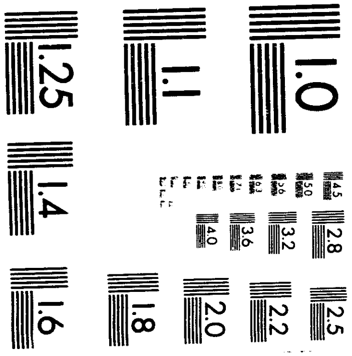
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ANL/CHM/PP--80545

Three Methods to Measure RH Bond Energies

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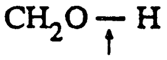
All chemists need to know bond energies. The energy changes associated with making and breaking bonds between atoms in a molecule are important practical concepts used everywhere in chemistry. In addition to being useful to synthetic chemists and material scientists, bond energies are also very good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

Bond dissociation energies (BDEs) offer an interesting window through which to view the 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] to the energy of the 2nd C-H bonds that lead to *ortho*-benzyne (79 kcal/mol), or *meta*-benzyne (89 kcal/mol), or *para*-benzyne (101 kcal/mol).

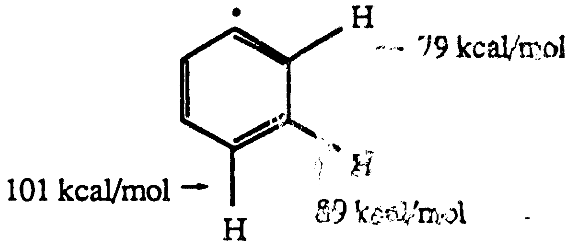
$H \underset{\uparrow}{-} CH_2O$

21 kcal/mol



$CH_2O \underset{\uparrow}{-} H$

29 kcal/mol



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

Many techniques[3] have been used to measure a huge number of BDE's and it is not our purpose to survey this massive field. Instead, we will discuss three approaches that are commonly used to determine the R-H bond energies of *gas phase*[4] polyatomic molecules: a) the study of radical kinetics, b) the use of negative ion thermochemical cycles, and c) photoionization mass spectroscopic techniques. It is essential to stress the *complementarity* of these three experimental methods; they are all inter-related. Our goal in this essay is to dissect each of our methods to describe how the measurements are carried out, what the limitations are, and to demonstrate by direct comparison that all give the same bond energies. An introduction to these three experimental programs is now in order.

a) Radical Kinetics

Suppose one measures the kinetics of equilibrium of a halogen atom, X, with a substrate, RH.

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

By monitoring the time dependence of [X] and [R] after flash photolysis, by atomic fluorescence, and/or resonance lamp photoionization detection, one can determine the absolute rate constants k_1 and k_{-1}. These rate constants fix the equilibrium constant, $K_{equi}(1)$, which permits one to determine $\Delta G_{rxn}(1)$, from which the enthalpy, $\Delta H_{rxn}(1)$, can be extracted. If the heats of formation ($\Delta H_f^o(RH)$, $\Delta H_f^o(X)$, and $\Delta H_f^o(XH)$) are known, $\Delta H_{rxn}(1)$ permits one to find $\Delta H_f^o(R)$ which fixes the bond energy, BDE(R-H).

b) Negative Ion Cycles

Ion chemistry can be used to deduce the gas phase acidity of a target molecule, RH. The acidity, ΔH_{acid}, is the enthalpy for the proton abstraction reaction.

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

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

$$\Delta H_{acid}(R\text{-}H) = BDE(R\text{-}H) + IP(H) - EA(R) \qquad (3)$$

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

c) Photoionization Mass Spectroscopy

By photoionization mass spectrometry (PIMS) one can measure the appearance energy [E_{AP}(R-H)] of the dissociative process: AP(R+, RH)

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

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

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

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 $\Delta H_{f,0K}$(RH) is known, $E_{AP}(R^{+}, RH)$ provides one with the heat of formation of the cation; $\Delta H_{f,0K}(R^{+}) = E_{AP}(R^{+}, RH) + \Delta H_{f,0K}(RH) - \Delta H_{f,0K}(H)$.

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 kcal/mol and ± 0.2 kcal/mol[5]. 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, 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[6].

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):

$$RH \rightarrow R + H \tag{6}$$

At 0 K the energy for process (6) is called the dissociation energy and is written[7] as D_0(R-H). This is the difference of the zero point energies:

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

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

$$H = E + pV \cong E + RT \tag{8}$$

Thus dissociation at room temperature, where most experiments are done, is properly[8] a dissociation enthalpy (which is sometimes referred to as a bond enthalpy).

$$DH_{0,298K}(R\text{-}H) \equiv \Delta H_{f,298K}(R) + \Delta H_{f,298K}(H) - \Delta H_{f,298K}(RH) \tag{9}$$

In order to relate D_0(R-H) to $DH_{0,298K}$(R-H), one makes use[9] of the integrated heat capacity.

$$DH_{0\ 298K}(R\text{-}H) = D_0(R\text{-}H) + \int_0^{298} dT\left[C_p(R) + C_p(H) - C_p(RH)\right] \tag{10}$$

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, H and R, will also be described by a Maxwell Boltzmann distribution. Equation (10) tells you that as T → 0 K, $DH_{0,T\,K}(R\text{-}H) \rightarrow D_0(R\text{-}H)$.

I. Experimental Probes of Bond Energies

A. Radical Kinetics

Studies of the kinetics of equilibria involving the reactions of halogen atoms (X = Cl, Br, I) with organic molecules R-H have been (for nearly 50 years)[10,11,12,13,14,15,16,17,18,19], 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 $\Delta H_{rxn}(1)$, obtained from E_1-E_{-1}, for the mid-temperature of the experiments is obtained directly. This is the **Second Law** method for obtaining ΔH_{rxn}. If k_1 and k_{-1} can be determined at only a single temperature (or over a very limited temperature range), $\Delta H_{rxn}(1)$ can still be obtained. In this case, the more limited kinetic information provides $K_{equi}(1) = k_1/k_{-1}$ and hence $\Delta G_{rxn}(1)$ at one temperature. $\Delta G_{rxn}(1)$ may be combined with $\Delta S_{rxn}(1)$ at the same temperature to obtain $\Delta H_{rxn}(1)$. $\Delta S_{rxn}(1)$ is obtained from calculated entropies of reactants and products using partition functions. This latter procedure for obtaining $\Delta H_{rxn}(1)$ 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 $\Delta G_{rxn}(1)$ and $\Delta H_{rxn}(1)$). 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 $\Delta H_{rxn}(1)$ and/or $\Delta G_{rxn}(1)$ are for a characteristic temperature of the experiments and are "corrected" to 298 K using tabulated or calculated heat capacities[20]. $\Delta C_{p,rxn}(1)$ is usually so small that this correction rarely is over 0.2 kcal/mol. Hence, if the Second Law method is used, $\Delta H_{rxn}(1)$ is obtained essentially directly from experiment without the need for other data or for assumptions. Since $\Delta H_f^o(RH)$, $\Delta H_f^o(X)$, and $\Delta H_f^o(HX)$ are known, $\Delta H_f^o(R)$ (and hence the BDE(R-H)) can be obtained from the experimental determination of $\Delta H_{rxn}(1)$.

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[17,21,22,23,24,25,26] and photoionization mass-spectrometry, which has been found to be extremely useful as a sensitive detector of polyatomic free radicals[27], 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 on the reverse reactions to obtain the desired thermochemical information on reaction (1)[14,15,16]. 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 $\Delta H_{rxn}(1)$, $\Delta H_{rxn}(1) = E_1(\text{measured}) - E_{-1}(\text{assumed})$[14,15]. 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 $\Delta H_{rxn}(1)$ 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[14] and by McMillen and Golden[15].

In the late-80's Gutman and coworkers 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 '88) based on measured activation energies for the R + HX reactions have generally yielded higher heats of formation (and R-H bond energies). These revised values are typically 2-4 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 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 by Tsang:[28,29] $R\text{-}H \rightleftharpoons R + H$ and $R\text{-}CH_3 \rightleftharpoons R + CH_3$. 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[19,26].

The apparatus used by Gutman and coworkers[27] to study the kinetics of R + HX reactions is shown in Fig. 1. Briefly, gas flowing through the heatable 1.05 cm 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 to 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[30,31]. 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 to 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.

