, and not CH_3O^+, which is much less stable. In the reaction of F atoms with CH_3OH, both CH_2OH and CH_3O are generated. Photoionization of these species produces ions with the same *m/e* 31. However, by using selectively deuterated samples (CD_3OH, CH_3OD), it is possible to distinguish the ionization potentials of these species. Thus, it was found[146] that IP(CH_2OH) = 7.553 ± 0.006 eV, whereas IP(CD_3O) = 10.762 ± 0.008 eV. The high value of IP(CD_3O) compared to IP(CH_2OH) provides further evidence that CH_3O^+ is much less stable than CH_2OH^+. In fact, CH_3O^+ was not observed. Apparently, there is a barrier to decomposition of this species, which is a triplet, into the singlet manifold of either CH_2OH^+ or the decomposition products $HCO^+ + H_2$. This leads to an isotope effect, enabling CD_3O^+ to survive during the characteristic lifetime of the experiment, but not CH_3O^+. By combining AP(CH_2OH^+) with IP(CH_2OH), one obtains D_0(H–CH_2OH) = 4.096 ± 0.007 eV (≡ 94.46 ± 0.15 kcal/mol).

D_0(H–CH_2SH). Thiomethanol displays some interesting differences from methanol, in both its thermochemistry and dynamics. In methanol, the O–H bond is stronger than the C–H bond, and hence CH_2OH is more stable than CH_3O. In thiomethanol, the reverse is true; the S–H bond is weaker than the C–H bond. This conclusion has been definitively established in recent studies. The lowest-energy fragment in the photoionization[147] of CH_3SH is not CH_2SH^+, but CH_2S^+. This decomposition proceeds through a "tight" transition state. The ion of *m/e* 47 (CH_3S^+/CH_2SH^+) begins to appear at a photon energy

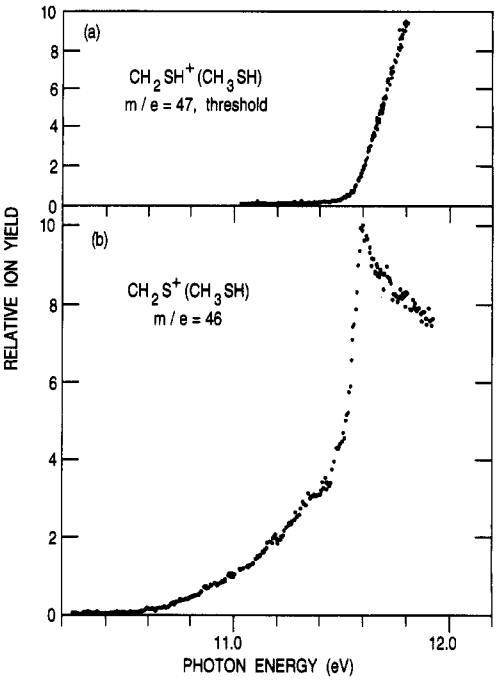


Figure 7. Photoion yield curve of the two lowest-energy fragment species from CH_3SH: (a) CH_2SH^+ (*m/e* 47), (b) CH_2S^+ (*m/e* 46). Note the abrupt decline of CH_2S^+ (+H_2) as it experiences competition from CH_2SH^+ (+H) at the onset of the latter process.

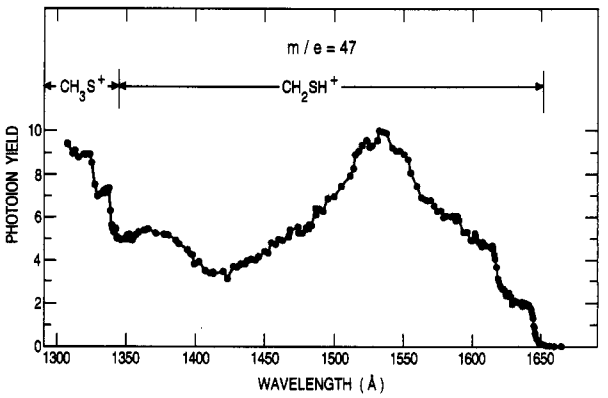


Figure 8. Photoion yield curve of *m/e* 47 upon reacting F atoms with CH_3SH. Both CH_2SH and CH_3S are generated in the reaction. The lower-energy onset corresponds to IP(CH_2SH), whereas a second onset at ≅1340 Å represents IP(CH_3S). This interpretation is demonstrably verified by using selectively deuterated CH_3SD and CD_3SH, where the two species occur at different *m/e*.

about 1 eV higher than CH_2S^+ but rapidly overtakes it in intensity (see Figure 7). In fact, when the *m/e* 47 ion initially appears, the relative cross section for CH_2S^+ abruptly declines, presumably due to strong competition from the more facile bond rupture process ("loose complex") associated with *m/e* 47. This behavior serves to establish AP = 11.611 ± 0.005 eV for *m/e* 47.

At the time of the original photoionization study, it was not clear whether *m/e* 47 was to be associated with CH_2SH^+ or CH_3S^+. Recent *ab initio* calculations[148] have clearly established that it is CH_2SH^+.

Reaction of F atoms with CH_3SH forms both CH_3S and CH_2SH. Once again, these species can be distinguished by selective deuteration (CH_3SD/CD_3SH). Photoionization of these species[149] (see Figure 8) yields IP(CH_2SH) at 1645.3 ± 0.7 Å (≡ 7.536 ± 0.003 eV) and IP(CH_3S) at 1338.6 ± 0.7 Å (≡ 9.262 ± 0.005 eV). The lower IP of CH_2SH is further evidence that the lowest-energy process forming *m/e* 47 ions from CH_3SH must have the CH_2SH^+ structure. By combining AP(CH_2SH^+) from CH_3SH with IP(CH_2SH), we obtain D_0(H–CH_2SH) = 4.075 ± 0.006 eV ≡ 93.97 ± 0.14 kcal/mol. Nicovich *et al.*[34] have recently determined $\Delta_f H_0°(CH_3S)$ = 31.44 ± 0.54 kcal/

mol by kinetic studies analogous to those presented in this review. When combined with $\Delta_f H_0°(CH_3SH) = -3.0 \pm 0.1$ kcal/mol, this leads to $D_0(CH_3S–H) = 86.1 \pm 0.6$ kcal/mol. Thus, the C–H bond is stronger than the S–H bond by about 8 kcal/mol.

A number of R–H bond energies in inorganic molecules have been successfully established by this approach. In fact, it has been possible to determine not just the first RH bond energy, but the successive ones in these molecules. For example, by determining the APs (or heats of formation) of NH_2^+ and NH^+ and the corresponding IP(NH_2) and IP(NH), one can deduce[150] $D_0(H_2N–H)$, $D_0(HN–H)$, and $D_0(N–H)$. Similar complete results have been obtained for PH_3, AsH_3, H_2Se, and SiH_4. Other systems, where not all of the sequential bond energies have been obtained, include $D_0(B_2H_5–H)$, $D_0(B_2H_4–H)$, $D_0(H_3Ge–H)$, $D_0(H_3SiSiH_2–H)$, $D_0(H_2SiSiH_2–H)$, $D_0(H_2NNH–H)$, and $D_0(HNNH–H)$. The pertinent references are included in Table 4.

c. Difficult Cases. $D_0(C_2H_3–H)$. While ethylene has the well-known planar, double-bonded structure, current evidence indicates that $C_2H_3^+$ has a bridged, nonclassical structure, the odd proton forming a three-membered ring with the two carbons.[151] Thus, the fragmentation reaction $C_2H_4 + h\nu \rightarrow C_2H_3^+ + H + e^-$ requires considerable rearrangement. Two high-quality photoionization studies[152,153] had arrived at AP($C_2H_3^+$) from C_2H_4 of 13.25 ± 0.05 and 13.22 ± 0.02 eV, equivalent to $\Delta_f H_0°(C_2H_3^+) = 268.4 \pm 1.2$ and 267.8 ± 0.5 kcal/mol. However, a recent study[154] of the reaction $HCCH^+$ with hydrogen at collision energies of less than 0.5 meV concluded that $\Delta_f H_0°(C_2H_3^+) = 265^{+1.1}_{-2.1}$ kcal/mol.

$$C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H \qquad (35)$$

Consequently, a barrier of 2–3 kcal/mol magnitude may exist in the fragmentation of C_2H_4 into $C_2H_3^+ + H$, preventing the attainment of a true threshold.

The vinyl radical C_2H_3 is known to have an ethylene-like structure (missing an H atom). Given the aforementioned structure for $C_2H_3^+$, the Franck–Condon factors connecting C_2H_3 and $C_2H_3^+$ should be weak (perhaps *very* weak) near threshold. Two recent photoionization studies, one by PIMS[155] and the other by photoelectron spectroscopy[156] (PES), have attempted to determine the adiabatic IP of C_2H_3. In the PIMS experiments, two different sources of C_2H_3 were utilized: the $F + C_2H_4$ reaction and the pyrolysis of $Hg(C_2H_3)_2$, divinylmercury. Similar photoion yield curves were obtained, displaying autoionization structure in the vicinity of 1180–1340 Å and a gradually declining intensity to longer wavelengths. With the H abstraction source, the lowest detectable signal occurred at roughly 1448 Å ≡ 8.56 eV. The vinyl radical is believed to equilibrate to near room temperature in this type of experiment. With the pyrolysis source operating at about 1200 K, the lowest detectable signal was at roughly 1476 Å ≡ 8.40 eV. It was concluded that the lower-energy threshold in the pyrolysis experiment was attributable to hot bands. With additional analysis, an upper limit of 8.59 ± 0.03 eV was selected for IP(C_2H_3).

The PES experiment employed a pulsed nozzle pyrolysis source, a pulsed laser line source, and time-of-flight analysis of the photoelectrons. Two different precursors, $C_2H_3CO_2C(CH_3)_3$ and $C_2H_3NO_2$, were pyrolyzed. The published photoelectron spectrum was obtained with $h\nu_0 = 10.49$ eV and displays a declining photoelectron intensity from about 1-eV kinetic energy out to more than 3 eV. A point on this curve has been chosen, near the asymptotic base line, which corresponds to an adiabatic IP of $8.25^{+0.20}_{-0.05}$ eV. The authors argue that their method of preparation provides vibrationally cold vinyl radicals and therefore that 8.25 eV is an unambiguous lower bound to IP(C_2H_3). It should be noted that a time-of-flight spectrum, which is linear in velocity, becomes compressed with increasing kinetic energy on an energy scale. With IP of 8.25- and 10.49-eV photons, the photoionized electrons have a kinetic energy of 2.24 eV and appear in such a compressed region.

In summary, there is an ambiguity of 2–3 kcal/mol in $\Delta_f H_0°(C_2H_3^+)$ and upper and lower bounds to IP(C_2H_3) which differ by 0.34 eV ≡ 7.8 kcal/mol. The various combinations allow for a broad range of $D_0(C_2H_3–H)$. Thus, with $\Delta_f H_0°(C_2H_3^+) = 267.8$ kcal/mol, $D_0(C_2H_3–H) \geq 106.8 \pm 0.9$ or $114.6^{+1.1}_{-4.6}$ kcal/mol. Alternatively, using $\Delta_f H_0°(C_2H_3^+) = 265$ kcal/mol, $D_0(C_2H_3–H) \geq 104.0 \pm 0.9$ or $111.8^{+1.1}_{-4.6}$ kcal/mol. The other methods described in this review unfortunately do not help to resolve the discrepancy. The kinetic approach yields $D_0(C_2H_3–H) = 105.1 \pm 0.3$ kcal/mol, whereas the method based on gas-phase acidity arrives at 109.7 ± 0.8 kcal/mol.

$D_0(C_6H_5–H)$. Even though $C_6H_5^+$ is the lowest-energy fragment 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 decay 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 clearly separate *m/e* 78 ($C_6H_6^+$) from *m/e* 77 ($C_6H_5^+$). Two alternative approaches have been employed that bear upon this problem.

(i) Instead of C_6H_6, halobenzene targets have been used. This 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, whereas, for example, $\Delta_f H_0°(C_6H_5I)$ has an uncertainty of ±1.4 kcal/mol. Dannacher *et al.*[157] performed such a coincidence measurement on C_6H_5I and inferred $\Delta_f H_0°(C_6H_5^+) = 270.8 \pm 1.4$ kcal/mol. Malinovich and Lifshitz[158] determined the decay rate at longer times (millisecond as well as microsecond), utilizing a cylindrical ion trap to contain the ions. Modeling of their data by quasi-equilibrium theory led to $\Delta_f H_0°(C_6H_5^+) = 272.7 \pm 2.4$ kcal/mol. More recently, Lifshitz *et al.*[159] obtained a slightly higher value, 274.4 kcal/mol, from a modeling of the corresponding C_6H_5Br problem.

(ii) Kuhlewind *et al.*[160] solved the mass separability problem in C_6H_6 by using a reflectron time-of-flight mass spectrometer, which has superior resolution. Their method of establishing the internal energy of $C_6H_6^+$ 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 yielded $E_0 = 3.66$ eV for this reaction. With IP(C_6H_6) = 9.2459 ± 0.0002 eV, the AP of $C_6H_5^+$ from C_6H_6 becomes 12.90_6 eV or $\Delta_f H_0°(C_6H_5^+) = 270.0$ kcal/mol. Using the same data but a "thermodynamic model" based on the Arrhenius equation, Klots[161] obtained $E_0 = 3.72$ eV. Still more recently,[162] 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. But the premise was that $C_6H_5^+$ was formed in its excited triplet state ($^3B_1$) rather than in the ground $^1A_1$ state. They estimate the excitation energy to be roughly 0.2 eV so that for the ground state they approximate $E_0 \cong 3.68$ eV. The use of $E_0 \cong 3.68$ or 3.72 eV would imply an AP($C_6H_5^+$,C_6H_6) of 12.92_6 and 12.96_6 eV and $\Delta_f H_0°(C_6H_5^+) = 270.5$ or 271.4 kcal/mol, respectively. We choose an average value for 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.

The IP(C_6H_5) was measured by Sergeev *et al.*[163] by PIMS, using pyrolysis of azobenzene as a source. These authors obtained a value of 8.1 ± 0.1 eV. More recently, Butcher *et al.*[164] prepared C_6H_5 by the $F + C_6H_6$ reaction and obtained a He I photoelectron spectrum. Their lowest observed ionization band occurred at IP(C_6H_5) = 8.32 ± 0.04 eV. However, their *ab initio* calculations led them to conclude that the lowest electronic state of the cation

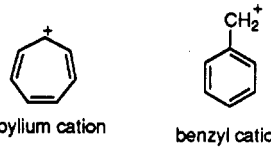
($^1A_1$) was not being observed, but rather the excited $^3B_1$ state, which is favored by Franck–Condon overlap. They consequently estimated that the adiabatic IP(C_6H_5), [$C_6H_5^+(\tilde{X}^1A_1) \leftarrow C_6H_5(\tilde{X}^2A_1)$], is 8.0 ± 0.1 eV. If we accept their interpretation, the range of IPs (8.1 ± 0.1, 8.0 ± 0.1 eV) and the range of APs (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.

We have noted above that Klippenstein *et al.*[162] modeled their dissociative ionization process assuming that the product $C_6H_5^+$ was formed in its excited state, and Butcher *et al.*[164] concluded that their measured IP(C_6H_5) also referred to the excited triplet state. With E_0 = 3.88 ± 0.05 eV (they demonstrated that E_0 = 3.78 and 3.98 eV provided distinctly poorer fits), we obtain AP($C_6H_5^+$,$\tilde{a}^3B_1$) = 13.13 ± 0.05 eV and, when combined with IP[$C_6H_5^+$,($\tilde{a}^3B_1$) ← $C_6H_5(\tilde{X}^2A_1)$] = 8.32 ± 0.04 eV, yields $D_0(C_6H_5–H)$ = 4.81 ± 0.06 eV ≡ 110.9 ± 1.5 kcal/mol. This latter value, though obtained in an unorthodox fashion (since neither the AP nor IP corresponds to the ground state of $C_6H_5^+$), is in reasonable agreement with the value 109.6 ± 2.1 kcal/mol obtained by the gas-phase acidity/EA cycle (see Table 2).

$D_0(C_6H_5CH_2–H)$. (*i*) *$\Delta_fH_0°(C_6H_5CH_2^+)$*. Photoion–photoelectron coincidence measurements determine the fractional abundance of parent and fragment ion as a function of photon energy. The data are often presented in a so-called breakdown diagram. Unimolecular decay theory, which involves an activation energy and the assumed entropic properties (vibrations, structure) of a transition state, can then be used to simulate the experimental breakdown diagram. Consider the dissociative ionization of toluene:

$$C_6H_5CH_3 + h\nu \rightarrow C_7H_7^+ + H + e^- \qquad (36)$$

Bombach *et al.*[165] obtained such a diagram corresponding to the process $C_7H_8^+ \rightarrow C_7H_7^+ + H$ but could not simulate the curve as long as a single transition state was employed. They were not surprised, since earlier work had demonstrated that two isomers of $C_7H_7^+$ could be formed—the more stable tropylium ion and the benzyl cation.



tropylium cation benzyl cation (37)

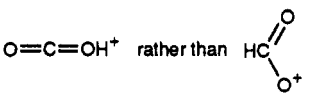
However, by using a model employing two transition states and two products, each with its own activation energy, they were able to obtain a good fit. From this simulation, they derived the threshold energies for tropylium cation and benzyl cation. The latter quantity enabled them to compute $\Delta_fH_0°(C_6H_5CH_2^+)$ = 223.5 ± 2.2 kcal/mol. It is apparent that this type of study involves a more complex experiment and analysis than conventional PIMS. The latter would, at best, yield the appearance potential of tropylium cation, but even that value would experience a kinetic shift.