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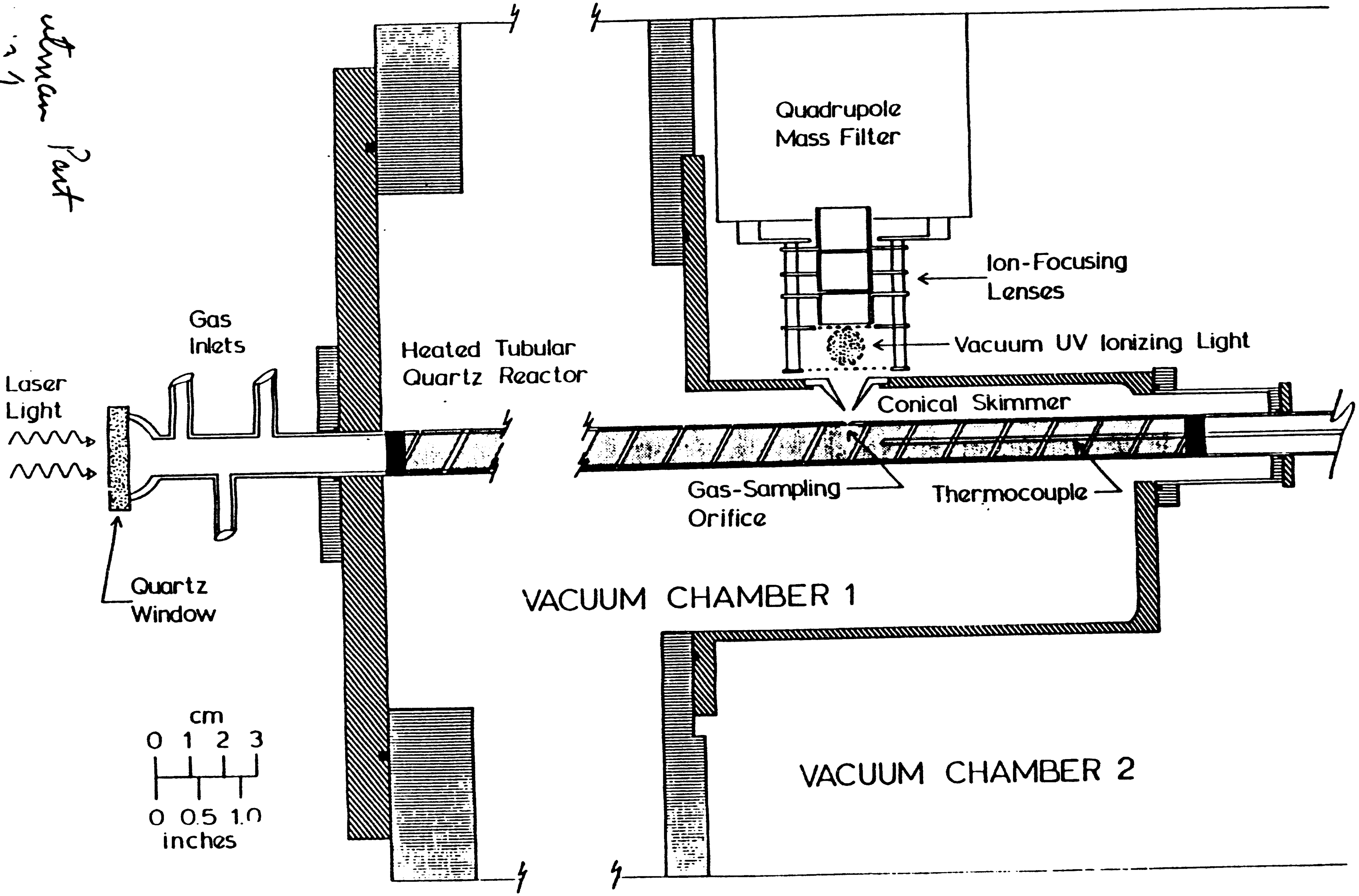
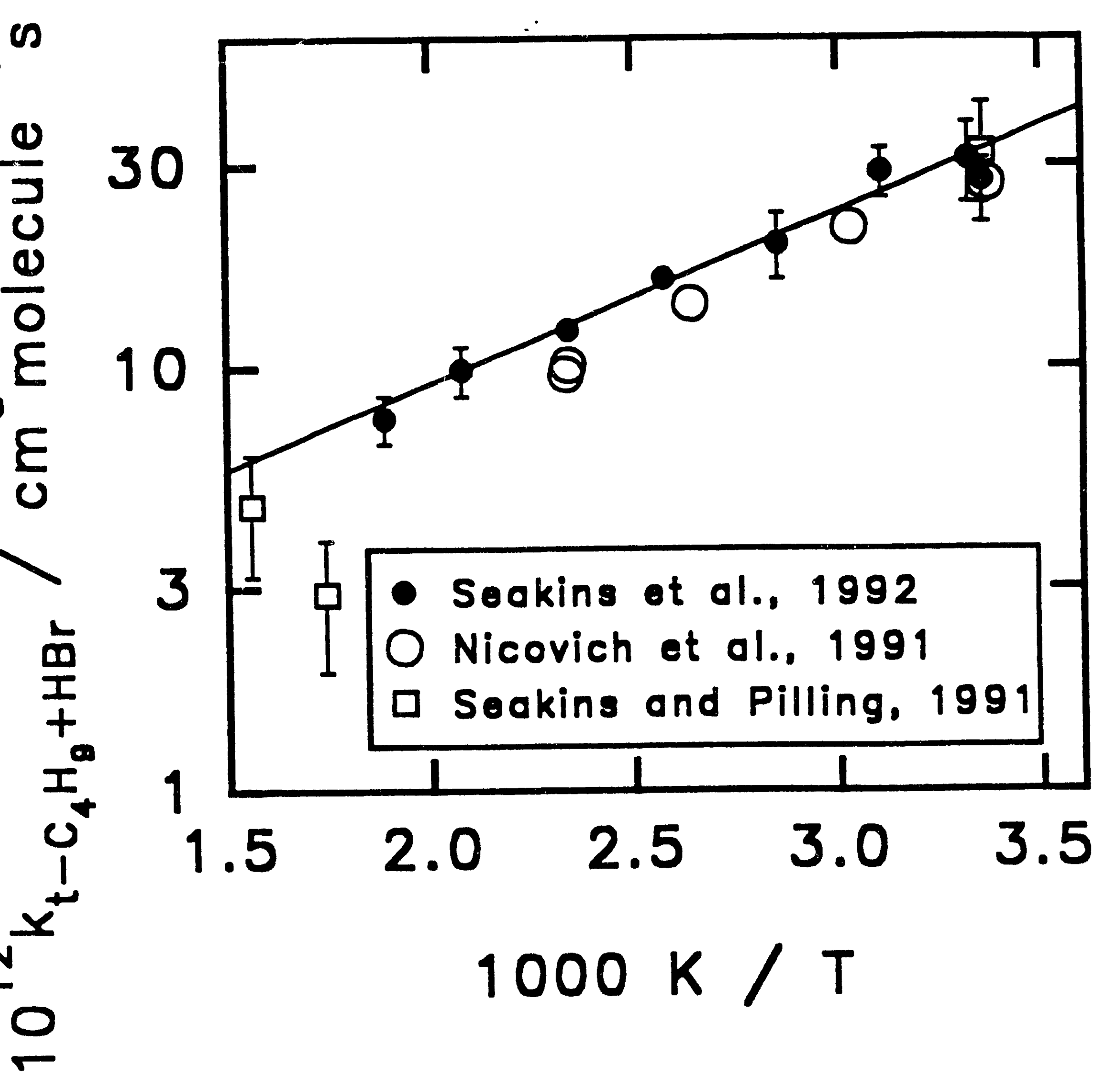
1


Quadrupole Mass Filter
Ion-Focusing Lenses
Vacuum UV Ionizing Light
Gas Inlets
Heated Tubular Quartz Reactor
Laser Light
Conical Skimmer
Gas-Sampling Orifice
Thermocouple
Quartz Window
VACUUM CHAMBER 1
VACUUM CHAMBER 2
cm
0 1 2 3
0 0.5 1.0
inches

The use of atomic resonance fluorescence to monitor the kinetics of atom-molecule reactions is well documented. Wine and coworkers[22,24,26] as well as Pilling and coworkers[21,23,25] 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 I. Both groups have extended the method to include monitoring Br formation in R + 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 Fig. 2. They include values obtained by monitoring Br-atom production using atomic fluorescence by Nicovich *et al.*.[24] and by Seakins and Pilling[23] and from monitoring $C(CH_3)_3$ radical decay using photoionization mass spectrometry by Seakins *et al.*[25]. 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. $\frac{1000K}{T}$ 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.