Baer *et al.*[166] opted for an alternative approach. Other evidence had demonstrated that benzyl bromide produces only benzyl cation (not tropylium) upon dissociative ionization. They thereupon chose to study $C_6H_5CH_2Br$ by photoion–photoelectron coincidence spectroscopy and to obtain a breakdown diagram. Their analysis of this curve by RRKM/QET calculations led them to $\Delta_fH_0°(C_6H_5CH_2^+)$ = 219 ± 1.2 kcal/mol. A discrepancy of about 4 kcal/mol persists. The heat of formation of benzyl bromide is not as well known as that of toluene, but according to Pedley *et al.*[61] its uncertainty is ±0.5 kcal/mol, which cannot account for the difference.

(*ii*) *$IP(C_6H_5CH_2)$*. A recent experiment performed by Eiden and Weisshaar[167,168] on $C_6H_5CH_2$ is perhaps a harbinger of the precision in the determination of ionization potentials which will become available in the near future, even for larger radicals. These authors prepared a beam of cold benzyl radicals by laser photolysis of diluted toluene, expanded through a supersonic nozzle. Thereupon, photoionization is achieved by using two tunable dye lasers, one tuned to a vibronic state of benzyl radical and the other scanning through the ionization region. The benzyl ions formed are detected by time-of-flight mass spectrometry. The adiabatic ionization potential is determined from the onset of ionization and found to be 7.2487 ± 0.0006 eV.

The combination of $\Delta_fH_0°(C_6H_5CH_2^+)$ from Bombach *et al.* together with IP($C_6H_5CH_2$) and $\Delta_fH_0°$(toluene) leads to $D_0(C_6H_5CH_2–H)$ = 90.4 ± 2.1 kcal/mol. With $\Delta_fH_0°(C_6H_5CH_2^+)$ from Baer *et al.*, one obtains 86.6 ± 1.1 kcal/mol. For comparison, recent kinetics studies by Hippler and Troe[169] and Walker and Tsang[170] enable one to arrive at $D_0(C_6H_5CH_2–H)$ = 89.0 ± 1.0 and 87.2 kcal/mol, respectively. The essential difference in the two kinetics studies is their choice of $S°(C_6H_5CH_2)$. We have reexamined this quantity,[171] availing ourselves of recently calculated *ab initio* frequencies for benzyl radical, as well as experimental ones, where possible. Our resulting $S°(C_6H_5CH_2)$ is much closer to that of Walker and Tsang. Consequently, we favor their value for $D_0(C_6H_5CH_2–H)$ of 87.2 ± 1.5 kcal/mol and $DH_{298}(C_6H_5CH_2–H)$ of 88.6 ± 1.5 kcal/mol; these values are in excellent agreement with the values based on gas-phase acidity measurements (see Table 2).

$D_0(H–COOH)$. The appearance potential of $COOH^+$ from HCOOH has been reinvestigated recently by photoion–photoelectron coincidence spectroscopy.[172] A value of 12.30 ± 0.02 eV was obtained. The structure of the *m/e* 45 ion was established to be



From this measurement, one can derive the proton affinity (PA) of CO_2 to be 129.2 ± 0.5 kcal/mol, in good agreement with a contemporary direct measurement,[173] PA(CO_2) = 128.5 ± 1 kcal/mol.

The products of the F + HCOOH reaction were studied by PIMS.[174] It was established by selective deuteration that HCOO + $h\nu \rightarrow HCOO^+ + e^-$ could not be observed, whereas COOH + $h\nu \rightarrow COOH^+ + e^-$ was detected. A steplike structure was noted in the photoion yield curve near threshold, indicative of a Franck–Condon progression, and hence a geometry change upon photoionization. The primary progression appears to be the C–O stretch, with a frequency of roughly 2300 cm^{-1}. The lowest step observed corresponds to an adiabatic IP(COOH) = 8.486 ± 0.012 eV, but a still weaker, lower step is not ruled out. The presence of such a step would lower the IP to 8.20 eV. Thus, D_0(H–COOH) = (12.30 eV – 8.468 eV) ≥ 3.81 eV [≡ 88 kcal/mol] and possibly D_0 = 12.30 – 8.20 = 4.10 eV [≡ 94.5 kcal/mol]. A recent *ab initio* calculation[175] arrives at 93.9 kcal/mol for this bond energy, suggesting that there may exist a heretofore unobserved lower step in the photoion yield curve.

4. Cases Solved by Photoion-Pair Formation. Attempts to determine the R–H bond energies of two small molecules, HCN and C_2H_2, by the AP/IP approach using IP(R) have thus far been thwarted. In both cases, the direct determination of the adiabatic IP of the free radical (CN and C_2H) has not been accomplished. For the example of HCN, discussed previously, this does not present a problem for establishing D_0(H–CN), since the lowest AP corresponds to formation of H^+, rather than CN^+. However, in the dissociative photoionization of acetylene, the lowest-energy fragmentation involves $C_2H^+ + H + e^-$, and hence one needs IP(C_2H). In addition, there remains some controversy regarding AP(C_2H^+) from C_2H_2.

Fortunately, both HCN and C_2H_2 (which are isoelectronic) manifest the photoion-pair formation process. In a search for C_2H^- upon photoexcitation of C_2H_2, Ruscic and Berkowitz[176] were surprised to observe two bands. The dependence of one

CHART 1: Ethane Experimental Bond Strengths (D_0 in kcal/mol)

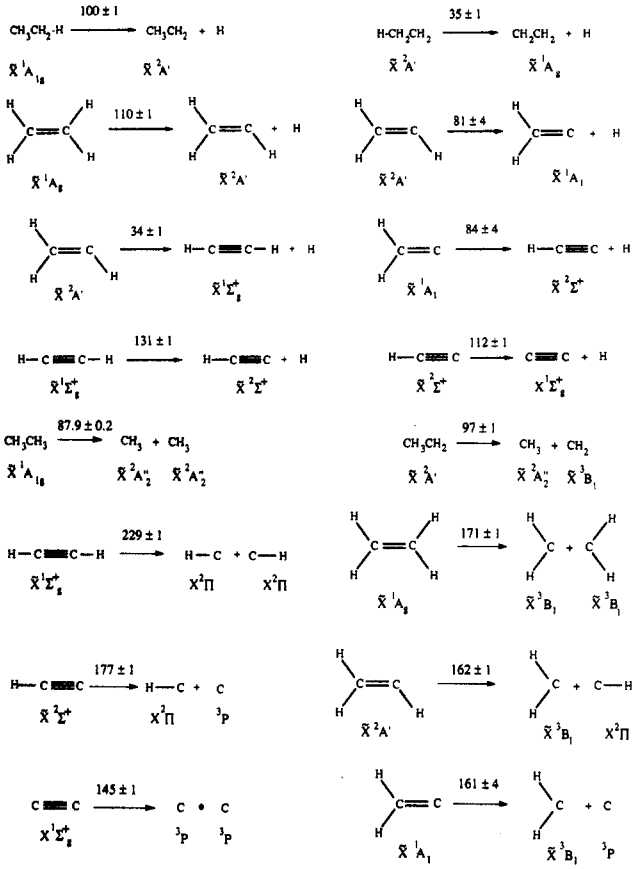


CHART 2: Acetaldehyde Experimental Bond Strengths (D_0 in kcal/mol)

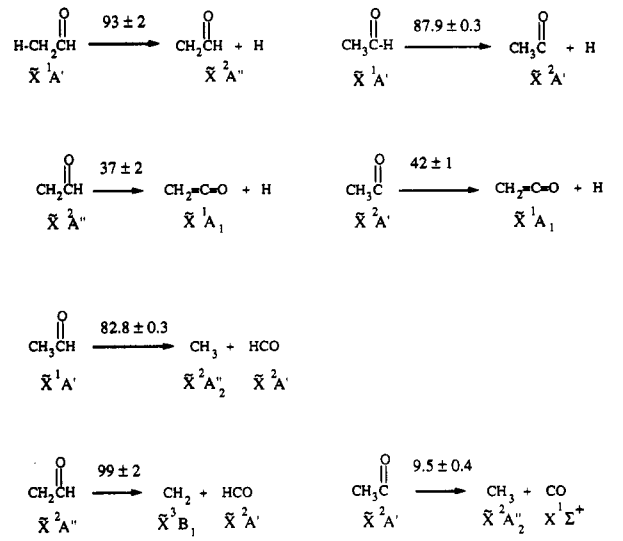
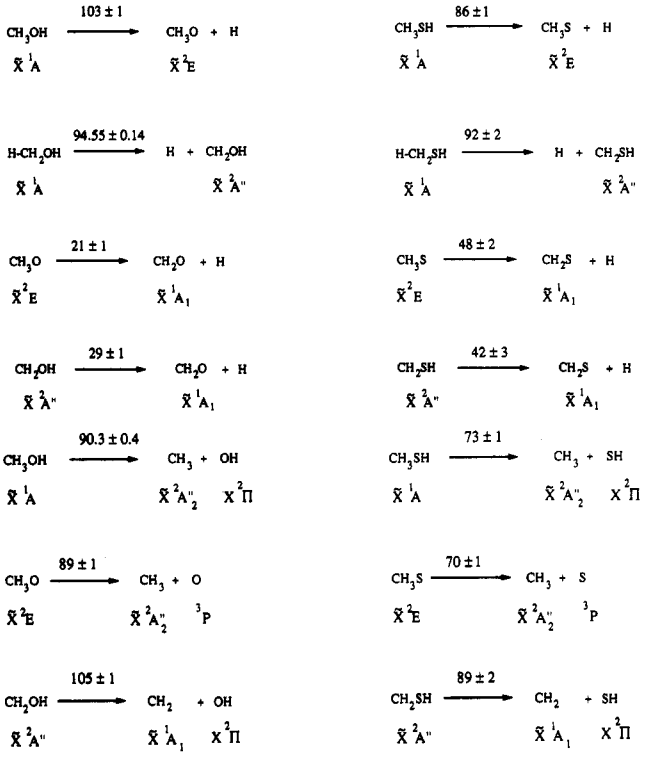


CHART 3: Methanol Experimental Bond Strengths (D_0 in kcal/mol)



band on the partial pressure of C_2H_2 was linear and the other quadratic. The linearly-dependent process, associated with photoion-pair production ($H^+ + C_2H^-$), had a threshold at $16.33_5 \pm 0.02$ eV. This threshold, together with IP(H) and the electron affinity,[177] EA(C_2H) = 2.969 ± 0.010 eV, gives D_0(HCC–H) ≤ $5.70_6 \pm 0.02_2$ eV [≡131.6 ± 0.5 kcal/mol]. The quadratically-dependent process was interpreted as the two-step reaction:

$$C_2H_2 + h\nu \rightarrow C_2H_2^+ + e^-(KE) \qquad (38a)$$

$$e^-(KE) + C_2H_2 \rightarrow C_2H^- + H \qquad (38b)$$

The kinetic energy of the scattered electron, e^-(KE), is fixed by the IP(HCCH) and the photon's energy, $h\nu$. The threshold for (38a) is the IP of C_2H_2, 11.400 eV. Photon energies higher then this value continue to form $C_2H_2^+$ in its ground vibronic state, the excess energy being carried away by the photoelectron. Process 38b, referred to as dissociative attachment, has a threshold at 14.072 eV. This corresponds to a photoelectron kinetic energy of 2.672 eV. (In fact, this process had been investigated previously using thermally generated, accelerated electrons.[178] The observed threshold was 2.8 ± 0.2 eV.) A detailed analysis of the dissociative attachment threshold in (38b) arrives at a value of $E_0 = 2.71_5 \pm 0.03_2$ eV and E_0(38b) = D_0(HCC–H) – EA(CCH). When combined with the aforementioned EA(C_2H), this process leads to D_0(HCC–H) = $5.68_4 \pm 0.03_4$ eV ≡ 131.1 ± 0.8 kcal/mol, in very good agreement with the value obtained from the photoion-pair threshold.

Bond Energies

In this essay, we have concentrated on three *methods* to determine R–H bond energies, although two techniques (kinetics and PIMS studies) can generally be applied to other bond energies. The EA/acidity measurements are, by definition, restricted to R–H bond energies only, but well-established thermochemical data bases[61] make it possible to complete a large number of separate cycles. To conclude, we give some examples in Chart 1 (C–H bonds starting from ethane) and (CC bonds starting from ethane),[179] Chart 2 (CH and CC bonds from acetaldehyde), and Chart 3 (CH bonds from methanol and thiomethanol) and (CO and CS bonds from methanol and thiomethanol). For a pointed discussion of the far-reaching implications of several of these $\Delta_f H°$(radicals), see the article by Doering.[180]

(*a*) *CH_4.* The removal of successive hydrogen atoms from methane requires 103, 109, 101, and 80 kcal/mol, respectively.[181] Thus, the strongest bond is that corresponding to $D_0(H_2C–H)$. In contrast, the corresponding bond in silane and germane, $D_0(H_2Si–H)$ and $D_0(H_2Ge–H)$, is the weakest one in those sequences. This is graphically illustrated in Figure 9. The explanation for this disparate behavior is intimately related to the ground states of the dihydrides. In CH_2 it is $^3B_1$ while SiH_2 and GeH_2 are singlets, $^1A_1$. The two nonbonding electrons of the radical are unpaired in methylene but are coupled to form singlets

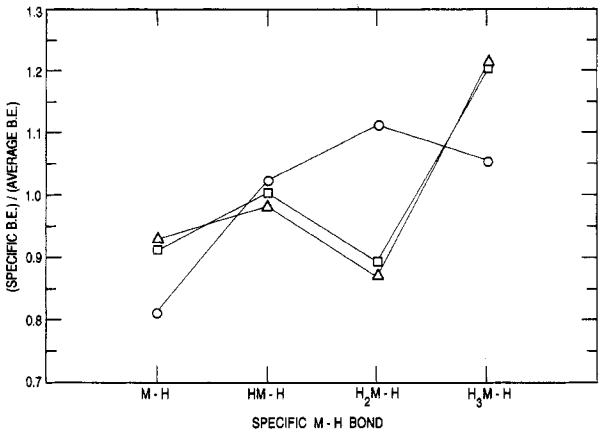


Figure 9. Ratio of a particular bond energy to the average bond energy, plotted against the sequential bonds M–H, HM–H, H_2M–H, and H_3M–H, where M is (○) C, (□) Si, or (△) Ge.

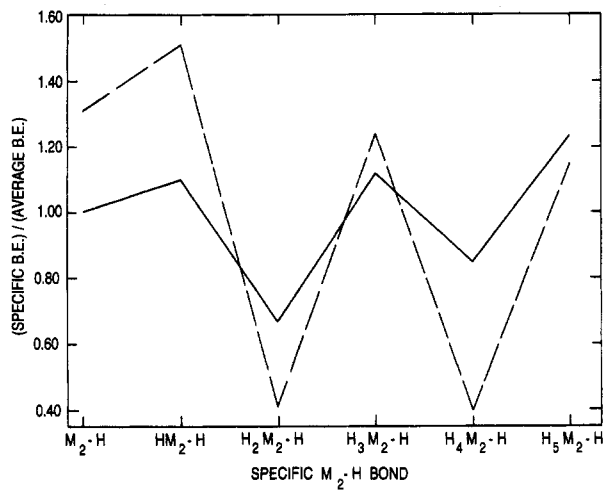


Figure 10. Plot representing the fraction of the average bond energy of successive bonds M_2–H_n, as a function of the particular bond: — for M_2 is Si_2 and - - - for the case of M_2 is C_2.

in silylene and germylene. Consequently, in order to add a H atom to the latter, it is necessary to supply energy to uncouple the singlet pair, effectively forming the excited $^3B_1$ state. This expenditure of energy manifests itself in a weaker $D_0(H_2Si–H)$ and $D_0(H_2Ge–H)$.

(*b*) *CH_3CH_3*. The C–H bond energy in ethane (99.5 ± 0.5 kcal/mol) is slightly weaker than that in methane. Although the precise value is still controversial, the C–H bond in ethylene is 107.5 ± 2.5 kcal/mol, distinctly larger than in ethane. In acetylene, there is a substantial increase to 131.3 ± 0.6 kcal/mol. By contrast, removal of a H atom from the ethyl radical requires only 34.2 ± 0.4 kcal/mol and from vinyl radical, 35.7 ± 2.5 kcal/mol (Chart 1). These anomalously low bond energies are readily understood when one recognizes that the products of bond rupture form additional bonds and hence gain stability. Thus, ethyl radical decomposes to generate ethylene with a C=C bond. Likewise, vinyl radical loses a H atom to produce acetylene with its C≡C bond. The oscillation in these bond energies in C_2H_6 and also Si_2H_6 (but with smaller amplitude) can be seen in Figure 10.

In a similar manner, one can anticipate weak bonds in many of the radicals derived from acetaldehyde, methanol, and thiomethanol.

Conclusions

These three different techniques have only a few disagreements among them; the case of ethylene is the most serious. *For the overwhelming number of studies, all measurements lead to bond energies within each other's error bars.* Likewise, the agreement between the photoion-pair thresholds (Table 3) and the gas-phase acidities (Table 2) is satisfactory.