Gutman Part
Figure 2

In the cases 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, can be isolated for direct study, and absolute rate constants 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 $\Delta H_{rxn}(1)$ (ignoring the magnitudes of k_1 and k_{-1}) whilst the latter uses only the magnitudes of the two rate constants at a particular temperature to obtain $K_{rxn}(1)$ and $\Delta G_{rxn}(1)$ (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 I. The close agreement between the values of the two radical heats of formation obtained from these two quite different properties of the measured rate constants (differences in ΔH_f^o 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 to 0.5 kcal/mol).

The I + RH reactions are quite endothermic (typically $\Delta H_{rxn}(1)$ 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 rate of the 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 to 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[19] radicals, the silyl radical[21], (SiH_3), and the hydroxymethyl[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)[32,33], (Cl + C_2H_4)[34,35], and (Cl + CH_3OH) systems[36]. 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[37]. The forward Cl + C_2H_4 reaction is the elementary reaction involved in these three systems that was not studied directly[33], 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[38]. 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.

Dobe[36], studying Cl + CH_3OH, obtained $\Delta H_{f298}{}^{o}(CH_2OH) = -2.1 \pm 1.0$ kcal/mol (2^{nd} law) and -3.3 ± 0.5 kcal/mol (3^{rd} law). Seetula and Gutman[1] obtained -2.2 ± 0.4 kcal/mol (Br + CH_3OH, 3^{rd} law), -2.1 ± 1.8 kcal/mol (I + CH_3OH, 2^{nd} law) and -1.9 ± 1.9 kcal/mol (I + CH_3OH), 3^{rd} law). The results appear to be in close agreement. However, Dobe used a different value for $S_{298}(\dot{C}H_2OH)$ than did Seetula and Gutman. The latter selected $S_{300}(CH_2OH) = 61.08$ cal/mol•deg given by Tsang[39], and based upon free rotation about the C-O bond. The value used by Dobe is based on expressions given by Burcat[40], which assume hindered rotation. From these expressions, we calculate $S_{298}(CH_2OH) = 57.88$ cal /mol•deg. Since there is strong evidence that CH_2OH is a hindered rotor, the entropy used by Dobe is expected to be more nearly correct. (We calculate $S_{298}(CH_2OH) = 58.71$ cal/mol•deg, using the most recently available information [41] on the structure, vibrational frequencies and barrier to rotation of CH_2OH). When we apply our entropy for CH_2OH to the Br + CH_3OH, 3^{rd} law determination of Seetula and Gutman, we obtain $\Delta H_{f298}{}^{o}(CH_2OH) = -2.9 \pm 0.4$ kcal/mol, close to the 3^{rd} law result for the Cl + CH_3OH reaction, -3.3 ± 0.5 kcal/mol. From these latter values, we can deduce $DH_{0,298K}(H\text{-}CH_2OH) = 97.2 \pm 0.4$ kcal/mol (Seetula and Gutman), and 96.8 ± 0.5 kcal/mol (Dobe), in good agreement with the AP/IP combination of $D_0(H\text{-}CH_2OH) = 95.0 \pm 0.7$ kcal/mol obtained from PIMS (see §C below).

B. Negative Ion Cycles

Rather than attempt the direct measurement of a bond energy, $D_0(R\text{-}H)$, an alternative method is to embed the BDE in a negative ion thermochemical cycle. This cycle, eq. (3), involves the acidity of RH [$\Delta H_{acid}(R\text{-}H)$], the electron affinity of R, [EA(R)] and the ionization potential[42] of H atom [IP(H)]. The strategy is to measure $\Delta H_{acid}(R\text{-}H)$ 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 ΔH_{acid}(R-H) or EA(R) will propagate into BDE(R-H). Use of the acidity/EA cycle is only useful if ΔH_{acid}(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[43] to connect the acidity to the bond dissociation energy and the electron affinity of the final radical is:

$$\Delta H_{acid}(\text{R-H}) = DH_{0,298K}(\text{R-H}) + IP_{0K}(\text{H}) - EA_{0K}(\text{R}) - \text{thermal correction} \qquad (11)$$

The thermal correction is simply the proper integrated heat capacities,

$$\text{Thermal corr'n} = \int_0^{298} dT \left[C_p(\text{R}) - C_p(\text{R}^-) + C_p(\text{H}) - C_p(\text{H}^+) \right] \qquad (12)$$

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[44]; consequently it is standard procedure in (11) to simply equate ΔH_{acid}(R-H) with $\{DH_{0,298K}(\text{R-H}) + IP(\text{H}) - EA(\text{R})\}$.

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, $\Delta H_{acid}(\text{R-H}) \cong 100 + 313 - 23$ or 390 kcal/mol. For example some representative acidities (out of several hundred examples)[45] are:

	Molecule	ΔH_{acid} (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 $DH_{0,298K}$(R-H), one needs separate measurements of (1) the acidity and (2) the electron affinity.

1. Gas Phase Acidities

The acidity[46], ΔH_{acid}, is the enthalpy for the proton abstraction reaction, eq (2) and most often is measured in ICR spectrometers[47] or flowing afterglow devices[48]. We will discuss several ways to find ΔH_{acid}(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.[49]

(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[50] than any acidity measurements; some of these are collected together in Table II. Consequently the acidities for these species are **computed** with eqs. (11) and (12) using EA(R) and $D_{0,0K}$(R-H). Table II flags these acidities with the ≡ sign. 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 ΔH_{acid}; temperature-dependent and temperature-independent measurements. Suppose one has an unknown acid, HU. A common measurement of ΔH_{acid}(H-U) 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.

$$U^- + HA \rightleftharpoons HU + A^- \tag{13}$$

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 ratios,($[A^-][HU]/[U^-][HA]$).

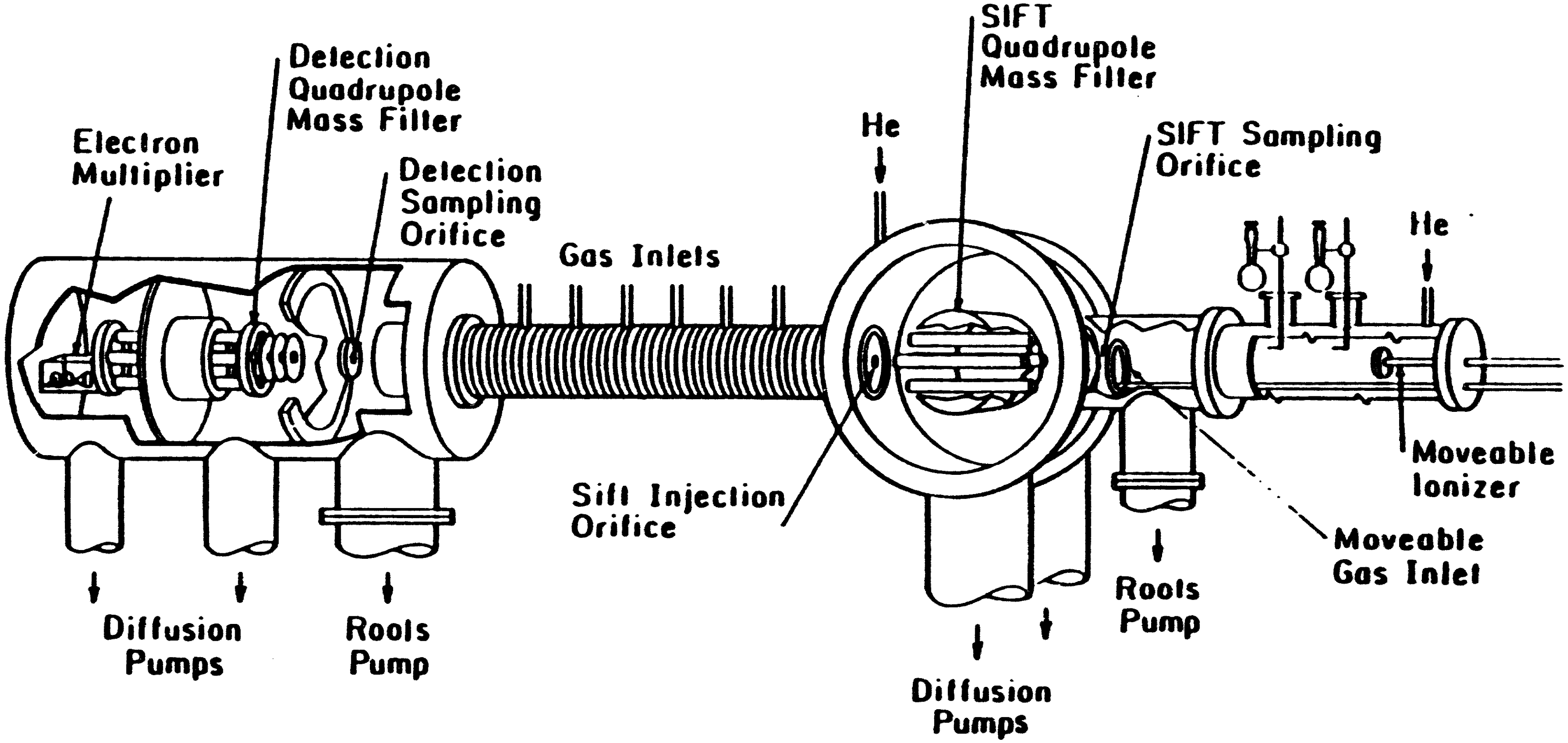
$$K_{13} = \frac{k_{13}}{k_{-13}} = \frac{[A^-][HU]}{[U^-][HA]} = e^{\frac{-\Delta G acid}{RT}} \tag{14}$$

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 HCC-H as an example.

Fig. 3 is a schematic diagram of a tandem Flowing Afterglow/Selected Ion Flow Tube[51] which can be used to study proton transfer kinetics. Consider an acidity measurement which connects the acidity of HCC-H to that of HF. From the definition (2), $\Delta G_{rxn298K}(15)$ is the difference $[\Delta G_{acid298K}(HCCH) - \Delta G_{acid298K}(HF)]$.

$$F^- + HCCH \rightleftharpoons HF + HCC^- \tag{15}$$

The acidity of HCCH was studied[37] 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.


Detection Quadrupole Mass Filter
Electron Multiplier
Detection Sampling Orifice
Gas Inlets
He
SIFT Quadrupole Mass Filter
SIFT Sampling Orifice
He
Moveable Ionizer
Sift Injection Orifice
Moveable Gas Inlet
Diffusion Pumps
Roots Pump
Diffusion Pumps
Roots Pump

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 Fig. 3 and this permits a simple determination of the ion-molecule kinetic rate constant.

The resulting bimolecular rate constants were found to be $k_{15} = 1.0\ (\pm 0.3)\times10^{-12}$ cm^3 sec^{-1} and $k_{-15} = 1.3\ (\pm 0.2)\times10^{-9}$ cm^3 sec^{-1}. The ratio of these rate constants is the equilibrium constant, $K_{equi}(15) = k_{15}/k_{-15}$ or 0.0008 ± 0.0003. The equilibrium constant yields the free energy, $\Delta G_{rxn298K}(15) = 4.2 \pm 0.2$ kcal/mol. The free energy change for (15) can be expressed in terms of the gas phase acidities: $\Delta G_{rxn298K}(15) = \Delta G_{acid298K}(\mathrm{HCCH}) - \Delta G_{acid298K}(\mathrm{HF})$. So if the acidity of HF can be established as an anchor, $K_{equi}(15)$ will yield the acidity of HCCH, $\Delta G_{acid298K}(\mathrm{HCCH})$.

As mentioned earlier in §1(a), the gas phase acidity of HF has been established by using the precise values of $DH_{0,298K}(\mathrm{HF})$, IP(H), EA(F) in eq(11). $D_0(\mathrm{HF})$ is known[52] to be 135.2 ± 0.2 kcal/mol and the electron affinity[53] of fluorine atom is EA(F) = 3.401 190 ± 0.000 004 eV; consequently $\Delta H_{acid,0K}(\mathrm{HF}) = 370.5 \pm 0.2$ kcal/mol. If the appropriate heat capacity corrections are applied, one finds $\Delta H_{acid,298K}(\mathrm{HF}) = 371.4 \pm 0.2$ kcal/mol [see Table II]; entropies of H^+, F^-, and HF lead to $\Delta S_{acid,298K}(\mathrm{HF}) = 19.30 \pm 0.01$ cal/mol•K so eq.(11) leads to $\Delta G_{acid,298K}(\mathrm{HF}) = 365.6 \pm 0.2$ kcal/mol. Consequently we see that $\Delta G_{rxn298K}(15) = 4.2 \pm 0.2$ kcal/mol implies that $\Delta G_{acid298K}(\mathrm{HCC\text{-}H}) = 369.8 \pm 0.3$ kcal/mol. We desire $\Delta H_{acid298K}(\mathrm{HCC\text{-}H})$ so we have a final entropic correction to make; we need $\Delta S_{acid298K}(\mathrm{HCC\text{-}H})$. This is found[54] to be $\Delta S_{acid298K}(\mathrm{HCC\text{-}H}) = 26.8$ cal/mol•K, and finally[55] we are led to $\Delta H_{acid298K}(\mathrm{HCC\text{-}H}) = 369.9 \pm 0.3 + (298)(0.0268) = 377.8 \pm 0.6$ 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 II). 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[56] to be greater than CH_3CN (373 kcal/mol) and less than CH_3NO_2 (356 kcal/mol).

$CH_2CO + NH_2^- \rightarrow HCCO^- + NH_3$ (fast) (16a)
$CH_2CO + CH_3O^- \rightarrow HCCO^- + CH_3OH$ (fast) (16b)
$CH_2CO + CH_2CN^- \rightarrow HCCO^- + CH_3CN$ (fast) (16c)
$CH_2CO + CH_3COCH_2^- \rightarrow HCCO^- + CH_3COCH_3$ (equ'l'n) (16d)
$CH_2CO + CH_2CHO^- \rightarrow HCCO^- + CH_3CHO$ (equ'l'n) (16e)
$CH_2CO + CF_3CH_2O^- \rightarrow HCCO^- + CF_3CH_2OH$ (slow) (16f)
$CH_2CO + CH_2NO_2^- \rightarrow HCCO^- + CH_3NO_2$ (no rxn) (16g)

The equilibrium (16e) was studied in detail. Measurement of the proton transfer rates (k_{16e} and k_{-16e}) lead to $K_{equi}(16e) = 6.8$ which corresponds to $\Delta G_{rxn298K}(16e) = -1.1 \pm 0.2$ kcal/mol. Now $\Delta G_{rxn298K}(16e) = [\Delta G_{acid}(CH_2CO) - \Delta G_{acid}(H\text{-}CH_2CHO)]$ so[57] $\Delta G_{acid}(CH_2CO) = 357.9 \pm 2.2$ kcal/mol. To extract the enthalpy, one has to compute $\Delta S_{acid}(CH_2CO)$ and finds[58] a value of 23.6 ± 2.2 cal/mol•K. Consequently the acidity we seek, $\Delta H_{acid}(CH_2CO)$, is 364.8 ± 2.1 kcal/mol.