When they can be successfully applied, both radical kinetic studies and PIMS measurements generally produce bond energies with an accuracy of better than ±1 kcal/mol. With few exceptions, the acidity/EA cycle is not as precise as kinetic determinations or AP/IP experiments. Since the acidity is almost always tied to a ladder of reference compounds, uncertainties of ±2 or ±3 kcal/mol are unavoidable for many molecules at the present time.

None of these methods is completely satisfactory. The kinetics of halogen abstraction with unsaturated molecules is sometimes complicated by addition reactions; thus, this method does not work with $CH_3C{\equiv}CH$ or $CH_2{=}CHCH{=}CH_2$. Likewise, PIMS depends on finding an accurate and thermochemically significant appearance energy $E_{AP}(R–H)$. For example, since CH_3O^+ is roughly 80 kcal/mol less stable than $^+CH_2OH$, the appearance potential of this *m/e* 31 fragment must be expected to have the $^+CH_2OH$ structure; the higher-energy form will rearrange and not manifest a new onset. Hence, $D_0(H–CH_2OH)$ is accessible to determination by the AP/IP method, but not $D_0(CH_3O–H)$. In addition, PIMS requires a clean determination of the radical IP(R). Sometimes the proper (0,0) band of the IP cannot be easily found due to unfavorable Franck–Condon factors. Thus, there is still continued concern about the $IP(CH_2CH)$ and $IP(C_6H_5)$. Negative ion chemistry/spectroscopy also has its headaches. In many cases one cannot prepare the target ion {e.g., $(CH_3)_3C^-$ or $HOCH_2^-$ for example}, or the ion is simply too fragile to study its ion chemistry (e.g., CH_3N^- or BH_3^-). Sometimes the ion has a huge EA(R) and has not yet been detached ($CH_3CO_2^-$ for example), or the detachment process is complicated by photodissociation (CO_3^-). In spite of these limitations, these negative ion cycles are very useful since the breadth of the EA/acidity approach is huge. Thousands of molecular acidities are securely known, and the latest EA tabulation lists hundreds of radical electron affinities. Table 2 could be expanded to include several hundred species.

The combination of these three approaches leads to a large number of accurate, consistent bond dissociation energies. Clearly, these techniques will be extended to determine the energetics of larger and more complex molecules.

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As we were finishing the galley proofs of this article, our colleague and friend David Gutman lost his long battle with cancer. Without David's energetic writing and close attention to detail, this review would not have much of its scope and depth. It is

characteristic of Gutman that, even as he was dying, he was still trying to understand his molecules.

Goodbye Dave.

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$$E = E_0 + n_1\epsilon_1 + n_2\epsilon_2 + n_3\epsilon_3 + n_4\epsilon_4 + \ldots$$

The population $\{n_i\}$ is described by the Maxwell–Boltzmann law, and one can use the partition function, Q, to write the molecular energy:

$$E = E_0 + RT^2 \frac{\mathrm{d}(\ln Q)}{\mathrm{d}T}$$

Consequently, we can use (8) to arrive at a useful expression of the heat capacity, $C_p(T) \equiv (\partial H/\partial T)_p$.

$$C_p = R + R\frac{\mathrm{d}}{\mathrm{d}T}\left[T^2 \frac{\mathrm{d}(\ln Q)}{\mathrm{d}T}\right]$$

Assuming symmetric tops and harmonic vibrations but ignoring internal rotations, Herzberg derives explicit formulas for the $C_p(T)$ expressions for molecular translation, rotation, and vibration on p 512.

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species	$H_{298} - H_0$	S_{298}	harmonic frequencies/cm^{-1}	B/cm^{-1}
HC≡C $\tilde{X}^2\Sigma^+$	2.5	49.6	3600, 1840, 370, 370	1.46
HC≡C$^-$ $\tilde{X}^1\Sigma^+$	2.4	48.8	3200, 1800, 520, 520	1.39
HC≡CH $\tilde{X}^1\Sigma_g^+$	2.4	48.0	3374, 1974, 3289, 612, 612, 730, 730	1.1766

(69) Notice that if one just replaces $\Delta_{acid}S_{298}(HCC–H) \equiv [S_{298}(HCC^-) + S_{298}(H^+) - S_{298}(HCCH)]$ by $S_{298}(H^+)$, the approximation is reasonble. By explicit calculation, $\Delta_{acid}S_{298}(HCC–H) = 26.8$ cal/(mol K) while $S_{298}(H^+) = 26.0$ cal/(mol K).

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(72) Generally if you cannot compute the entropy exactly, one can make a conjecture: $\Delta_{acid}S(R–H) = [S(R^-) + S(H^+) - S(RH)] \cong S_{298}(H^+)$ or 26 ± 4 cal/(mol K). The error bars of ±4 cal/(mol K) are used since we assume $[S(R^-) - S(RH)] \cong 0$. To see that this is not always the case, notice that CH_3CHO has free rotation about the CC bond, but in the anion, $CH_2{=}CH–O^-$, this will certainly be lost and $[S(R^-) - S(RH)] \neq 0$.

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(75) We have had to make a choice about significant figures. Essentially, one has to choose between being conservative or being correct. Suppose a proper analysis leads to a bond energy which is 93.3 ± 2.1 kcal/mol. Now the uncertainty is correctly computed, and 2.1 kcal/mol is really the proper measure of the error associated with this bond. But it is all too common that large numbers of chemists lose track of the error bars. Thus, the BDEs are picked up from a table and used elsewhere without their accompanying uncertainties. Consequently, 93.3 ± 2.1 kcal/mol propagates about as 93.3 kcal/mol, and at some point there is an implication of an uncertainty of ±0.1 kcal/mol. To be conservative, in the charts we try to round our numbers carefully; thus, 93.3 ± 2.1 kcal/mol becomes 93 ± 2 kcal/mol. In the text and our tables, we try to be correct. Also, we notice that not all uncertainties are symmetric. Thus, $h\nu_{thresh}$ for the EA(CH_2CHO) is properly $14\,718^{+2}_{-5}$ cm^{-1}. However, in all cycles, we choose a symmetric uncertainty of ±5 cm^{-1} and report an EA(CH_2CHO) of 42.08 ± 0.01 kcal/mol.

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(179) Urdahl, R. S.; Bao, Y.; Jackson, W. M. *Chem. Phys. Lett.* **1991**, *178*, 425. Recently, a photodissociation experiment on HCCH has led to the significant revision of the heat of formation of $X^1\Sigma_g^+C_2$. This reference establishes $\Delta_f H_0(C_2)$ = 194.8 ± 0.5 kcal/mol.
(180) Doering, W. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279.
(181) The bond energies (kcal/mol) of methane are $D_0(H_3C–H)$ = 103.2 ± 0.1, $D_0(H_2C–H)$ = 108.7 ± 0.6, D_0(HC–H) = 100.7 ± 1.0, and D_0(C–H) = 79.9 ± 0.1. See: McCulloh, K. E.; Dibeler, V. H. *J. Chem. Phys.* **1976**, *64*, 4445. Herzberg, G. *Proc. R. Soc. London* **1961**, *A262*, 291. Leopold, D. G.; Murray, K. K.; Stevens Miller, A. E.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849. Helm, H. P.; Cosby, P. C.; Graff, M. M.; Moseley, J. T. *Phys. Rev.* **1982**, *25A*, 304. Gurvich *et al.* lists $\Delta_f H_0°(CH_4)$ = –15.92 ± 0.07 kcal/mol, for gaseous C atom, $\Delta_f H_0°(C)$ = 169.98 ± 0.11 kcal/mol, and $\Delta_f H_0°(H)$ = 51.633 ± 0.001 kcal/mol; consequently, the sum of the four C–H bonds in methane must add to 392.4 ± 0.1 kcal/mol.
(182) Based on the study of Cl + $CH_4 \rightleftharpoons CH_3$ + HCl equilibrium.
(183) Reliance on old, indirect kinetic data on Br + CH_3OH kinetics is responsible for the higher error limits of the CH_2OH heat of formation as well as the inability to provide a reliable second law determination. See text and footnote 49 for a discussion of the "best" entropy.
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(193) See Table 3.
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(236) Gurvich *et al.*, 1989, Vol. 1. This reports $\Delta_fH_0°(HF) = -65.31 \pm 0.17$ kcal/mol and $\Delta_fH_{298}°(HF) = -65.32 \pm 0.17$ kcal/mol. They also report the values of $\Delta_fH_0°(F)$ and $\Delta_fH_{298}°(F)$ in Table 5, which are fixed by the spectroscopic value for $D_0(F_2)$. Their value of $\Delta_fH_0°(F)$ is very slightly different from the spectroscopic value reported for $D_0(HF)$. Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Von Nostrand Reinhold: New York, 1979 list $D_0(HF) = 47\,333 \pm 60$ cm^{-1} or 135.3 ± 0.2 kcal/mol. Gurvich's value for $D_0(HF)$ is also just outside the error bars from values obtained by AP/IP methods shown in Table 4 (by about 0.5 kcal/mol). The explanation for this is not clear.