A word about uncertainties. 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[59] to an uncertainty of about ± 0.2 kcal/mol. In order to account for errors in anchoring the *entire* acidity scale, one has to include an additional ± 2 kcal/mol to the error bar. Converting ΔG_{acid} to ΔH_{acid} implies an additional uncertainty ($T\delta(\Delta S)$) of ± 0.6 kcal/mol. Consequently the final uncertainty in a typical acidity measurement[60] swells to $\pm \{0.2^2 + 2^2 + 0.6^2\}^{1/2}$ or ± 2.1

kcal/mol[61]. Unless great care is taken to tie the unknown acid, HU, to one of the primary anchors, the resulting acidity $\Delta H_{acid}(HU)$ 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^-, with 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[62] 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 (3rd law) method described above in (13) is to study the *temperature dependence* of the equilibrium (2nd law) in a pulsed electron beam mass spectrometer[63]. 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[64].

$$HO^- + CH_3OH \rightleftharpoons H_2O + CH_3O^- \tag{17}$$

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

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

Since $K_{equi}(T)$ and $\Delta G_{rxn}(17)$ are related, one can use:

$$\ln K_{equi}(T) = \frac{-\Delta H_{rxn}}{RT} + \frac{\Delta S_{rxn}}{R} \tag{19}$$

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

(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 methyleneimine, CH_2NH. One[65] can measure k_{20} but since CH_2NH is not an available reagent, k_{-20} cannot be found.

$$CH_2N^- + HA \rightarrow CH_2NH + A^- \qquad (20)$$

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

As a specific example[37], consider the vinylidene anion, H_2CC^-. If one prepares the H_2CC^- ion in a SIFT, one rapidly sees that the acidity is somewhere between water and

$$H_2CC^- + H_2O \rightarrow H_2CCH + HO^- \qquad (21a)$$

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

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/sec. 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); $k_{-21a} \equiv 1.4 \times 10^{-9}$ cm^3/sec. So $K_{21a} \leq 0.003$ and $\Delta G_{21a} \geq 3.5$ kcal/mol. From the acidity of water, this implies $\Delta G_{acid}(H_2CC\text{-}H) \leq 380.4 \pm 0.3$ 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/sec and k_{-21b} could not be measured. Consequently $\Delta G_{acid}(H_2CC\text{-}H)$ is greater than that of methanol[66], so $\Delta G_{acid}(H_2CC\text{-}H) \geq 375.1 \pm 0.6$ kcal/mol.

What is the bottom line? $\Delta G_{acid}(H_2CC\text{-}H)$ is estimated by splitting the difference between water and methanol; $\Delta G_{acid}(H_2CC\text{-}H) = 377.6 \pm 3.1$ kcal/mol. If we estimate that

$\Delta S_{acid}(H_2CC\text{-}H) \cong S_{298}(H^+) = 26 \pm 4$ cal/mole•K, one finally computes the acidity of the vinyl radical[67], $\Delta H_{acid}(H_2CC\text{-}H) = 385 \pm 3$ 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.

$$RH + h\nu_{Thresh} \rightarrow R^- + H^+ \tag{22}$$

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[68]. 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 pair potentials are listed in Table III. These thresholds are just the gas phase acidities at 0 K; consequently $\Delta H_{acid\ 0K}(RH)$ and $\Delta H_{acid\ 298K}(RH)$ are tabulated for comparison to Table II and the agreement is good.

(e) Recent progress in mass spectroscopy[69] has demonstrated the fact that collision-induced dissociation of proton bound dimer ions, $[U{\bullet}HA]^-$, reflects the relative acidities of the product acids. The ratio of product CID ions, U^-/A^-,

$$[U{\bullet}HA]^- + \mathrm{CID} \begin{cases} \xrightarrow{k_{HA}} U^- + HA \\ \xrightarrow{k_{HU}} A^- + HU \end{cases} \tag{23}$$

reflects only the difference in acidity, $\Delta G_{acid}(HU)$ and $\Delta G_{acid}(HA)$. 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[70], it is claimed that:

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

Such a CID approach may become an important avenue to secure thermochemical parameters for ultra-trace samples, or molecules with high molecular weights, 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[71] by CID studies of the cluster ions such as, $[CH_3CH_2O^-{\bullet}\ HOCD_2CD_3]$. 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, $C_2H_5O^-$.

$$(< 50\%)\ C_2H_5OH + C_2D_5O^- \leftarrow [C_2H_5O^- \bullet HOC_2D_5] \rightarrow (> 50\%)\ C_2H_5O^- + C_2D_5OH \quad (25)$$

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: $\Delta H_{acid}(CH_3CD_2O\text{-}H) = 377.85 \pm 0.15$ kcal/mol, $\Delta H_{acid}(CD_3CH_2O\text{-}H) = 377.70 \pm 0.15$ kcal/mol, and $\Delta H_{acid}(CD_3CD_2O\text{-}H) = 378.00 \pm 0.15$ 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, $[U \bullet HA]^-$, have similar acidities, $\Delta G_{acid}(HA) \cong \Delta G_{acid}(HU)$.

2. Electron Affinities

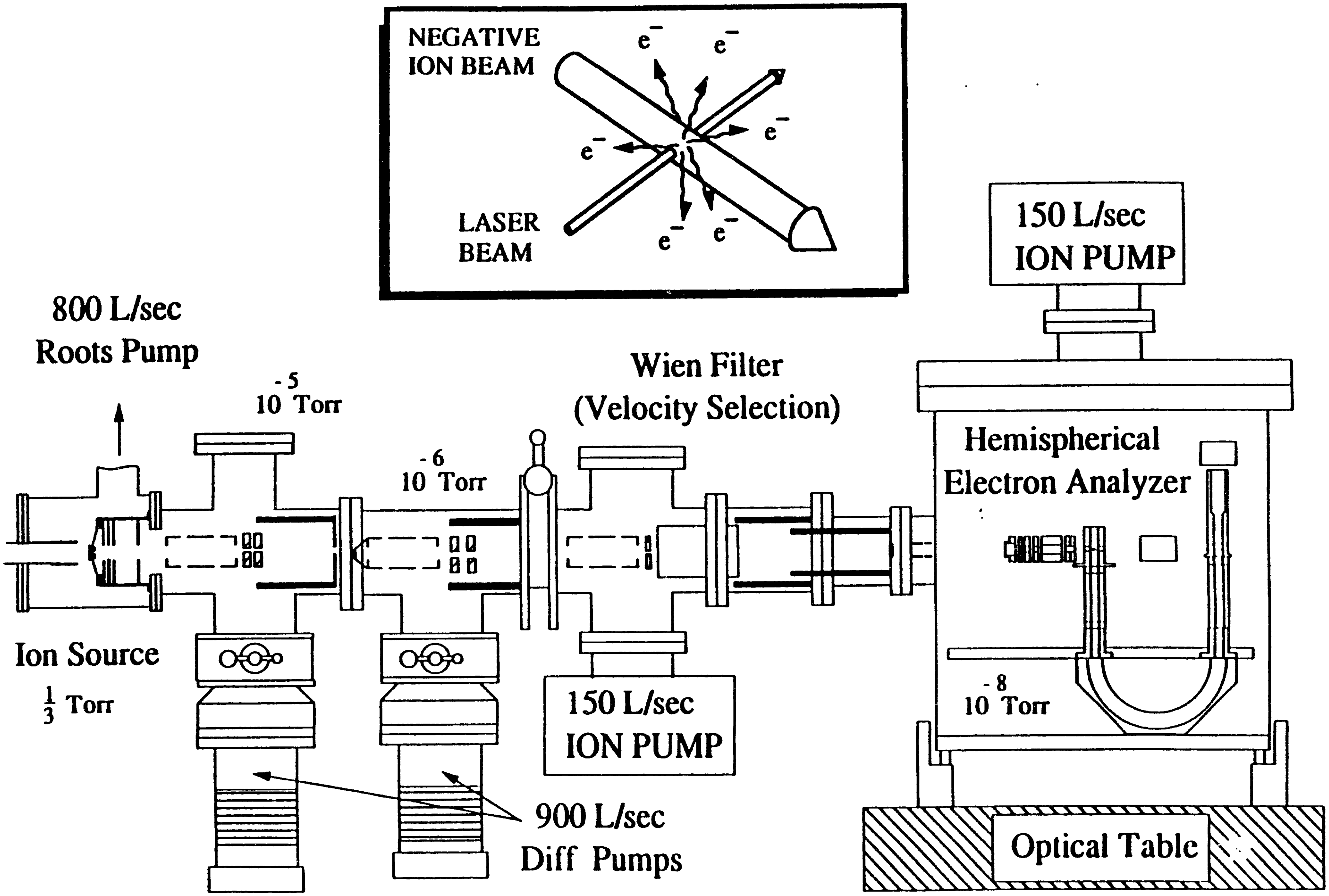
In a separate experiment, the electron affinity of radical R can be measured. Just as in the case of the acidity measurements, this is a gas phase measurement; the EA(R) is just the energy required to detach an electron.

$$R^- + h\nu \rightarrow R + e^- \quad (26)$$

There are several ways to utilize (26) to measure EA(R). A very precise method[72] is to scan the photon energy, hν, 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[73] for H^- at $6\,082.99 \pm 0.15$ cm^{-1}, corresponding to EA(H) = 0.754 195 ± 0.000 019 eV; the threshold for D^- was found to be $6\,086.2 \pm 0.6$ 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[74], the threshold for the detachment $CH_2CHO^- \rightarrow CH_2CHO$ is measured to be $\nu_{Thresh} = 14\,718^{+2}_{-5}$ cm^{-1} or EA(CH_2CHO) = 42.08 ± 0.01 kcal/mol.