(237) Gurvich *et al.*, 1989, Vol. 1. This reports $\Delta_fH_0°(HCl) = -22.02 \pm 0.03$ kcal/mol and $\Delta_fH_{298}°(HCl) = -22.06 \pm 0.03$ kcal/mol.

(238) Gurvich *et al.*, 1989, Vol. 1. This reports $\Delta_fH_0°(HBr) = -6.82 \pm 0.04$ kcal/mol and $\Delta_fH_{298}°(HBr) = -8.70 \pm 0.04$ kcal/mol.

(239) Gurvich *et al.*, 1989, Vol. 1. This reports $\Delta_fH_0°(HI) = 6.82 \pm 0.06$ kcal/mol and $\Delta_fH_{298}°(HI) = 6.30 \pm 0.06$ kcal/mol.

(240) Gurvich *et al.*, 1989, Vol. 1. This reports $\Delta_fH_0°(H_2O) = -57.102 \pm 0.010$ kcal/mol and $\Delta_fH_{298}°(H_2O) = -57.795 \pm 0.010$ kcal/mol. For hydroxyl radical, $\Delta_fH_0°(OH)$ comes from a spectroscopic determination of $D_0(OH)$ [=35 420 ± 15 cm^{-1}] by Carlone, C.; Dalby, F. W. *Can. J. Phys.* **1969**, *47*, 1945 which is to be compared with an earlier measurement by R. F. Barrow *Ark. Fys.* **1956**, *11*, 281 of 35 450 ± 100 cm^{-1}. Gurvich's values differ slightly (by roughly 0.4 kcal/mol) from the AP/IP results in Table 4. The precise reason is not known.

(241) Chuang, M. C.; Foltz, M. F.; Moore, C. B. *J. Chem. Phys.* **1987**, *87*, 3855. This papers reports D_0(H–CHO) and Δ_fH_{298}(HCO) = 9.99 ± 0.19 kcal/mol based on a value of $\Delta_fH_{298}°(CH_2O) = -25.95$ kcal/mol reported by: Baulch, D. L.; Cox, R. A.; Crutzen, P. J.; Hampson Jr., R. F.; Troe, J.; Watson, R. T. *J. Phys. Chem. Ref Data* **1982**, *11*, 493. We adopt Chuang *et al.*'s value for D_0(H–CHO) and compute $\Delta_fH_{298}°$(HCO) and $\Delta_fH_0°$(HCO) based on the values of $\Delta_fH_0°(CH_2O) = -25.06 \pm 0.12$ kcal/mol and $\Delta_fH_{298}°(CH_2O) = -25.98 \pm 0.12$ kcal/mol recommended by Gurvich *et al.* (1991).

(242) Gurvich *et al.*, 1989, Vol. 1. This reports $\Delta_fH_0°(NH_3) = -9.31 \pm 0.08$ kcal/mol and $\Delta_fH_{298}°(NH_3) = -10.98 \pm 0.08$ kcal/mol. Gibson, S. T.; Greene, J. P.; Berkowitz, J. *J. Chem. Phys.* **1985**, *83*, 4319 report $D_0(NH_3)$ and $\Delta_fH_0°(NH_2)$. Heat capacity corrections for NH_2 provide $\Delta_fH_{298}°(NH_2)$ and hence $DH_{298}(NH_3)$.

(243) Gurvich *et al.*, 1991, Vol. 2, Parts 1 and 2. This compilation recommends $\Delta_fH_0°(CH_4) = -15.92 \pm 0.07$ kcal/mol and $\Delta_fH_{298}°(CH_4) = -17.83 \pm 0.07$ kcal/mol; McCulloh, K. E.; Dibeler, V. H. *J. Chem. Phys.* **1976**, *64*, 4445 and Herzberg, G. *Proc. R. Soc. London* **1961**, *A262*, 291 find $D_0(CH_4)$. Appropriate heat capacity measurements yield a value for $DH_{298}(CH_4)$. The recommended kinetic $\Delta_fH_{298}°(CH_3)$ in Table 1 agrees very well.

(244) Gurvich *et al.*, 1991, Vol. 2, Parts 1 and 2. This compilation recommends $\Delta_fH_0°(HCN) = 31.6 \pm 1.0$ kcal/mol and $\Delta_fH_{298}°(HCN) = 31.5 \pm 1.0$ kcal/mol; Berkowitz, J.; Chupka, W. A.; Walter, T. A. *J. Chem. Phys.* **1969**, *50*, 1497 report AP(H^+,HCN) and use IP(H) to find D_0(H–CN). Heat capacity corrections yield DH_{298}(H–CN). This value overlaps that resulting from the acidity/EA cycle (Tables 2 and 3).

(245) Gurvich *et al.*, 1989, Vol. 1. This reports $\Delta_fH_0°(H_2S) = -4.22 \pm 0.12$ kcal/mol and $\Delta_fH_{298}°(H_2S) = -4.92 \pm 0.12$ kcal/mol. We have adopted $\Delta_fH_0°$(SH) and $\Delta_fH_{298}°$(SH) from: Nicovich, J. M.; Kreutter, K. D.; van Dijk, C. A.; Wine, P. H. *J. Phys. Chem.* **1992**, *96*, 2518. The $D_0(H_2S)$ and $DH_{298}(H_2S)$ values from the acidity/EA cycle (Table 2) are compatible with these values.

(246) Mills, K. C. *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*; Butterworths: London, 1974. Mills recommends $\Delta_fH_{298}°(H_2Se)$ as 7.0 ± 0.2 kcal/mol but Flogel, P. *Z. Anorg. Allg. Chem.* **1972**, *388*, 218 gives 6.4 ± 0.2 kcal/mol; we have chosen 6.7 ± 0.5 kcal/mol as a conservative average. Gibson, S. T.; Greene, J. P.; Berkowitz, J. *J. Chem. Phys.* **1986**, *85*, 4815 have determined $D_0(H_2Se)$. Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11* (*Suppl. No. 2*) gives $(H_{298} - H_0)$ for H_2Se as 2.391 kcal/mol and we find $(H_{298} - H_0)$ for SeH to be 2.075 kcal/mol. This leads to $DH_{298}(H_2Se)$. From $DH_{298}(H_2Se)$ and other given quantities, one finds $\Delta_fH_{298}°$(SeH); use of $(H_{298} - H_0)$ for Se(solid), H_2 and SeH leads to $\Delta_fH_0°$(SeH). There is a discrepancy with the acidity/EA cycle (Table 2). The value for $\Delta_{acid}H_{298}°(H_2Se)$ is over 20 years old and probably needs to be reexamined.

(247) Gunn, S. R. *J. Phys. Chem.* **1964**, *68*, 949. Gunn reports $\Delta_fH_{298}°(H_2Te)$ as 23.8 ± 0.2 kcal/mol. Gal, J.-F.; Maria, P.-C.; Decouzon, M. *Int. J. Mass Spectrosc. Ion Processes* **1989**, *93*, 87. Friedhoff, C. B.; Snodgrass, J. T.; Coe, J. V.; McHugh, K. M.; Bowen, K. H. *J. Chem. Phys.* **1986**, *84*, 1051 combine $\Delta_{acid}H(H_2Te)$ and EA(TeH) and report $DH_{298}(H_2Te)$. Using $(H_{298} - H_0)$ for H_2Te from Altshuler, *J. Phys. Chem.* **1957**, *61*, 509 and a value of $(H_{298} - H_0)$ for TeH of 2.074, we find $D_0(H_2Te)$. From the definition of heat of formation and $(H_{298} - H_0)$ for Te(solid), we find $\Delta_fH_0°$(TeH).

(248) Berkowitz, J.; Curtiss, L. A.; Gibson, S. T.; Greene, J. P.; Hillhouse, G. L.; Pople, J. A. *J. Chem. Phys.* **1986**, *84*, 375. This paper reports $D_0(PH_3)$ and $\Delta_fH_0°(PH_2)$. JANAF, Gurvich, and Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11* (*Suppl. No. 2*) all agree that the standard state of phosphorus is white phosphorus although red phosphorus is more stable. All seem to accept the heat of formation of PH_3 from Gunn and Green (*J. Phys. Chem.* **1961**, *65*, 779), which is 1.3 ± 0.4 kcal/mol at 298 K. Both Gurvich and Wagman *et al.* adopt $\Delta_fH_0°(PH_3) = 3.2 \pm 0.4$ kcal/mol. Now we need $DH_{298}(PH_3)$ and $\Delta_fH_{298}°(PH_2)$. JANAF and Wagman *et al.* give $(H_{298} - H_0)PH_3$ while JANAF and Gurvich give $(H_{298} - H_0)PH_2$. Thus, $DH_{298}(PH_3) = D_0(PH_3) + 1.447$ kcal/mol (Gurvich + NBS) or $DH_{298}(PH_3) = D_0(PH_3) + 1.449$ (JANAF). Therefore, $DH_{298}(PH_3) = 83.91 \pm 0.46$ kcal/mol. Now Gurvich gives the values of both $\Delta_fH_{298}°(PH_2)$ and $\Delta_fH_0°(PH_2)$, the difference being 0.919 kcal/mol. Using our value for $\Delta_fH_0°(PH_2)$ and this difference, we find $\Delta_fH_{298}°(PH_2)$. The values extracted from the acidity/EA cycle (Table 2) have barely overlapping error bars.