Alternatively[75] one can find EA(R) by irradiating with a fixed frequency laser, $h\nu_0$, and measuring the kinetic energies of the scattered photoelectrons. Fig. 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 $\geq$ 3.5 eV) cannot be studied. In Fig. 4, the scattered photoelectrons are energy analyzed with a hemispherical electrostatic analyzer. As an example of negative ion photoelectron spectroscopy[76], 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 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[77] photodetached. Recent developments[78] 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[79].



Negative Ion Photoelectron Spectrometer

We now present a partial survey of the acidity/EA technique. Table II collects about 30 representative molecules for which the acidities, electron affinities, and bond enthalpies are available. The species *above* the solid line have their acidities **computed** from known EA(R) and $D_{0,0K}$(R-H) values; those below the line use the measured EA(R) and ΔH_{acid}(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[80] acidity for CH_2O is ΔH_{acid}(H-CHO) = 402 ± 5 kcal/mol but this value is now known to be incorrect. From the extensive, thorough studies of the photochemistry of formaldehyde[81], the bond energy is now established as D_0(H-CHO) = 86.57 ± 0.16 kcal/mol while the EA(HCO) is measured[82] to be 0.313 ± 0.005 eV. The acidity computed *via* eq (11) is ΔH_{acid}(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 I and IV. In general, it is straightforward to use these negative ion measurements to find the bond enthalpies of several hundred compounds.

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 §C. This high bond energy in Table II results from measurements of EA(CH_2CH) and ΔH_{acid}(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 our 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 roughly 0.46 eV. This was checked by searching for charge transfer to O_2 since EA(O_2) is[83] 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 0.46 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^3s^{-1} and $k_{-27} = (5.5 \pm 0.9) \times 10^{-10}$ cm^3s^{-1}]. The exceedingly slow rate, k_{27}, was independently checked by calibration with an internal HCCH standard; this cross check lead to $k_{27} = 2.6 \times 10^{-13}$ cm^3s^{-1} in good agreement with the directly determined k_{27}. The rate constants lead to $\Delta G_{rxn}(27) = 4.5 \pm 0.2$ kcal/mol. Now the gas phase acidity of ammonia anchors ethylene since $\Delta G_{rxn}(27) = \Delta G_{acid}(CH_2CH_2) - \Delta G_{acid}(NH_3)$; but Table II shows that $\Delta G_{acid}(NH_3)$ is known from PIMS studies and the EA(NH_2). All of these negative ion studies suggests that a CH bond energy of 104-105 kcal/mol is incompatible with the measured EA(CH_2CH) and $\Delta G_{acid}(CH_2CH_2)$.

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 II), one can control the uncertainties to less than 1 kcal/mol but this is not commonly done. However the range of the acidity/EA cycle is impressive. There are over 2,500 negative ions that have been prepared and studied. In a great number of cases[84], 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[85] 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[86] and are not prone to rearrangements.

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?

$$\text{H-CH}_2\text{CHO} \rightarrow \text{CH}_2\text{CHO}^- + \text{H}^+ \tag{28a}$$

$$\text{CH}_3\text{CO-H} \rightarrow \text{CH}_3\text{CO}^- + \text{H}^+ \tag{28b}$$

The acetaldehyde enolate ion, $(CH_2CHO)^-$, is the easiest to prepare by removal of the most

$$\text{HO}^- + \text{CH}_3\text{CHO} \rightarrow \text{H}_2\text{O} + (\text{CH}_2\text{CHO})^- \tag{29a}$$

acidic methyl proton. ICR studies[87] report $\Delta H_{acid}(H\text{-}CH_2CHO) = 365.8 \pm 2.2$ kcal/mol while threshold photodetachment studies[74] find $EA(CH_2CHO) = 1.8248 \pm 0.0006$ eV. These findings lead to the bond energies, $DH_{0,298K}(H\text{-}CH_2CHO) = 94.3 \pm 2.2$ kcal/mol, and $D_0(H\text{-}CH_2CHO) = 92.8 \pm 2.2$ 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.

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

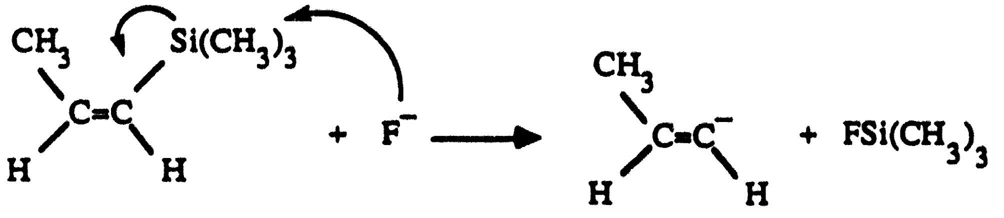
In this way the acidity of the acyl proton in acetaldehyde, (28b), has been studied. At 298 K, the acidity has been measured in a flowing afterglow[88], $\Delta H_{acid}(CH_3CO\text{-}H) = 391.1 \pm 2.1$ kcal/mol. Likewise the electron affinity is reported[89] as $EA(CH_3CO) = 0.423 \pm 0.037$ eV; consequently use of eq (11) determines the bond energy, $DH_{0,298K}(CH_3CO\text{-}H) = 87.2 \pm 2.3$ kcal/mol. With a heat capacity correction, the bond energy becomes, $D_0(CH_3CO\text{-}H) = 85.7 \pm 2.3$ kcal/mol.

Some other pairs of isomeric ions that have been synthesized are: Acetic acid[90] $(HOOCCH_2^-, CH_3COO^-)$, Thiomethanol[91] $(HSCH_2^-, CH_3S^-)$, Formic acid[92] $(HOOC^-, HCOO^-)$, and the isomeric nitriles[93] (CH_2NC^-, CH_2CN^-). As Table II 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 $CH_2{=}CH\text{-}CH_3$ to consider; the methyl C-H and three distinct vinyl C-H bonds. As Table II shows, study of the allylic ion has furnished $D_0(CH_2CHCH_2\text{-}H) = 86.7 \pm 2.1$ kcal/mol. Since the methyl C-H is the most acidic site, the $(CH_2CHCH_2)^-$ ion is readily formed by an appropriate base.

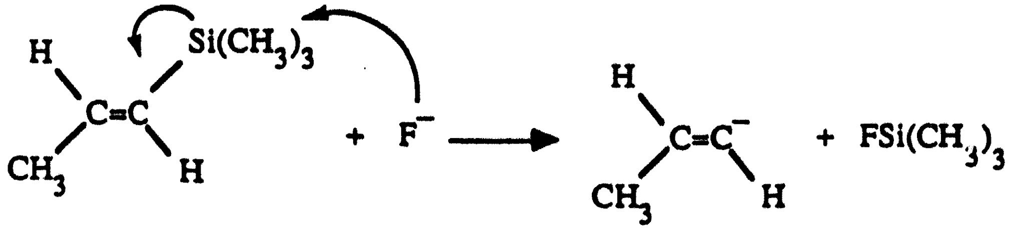
$$HO^- + H\text{-}CH_2CHCH_2 \rightleftharpoons H_2O + [CH_2CHCH_2]^- \qquad (30)$$

Using technology based on the fluorodesilylation of substituted trimethylsilanes[94], it has been possible to synthesize two *stereoisomeric* 1-propenyl anions[95].