(249) Gunn, S. R.; Jolly, W. L.; Green, L. G. *J. Phys. Chem.* **1960**, *64*, 1334. These workers find $\Delta_fH_{298}°(AsH_3) = 15.87 \pm 0.25$ kcal/mol; Berkowitz, J. (*J. Chem. Phys.* **1988**, *89*, 7065) finds $D_0(AsH_3)$. To correct $D_0(AsH_3)$ to $DH_{298}(AsH_3)$, one employs $(H_{298} - H_0)$ of AsH_3 from Wagman *et al.* and a value of $(H_{298} - H_0)$ for AsH_2 and finds $DH_{298}(AsH_3)$. This produces $\Delta_fH_{298}°(AsH_2)$. The values of $D_0(AsH_3)$ and $DH_{298}(AsH_3)$ from the acidity/EA cycle do not have overlapping error bars. Both $\Delta_{acid}H_{298}°(AsH_3)$ and EA(AsH_2), now over 20 years old, need reexamination.

(250) Ruscic, B.; Berkowitz, J. *J. Chem. Phys*, in press. This paper reports $D_0(SbH_3)$ and $\Delta_fH_0°(SbH_2)$. Using values of $(H_{298} - H_0)$ of SbH_3 and SbH_2, we find $DH_{298}(SbH_3)$. With $DH_{298}(SbH_3)$ and $\Delta_fH_{298}°(SbH_3) = 34.61$ kcal/mol from: Gunn, S. R. *J. Phys. Chem.* **1964**, *68*, 949, we extract $\Delta_fH_{298}°(SbH_2) = 51.4 \pm 0.6$ kcal/mol. An alternate way of going from $\Delta_fH_0°(SbH_2)$ to $\Delta_fH_{298}°(SbH_2)$ is from the definition, which requires $(H_{298} - H_0)$ of Sb(solid) which is listed by D. D. Wagman *et al.* (1982). From this and previously determined quantities, $\Delta_fH_{298}°(SbH_2) = \Delta_fH_0°(SbH_2) = 1.056$ or $\Delta_fH_{298}°(SbH_2) = 51.4 \pm 0.6$ kcal/mol, in agreement with the other calculation.

(251) Gurvich *et al.*, 1989, Vol. 1. It is recommended that $\Delta_fH_0°(SiH_4) = 10.6 \pm 0.4$ kcal/mol and $\Delta_fH_{298}°(SiH_4) = 8.3 \pm 0.4$ kcal/mol. Seetula, J. A.; Feng, Y.; Gutman, D.; Seakins, P. W.; Pilling, M. J. *J. Phys. Chem.* **1991**, *95*, 1658 have measured $\Delta_fH_{298}°(SiH_3)$ and hence $DH_{298}(SiH_3$–H).

$D_0(SiH_4)$ is computed from $DH_{298}(SiH_4)$. The values from the acidity/EA cycle (Table 2) and the AP/IP cycle (Table 4) are compatible with these values.

(252) Ruscic, B.; Schwarz, M.; Berkowitz, J. *J. Chem. Phys.* **1990**, *92*, 1865. These workers have measured $D_0(GeH_4)$ and $\Delta_f H_0°(GeH_3)$. The frequencies of both GeH_4 and GeH_3 are reported in: Krasnov, K. S. *Molekulyarnie postoyannie neorganicheskikh soedineni*; Khimia: Leningrad, 1979. Use of these frequencies leads to $(H_{298} - H_0)$ for GeH_4 = 2.568 kcal/mol and $(H_{298} - H_0)$ for GeH_3 = 2.485 kcal/mol. Therefore, $DH_{298}(GeH_4) = D_0(GeH_4) + 1.398$ kcal/mol. From the definition of $\Delta_f H_{298}°$ and $(H_{298} - H_0)$ of solid germanium as 1.105 kcal/mol from Wagman *et al.*, one finds that $\Delta_f H_{298}°(GeH_3) = \Delta_f H_0°(GeH_3) = 1.708$ kcal/mol. The acidity/EA values in Table 2 have overlapping error bars.

(253) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1993**, *98*, 2568. This paper reports $D_0(H_2CS)$, $\Delta_f H_0°(H_2CS)$, and $\Delta_f H_0°(HCS)$; $(H_{298} - H_0)$ for H_2CS = 2.44 kcal/mol and $(H_{298} - H_0)$ for HCS = 2.439 kcal/mol so $DH_{298}(H_2CS) = D_0(H_2CS) + 1.48$ kcal/mol. To get $\Delta_f H_{298}°(HCS)$, one uses the $(H_{298} - H_0)$ values of graphite (0.251 kcal/mol) and solid sulfur (1.054 kcal/mol) from Wagman *et al.* and finds $\Delta_f H_{298}°(HCS) = \Delta_f H_0°(HCS) + 0.1045$.

(254) Gurvich *et al.*, 1991, Vol. 2, Parts 1, 2. This compilation recommends $\Delta_f H_0°(HCCH) = 54.48 \pm 0.19$ kcal/mol and $\Delta_f H_{298}°(HCCH) = 54.35 \pm 0.19$ kcal/mol. Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750 report $D_0(HCCH)$ and $DH_{298}(HCCH)$; the values based on ion-pair and dissociative attachment thresholds reported by Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1990**, *93*, 5586 are in excellent agreement.

(255) Gurvich *et al.*, 1991, Vol. 2, Parts 1, 2. This compilation recommends $\Delta_f H_0°(H_2CCH_2) = 14.56 \pm 0.12$ kcal/mol and $\Delta_f H_{298}°(H_2CCH_2) = 12.52 \pm 0.12$ kcal/mol; we adopt $D_0(H_2CCH–H)$ from: Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750. See text for a discussion of the discrepancies with kinetic measurements and AP/IP cycles.

(256) It is recommended that $\Delta_f H_{298}°(C_6H_6) = 19.7 \pm 0.2$ kcal/mol, and we use $\Delta_f H_0°(C_6H_6) = 23.9 \pm 0.3$ kcal/mol. We adopt the C_6H_6 acidity and $EA(C_6H_5)$ from footnote 205 to compute $DH_{298}(C_6H_5–H) = 111.2 \pm 0.8$ kcal/mol and $D_0(C_6H_5–H) = 109.8 \pm 0.8$ kcal/mol. See text for discussion of AP/IP cycles.

(257) Pedley *et al.*, 1986, Vol. 1. It is recommended that $\Delta_f H_{298}°(CH_2CHCH_3) = 4.8 \pm 0.2$ kcal/mol and we use $\Delta_f H_0°(CH_2CHCH_3) = 8.4 \pm 0.3$ kcal/mol: McKay, G. I.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Can. J. Chem.* **1978**, *56*, 131. Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734. Polak, M. L.; Lineberger, W. C. Unpublished, 1992. $D_0(CH_2CHCH_2–H)$ computed from $DH_{298}(CH_2CHCH_2–H) - {}^5/_2RT$.

(258) Pedley *et al.*, 1986, Vol. 1. It is recommended that $\Delta_f H_{298}°(C_6H_5CH_3) = 12.0 \pm 0.1$ kcal/mol, and we use $\Delta_f H_0°(C_6H_5CH_3) = 17.4 \pm 0.3$ kcal/mol; see text and footnote 171 for $D_0(C_6H_5CH_2–H)$ assessment.

(259) Pedley *et al.*, 1986, Vol. 1. This compilation lists $\Delta_f H_{298}°(CH_3CHO) = -39.7 \pm 0.1$ kcal/mol, and we use $\Delta_f H_0°(CH_3CHO) = -37.2 \pm 0.2$ kcal/mol; Bartmess, J. E.; Scott, J. A.; McIver Jr., R. T. *J. Am. Chem. Soc.* **1979**, *101*, 6047. Mead, R. D.; Lykke, K. R.; Lineberger, W. C.; Marks, J.; Brauman, J. I. *J. Chem. Phys.* **1984**, *81*, 4883. $D_0(H–CH_2CHO)$ is computed from $DH_{298}(H–CH_2CHO) - {}^5/_2RT$.