(Z)-1-propenyl carbanion

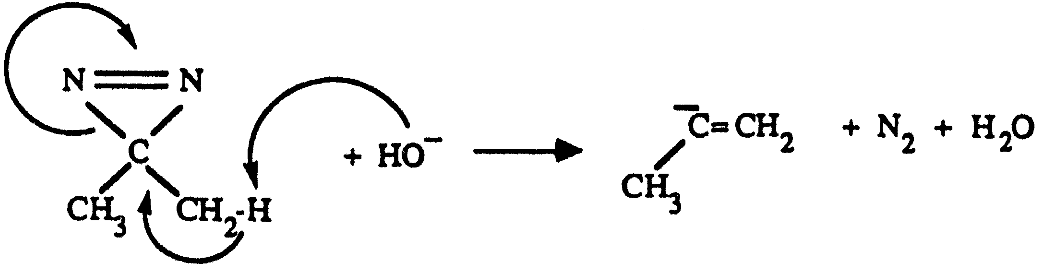
(31a)



(E)-1-propenyl carbanion

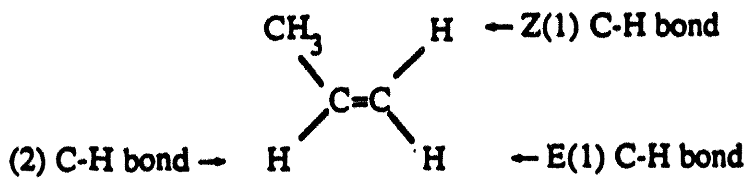
(31b)

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



(31c)

pioneered by Kass[96]. 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 radicals, 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[97] 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. As a result, an avenue is open to the thermochemical properties of the corresponding diradicals[98,99,100,101,102]: CX_2, CH_2C, C_6H_4, CHCN, and (CH_2COCH_2).

$$O^- + H_2CX_2 \rightarrow H_2O + [CX_2]^- \qquad (33a)$$
$$O^- + H_2CCH_2 \rightarrow H_2O + [CH_2C]^- \qquad (33b)$$
$$O^- + C_6H_6 \rightarrow H_2O + [C_6H_4]^- \qquad (33c)$$
$$O^- + H_3CC{\equiv}N \rightarrow H_2O + [HCCN]^- \qquad (33d)$$
$$O^- + CH_3COCH_3 \rightarrow H_2O + [CH_2COCH_2]^- \text{ and } [CH_3COCH]^- \qquad (33e)$$

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 $\Delta H_f^o(R^+)$, $\Delta H_f^o(R)$ and $D_0(R\text{-}H)$.

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:

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 ($\frac{1}{r^4}$) 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 $0 \rightarrow 0$ 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 $C_7H_7^+$ from toluene ($C_6H_5CH_3$) it may be a few tenths of an eV, which could be corrected by experiments employing longer characteristic times, but for C_{58}^+ from C_{60}, it may be[103] 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 ion optics for introduction of ions to a mass analyzer, with subsequent detection. It nis also necessary to monitor simultaneously the intensity of the VUV radiation, in order to construct a normalized photoion yield curve, i.e. normalized ion intensity as a function of photon energy, hv. Nowadays, the light source may be a) capillary discharge in H_2, He, Ar; b) synchrotron radiation; or c) a VUV 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 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[104] that, if the inherent fragment photoion yield curve is linear (i.e. if a hypothetical experiment at 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 Fig. 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 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. $HCOOH \rightarrow (^+COOH \text{ or } HCOO^+) + H$, $CH_3OH \rightarrow (^+CH_2OH \text{ or } CH_3O^+) + H$, and $CH_3SH \rightarrow (^+CH_2SH \text{ or } CH_3S^+) + H$. In these cases, the appropriate process (which corresponds to the least endothermic fragmentation) has been proven by selective deuterium substitution.

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 one order of magnitude in partial pressure of sample, compared to 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 Fig. 6. A more extensive discussion, and a list of species prepared by various means, appears elsewhere[105].

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[106] 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) = 13.5985 eV, one uses eq. (5) to obtain $D_0(HF) = 5.85 \pm 0.01$ eV. An independent experiment yielded $D_0(DF) = 5.91_2 \pm 0.005$ eV, consistent with zero point energy differences. Subsequently, Di Lonardo and Douglas[107] obtained $D_0(HF) = 5.869 \pm 0.007$ 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 3.401190 ± 0.000004 eV as the electron affinity[53] of F, and the aforementioned IP(H), one obtains $D_0(HF) \leq 5.84$ 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[108] to be 19.00 ± 0.01 eV, and hence $D_0(H\text{-}CN) = 5.40 \pm 0.01$ eV[109]. 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[110] by optogalvanic spectroscopy and reported to be 3.821 ± 0.004 eV. More recently[111] 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)

$D_0(H\text{-}C_2H_5)$

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 $\Delta H_f^\circ(C_2H_5^+)$ and the photolysis of ethyl iodide was used to accomplish just this.

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

Rosenstock *et al.*[112] 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 $\Delta H_{f0}^\circ(C_2H_5^+) = 218.8 \pm 0.5$ kcal/mol. Ruscic *et al.*[113]prepared C_2H_5 by the reaction of $F + C_2H_6$. The photoion yield curve yields $IP(C_2H_5) = 8.117 \pm 0.008$ eV. Thus, $\Delta H_{f0}^\circ(C_2H_5) = \Delta H_{f0}^\circ(C_2H_5^+) - IP(C_2H_5) = 31.6 \pm 0.5$ kcal/mol. The heats of formation of C_2H_6 ($\Delta H_{f0}^\circ = -16.3 \pm 0.1$ kcal/mol), and H ($\Delta H_{f0}^\circ = 51.634$ kcal/mol) are well established. Thus, $D_0(H\text{-}C_2H_5) = 99.5 \pm 0.5$ kcal/mol.

$D_0(H\text{-}CH_2OH)$

The AP of CH_2OH^+ from CH_3OH has been reported[114] to be 11.67 ± 0.03 eV at 0 K. 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[115] that IP (CH_2OH) = 7.549 ± 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 $CH2OH^+$. 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) = 4.12 ± 0.03 eV ≡ 95.0 ± 0.7 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[116] 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 about 1 eV higher than CH_2S^+, but rapidly overtakes it in intensity. (see Fig. 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[117] 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[118] (see Fig. 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 $D_0(H\text{-}CH_2SH) = 4.075 \pm 0.006$ eV ≡ 93.97 ± 0.14 kcal/mol. Nicovich *et al.*[26] have recently determined $\Delta H_{f0}°(CH_3S) = 31.44 \pm 0.54$ kcal/mol by kinetic studies analogous to those presented in this review. When combined with $\Delta H_{f0}°(CH_3SH) = -3.0 \pm 0.1$ kcal/mol, this leads to $D_0(CH_3S\text{-}H) = 86.1 \pm 0.6$ kcal/mol. Thus, the C-H bond is stronger than the S-H bond, by about 8 kcal/mol.

A number of R-H bonds 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 AP's (or heats of formation) of NH_2^+ and NH^+, and the corresponding IP(NH_2) and IP(NH), one can deduce $D_0(H_2N\text{-}H)$, $D_0(HN\text{-}H)$ and $D_0(N\text{-}H)$. 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 $D_0(B_2H_5\text{-}H)$, $D_0(B_2H_4\text{-}H)$, $D_0(H_3Ge\text{-}H)$, $D_0(H_3SiSiH_2\text{-}H)$, $D_0(H_2SiSiH_2\text{-}H)$, $D_0(H_2NNH\text{-}H)$ and $D_0(HNNH\text{-}H)$. The pertinent references are included in Table IV.

c. Difficult cases

$D_0(C_2H_3\text{-}H)$

While ethylene has the well-known planar, double-bonded structure, current evidence indicates that $C_2H_3^+$ has a bridged, non-classical structure, the odd proton forming a 3-membered ring with the two carbons[119]. Thus, the fragmentation reaction $C_2H_4 + h\nu \rightarrow C_2H_3^+ + H + e^-$ requires considerable rearrangement. Two high quality photoionization studies[120,121] had arrived at $AP(C_2H_3^+)$ from C_2H_4 of 13.25 ± 0.05 eV and 13.22 ± 0.02 eV, equivalent to $\Delta H_{f0}{}^o(C_2H_3^+) = 268.4 \pm 1.2$ kcal/mol and 267.8 ± 0.5 kcal/mol. However, a recent study[122] of the reaction $HCCH^+$ with hydrogen at collision energies of less than 0.5 meV concluded that $\Delta H_{f0}{}^o(C_2H_3^+) = 265^{+1.1}_{-2.1}$ 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[123] and the other by photoelectron spectroscopy[124] (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 $Hg(C_2H_3)_2$, divinyl mercury. 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 eV 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 $\Delta H_{f0}°(C_2H_3^+)$ 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 $D_0(C_2H_3\text{-}H)$. Thus, with $\Delta H_{f0}°(C_2H_3^+)$ = 267.8 kcal/mol, $D_0(C_2H_3\text{-}H) \geq 106.8 \pm 0.9$ kcal/mol, or $114.6^{+1.1}_{-4.6}$ kcal/mol. Alternatively, using $\Delta H_{f0}°(C_2H_3^+)$ = 265 kcal/mol, $D_0(C_2H_3\text{-}H) \geq 104.0 \pm 0.9$ kcal/mol 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 $D_0(C_2H_3\text{-}H) = 105.1 \pm 0.3$ kcal/mol, whereas the method based on gas phase acidity arrives at 109.7 ± 0.8 kcal/mol.