(260) Niiranen, J. K.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 5881. This paper reports a value for $\Delta_f H_{298}(CH_3CO)$ and thus $DH_{298}(CH_3CO–H)$ (see Table 1). $D_0(CH_3CO–H)$ computed from $DH_{298}(CH_3CO–H) - {}^5/_2RT$. These values are compatible with the results of the acidity/EA cycle (Table 2).

(261) Pedley *et al.*, 1986, Vol. 1. This compilation lists $\Delta_f H_{298}°(CH_2CO) = -11.4 \pm 0.4$ kcal/mol, and we use $\Delta_f H_0°(CH_2CO) = -10.6 \pm 0.4$ kcal/mol; Oakes, J. M.; Jones, M. E.; Bierbaum, V. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1983**, *87*, 4810. $D_0(CH_2CO)$ computed from $DH_{298}(CH_2CO) - {}^5/_2RT$.

(262) Gurvich *et al.*, 1991, Vol. 2, Parts 1 and 2. This compilation recommends $\Delta_f H_0°(CH_3OH) = -45.42 \pm 0.14$ kcal/mol and $\Delta_f H_{298}°(CH_3OH) = -48.04 \pm 0.14$ kcal/mol; Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1991**, *95*, 4033. Ruscic, B.; Berkowitz, J. *J. Phys. Chem.*, in press, find the value for $D_0(H–CH_2OH)$ and $DH_{298}(H–CH_2OH)$. The recommended kinetic value of $\Delta_f H_{298}°(CH_2OH)$ in Table 1 is compatible.

(263) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Phys. Chem.* **1986**, *90*, 6687. This reference together with Engelking, P. C.; Ellison, G. B.; Lineberger, W. C. *J. Chem. Phys.* **1978**, *69*, 1826 finds $DH_{298}(CH_3O–H)$; appropriate $(H_{298} - H_0)$ calculations for CH_3OH and CH_3O permit $D_0(CH_3O–H)$ to be extracted from $DH_{298}(CH_3O–H)$. The $\Delta_f H_0°(CH_3O)$ resulting from these acidity/EA measurements compares very well with the $\Delta_f H_0°(CH_3O) = 5.9 \pm 1.0$ kcal/mol recommended by: Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1991**, *95*, 4033.

(264) Gurvich *et al.*, 1991, Vol. 2, Parts 1 and 2. This compilation recommends $\Delta_f H_0°(CH_3CH_2OH) = -51.88 \pm 0.12$ kcal/mol and $\Delta_f H_{298}°(CH_3CH_2OH) = -56.12 \pm 0.12$ kcal/mol; Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750 report $DH_{298}(CH_3CH_2O–H)$; $D_0(CH_3CH_2O–H)$ computed from $DH_{298}(CH_3CH_2O–H) - {}^5/_2RT$.

(265) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1993**, *98*, 2568. This paper reports $\Delta_f H_0°(CH_3SH) = -3.0 \pm 0.1$ kcal/mol and $\Delta_f H_{298}°(CH_3SH) = -5.5 \pm 0.1$ kcal/mol; Nicovich, J. M.; Kreutter, K. D.; van Dijk, C. A.; Wine, P. H. *J. Phys. Chem.* **1992**, *96*, 2518.

(266) Pedley *et al.*, 1986, Vol. 1. This compilation lists $\Delta_f H_{298}°(CH_3CN) = 15.4 \pm 1.7$ kcal/mol and we use $\Delta_f H_0°(CH_3CN) = 17.1 \pm 1.7$ kcal/mol; Bartmess, J. E.; Scott, J. A.; McIver Jr., R. T. *J. Am. Chem. Soc.* **1979**, *101*, 6047. Moran, S.; Ellis, Jr., H. B.; DeFrees, D. J.; McLean, A. D.; Ellison, G. B. *J. Am. Chem. Soc.* **1987**, *109*, 5996. $D_0(CH_3CN)$ computed from $DH_{298}(CH_3CN) - {}^5/_2RT$.

(267) Pedley *et al.*, 1986, Vol. 1. This compilation lists $\Delta_f H_{298}°(CH_3NC) = 39.1 \pm 1.7$ kcal/mol and we use $\Delta_f H_0°(CH_3NC) = 40.6 \pm 1.7$ kcal/mol; Peerboom, R. A. L.; Ingemann, S.; Nibbering, N. M. M.; Liebman, J. F. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1825. Moran, S.; Ellis Jr., H. B.; DeFrees, D. J.; McLean, A. D.; Paulson, S. E.; Ellison, G. B. *J. Am. Chem. Soc.* **1987**, *109*, 6004. $D_0(CH_3NC)$ computed from $DH_{298}(CH_3NC) - {}^5/_2RT$.

(268) Gurvich *et al.*, 1991, Vol. 2, Parts 1 and 2. It is recommended that $\Delta_f H_0°(HCOOH) = -88.79 \pm 0.12$ kcal/mol and $\Delta_f H_{298}°(HCOOH) = -90.54 \pm 0.12$ kcal/mol. $D_0(H–COOH)$ is reported by: Ruscic, B.; Schwarz, M.; Berkowitz, J. *J. Chem. Phys.* **1989**, *91*, 6772. Ruscic, B.; Schwarz, M.; Berkowitz, J. *J. Chem. Phys.* **1989**, *91*, 6780. $DH_{298}(H–COOH)$ computed from $D_0(H–COOH)$ and $(H_{298} - H_0)$ values for HCOOH and COOH from Glushko *et al.*

(269) Berkowitz, J., 1993. The photoion yield curve of $(COOH^+, HCOOH)$ manifests step structure which becomes weaker near threshold. Therefore, it is quite possible that the (0,0) transition, corresponding to a weak Franck–Condon factor, has not been detected. Support for this view comes from *ab initio* calculations (Curtiss, L. A., private communication), which find IP(COOH) = 8.03 eV, compared to the lower experimental value, 8.486 ± 0.012 eV. The numbers in parentheses allow for this possibility.

(270) Gurvich *et al.*, 1991, Vol. 2, Parts 1 and 2. This compilation recommends $\Delta_f H_0°(CH_3CH_3) = -16.34 \pm 0.10$ kcal/mol and $\Delta_f H_{298}°(CH_3CH_3) = -20.08 \pm 0.10$ kcal/mol; Ruscic, B.; Berkowitz, J.; Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989**, *91*, 114 report $D_0(CH_3CH_2–H)$ while Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847 have measured $\Delta_f H_{298}°(CH_3CH_2)$ and hence $DH_{298}(CH_3CH_2–H)$; see Table 1 for recommended $\Delta_f H_{298}°(CH_3CH_2)$. These two bond energies are consistent.

(271) Pedley *et al.*, 1986, Vol. 1. This compilation lists $\Delta_f H_{298}°(CH_3CH_2CH_3) = -25.0 \pm 0.1$ kcal/mol and we use $\Delta_f H_0°(CH_3CH_2CH_3) = -19.9 \pm 0.2$; Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847 have measured $\Delta_f H_{298}°(CH_3CHCH_3)$ and hence $DH_{298}[(CH_3)_2CH–H]$; see Table 1 for recommended $\Delta_f H_{298}°(CH_3CHCH_3)$. $D_0[(CH_3)_2CH–H]$ computed from $DH_{298}[(CH_3)_2CH–H] - {}^5/_2RT$.

(272) Pedley *et al.*, 1986, Vol. 1. This compilation lists $\Delta_f H_{298}°(CH_3CH_2CH_2CH_3) = -30.0 \pm 0.2$ kcal/mol and we use $\Delta_f H_0°(CH_3CH_2CH_2CH_3) = -23.2 \pm 0.3$ kcal/mol; Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847 have measured $\Delta_f H_{298}°(CH_3CH_2CHCH_3)$ and hence $DH_{298}[CH_3CH_2C(CH_3)–H]$; see Table 1 for recommended $\Delta_f H_{298}°(CH_3CH_2CHCH_3)$. $D_0[CH_3CH_2C(CH_3)–H]$ computed from $DH_{298}[CH_3CH_2C(CH_3)–H] - {}^5/_2RT$.

(273) Pedley *et al.*, 1986, Vol. 1. This compilation lists $\Delta_f H_{298}°[(CH_3)_3CH] = -32.1 \pm 0.2$ kcal/mol and we use $\Delta_f H_0°[(CH_3)_3CH] = -25.3 \pm 0.3$ kcal/mol; Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847 have measured $\Delta_f H_{298}°[C(CH_3)_3]$ and hence $DH_{298}[(CH_3)_3C–H]$; see Table 1 for recommended $\Delta_f H_{298}°[C(CH_3)_3]$. $D_0[(CH_3)_3C–H]$ computed from $DH_{298}[(CH_3)_3C–H] - {}^5/_2RT$.