$D_0(C_6H_5\text{-}H)$

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 modelling 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 $\Delta H_{f0}°(C_6H_5^+)$, if $\Delta H_{f0}°(C_6H_5X)$ is well known. Some loss in accuracy does occur here, since $\Delta H_{f0}°(C_6H_6)$ is known to ± 0.2 kcal/mol, whereas for example, $\Delta H_{f0}°(C_6H_5I)$ has an uncertainty of ± 1.4 kcal/mol. Dannacher *et al.*[125] performed such a coincidence measurement on C_6H_5I, and inferred $\Delta H_{f0}°(C_6H_5^+) = 270.8 \pm 1.4$ kcal/mol. Malinovich and Lifshitz[126] determined the decay rate at longer times (msec as well as μsec), utilizing a cylindrical ion trap to contain the ions. Modelling of their data by quasi-equilibrium theory led to $\Delta H_{f0}°(C_6H_5^+) = 272.7 \pm 2.4$ kcal/mol.

ii) Kuhlewind *et al.*[127]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 modelling 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 $IP(C_6H_6) = 9.2459 \pm$

0.0002 eV, the AP of $C_6H_5^+$ from C_6H_6 becomes 12.90_6 eV, or $\Delta H_{f0}°(C_6H_5^+) = 270.0$ kcal/mol. Thus, an uncertainty of < 3 kcal/mol persists.

The IP (C_6H_5) was measured by Sergeev *et al.*[128] 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.*[129] 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 $^3B_1$, which is favored by Franck-Condon overlap. They consequently estimated the adiabatic IP (C_6H_5) to be 8.0 ± 0.1 eV. If we accept their interpretation, the range of IP's (8.1 ± 0.1; 8.0 ± 0.1 eV) and the range of AP's (12.906, 13.01 ± 0.10 eV) leads to a range of bond energies $D_0(C_6H_5\text{-}H)$ from 110.8 to 115.6 kcal/mol.

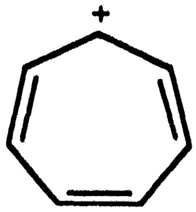
$D_0(C_6H_5CH_2\text{-}H)$

i) $\Delta H_{f0}°(C_6H_5CH_2^+)$

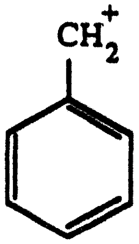
Photoion-photoelectron coincidence measurements determine the fractional abundance of parent and fragment ion as a function of photon energy. The data are often presented in a so-called breakdown diagram. Unimolecular decay theory, which involves an activation energy and the assumed entropic properties (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.*[130] 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 ion.



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 individual threshold energies for tropylium cation and benzyl cation. The latter quantity enabled them to compute $\Delta H_{f0}{}^{o}(C_6H_5CH_2{}^+)$ = 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.*[131] 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 $\Delta H_{f0}{}^{o}(C_6H_5CH_2{}^+)$ = 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.*[132] its uncertainty is ± 0.5 kcal/mol, which cannot account for the difference.

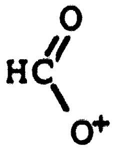
ii) IP $(C_6H_5CH_2)$

A recent experiment performed by Eiden and Weisshaar[133] 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, 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 $\Delta H_{f0}^{\circ}(C_6H_5CH_2^{+})$ from Bombach *et al.* together with IP $(C_6H_5CH_2)$ and ΔH_{f0}°(toluene), leads to $D_0(C_6H_5CH_2\text{-}H) = 90.4 \pm 2.1$ kcal/mol. With $\Delta H_{f0}^{\circ}(C_6H_5CH_2^{+})$ from Baer *et al.*, one obtains 86.6 ± 1.1 kcal/mol. For comparison, recent kinetics studies by Hippler and Troe[134] and Walker and Tsang[135] enable one to arrive at $D_0(C_6H_5CH_2\text{-}H) = 89.0 \pm 1.0$ kcal/mol, and 87.2 kcal/mol, respectively. The essential difference in the two kinetics studies is their choice of $S^{\circ}(C_6H_5CH_2)$. We have re-examined this quantity[136], availing ourselves of recently calculated *ab initio* frequencies for benzyl radical, as well as experimental ones, where possible. Our resulting $S^{\circ}(C_6H_5CH_2)$ is much closer to that of Walker and Tsang. Consequently we favor their value for $D_0(C_6H_5CH_2\text{-}H)$, which is also in good agreement with the valued based on gas phase acidity measurements, 86.8 ± 2.1 kcal/mol (see Table III).

D_0(H-COOH)

The appearance potential of $COOH^{+}$ from HCOOH has been re-investigated recently by photoion-photoelectron coincidence spectroscopy[137]. A value of 12.30 ± 0.02 eV was obtained. The structure of the m/e 45 ion was established to be:

$O{=}C{=}\overset{+}{O}H$ rather than 

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[138], PA(CO_2) = 128.5 ± 1 kcal/mol.

The products of the F + HCOOH reaction were studied by PIMS[139]. 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 step-like 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[140] 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[136] were surprised to observe two bands. The dependence of one band on the partial pressure of C_2H_2 was linear, 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[141], EA(C_2H) = 2.969 ± 0.010 eV, gives D_0(HCC-H) $\leq 5.70_6 \pm 0.02_2$ 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, hν. 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[142]. 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.

II. 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[129] make it possible to complete a huge number of separate cycles. To conclude we give some examples in Charts I, II, and III.

a) CH_4

The removal of successive hydrogen atoms from methane requires 103, 108, 101, and 80 kcal/mol respectively.[143] Thus the strongest bond is that corresponding to $D_0(H_2C\text{-}H)$. In contrast, the corresponding bond in silane and germane, $D_0(H_2Si\text{-}H)$ and $D_0(H_2Ge\text{-}H)$, is the weakest one in those sequences. This is graphically illustrated in Fig. 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 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 $D_0(H_2Si\text{-}H)$ and $D_0(H_2Ge\text{-}H)$.

b) CH_3CH_3

The C-H bond energy in ethane (99.6 ± 0.4 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 I) 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 Fig. 10.

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

III. 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 III) and the gas phase acidities (Table II) 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 $E_{AP}(R\text{-}H)$. 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 $D_0(H\text{-}CH_2OH)$ is accessible to determination by the AP/IP method, but not $D_0(CH_3O\text{-}H)$. 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 II 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.

Acknowledgement

We particularly thank Dr. W.H. Kirchhoff of the United States DOE for his series of combustion meetings which suggested this Review. GBE wishes to thank his colleagues Chuck DePuy, Veronica Bierbaum, C.J. Howard, Marin Robinson, Richard O'Hair, Michèle Krempp, Mark L. Polak, Lawrence B. Harding, and Carl Lineberger for their usual spirited comments. Special recognition to Prof. Kent M. Ervin for his consistent advice and skillful editorial help. Prof. John Bartmess has given us helpful advice about Gas Phase Acidities. The work in Boulder was supported by a grant from the Chemical Physics Program, United States Department of Energy (DE-FG02-87ER13695).

DG acknowledges support for this work from the National Science Foundation (CHE-9102038). Thanks is given to those who developed and conducted the photoionization mass spectrometry experiments discussed here: John J. Russell, Jorma A. Seetula, Paul W. Seakins, Yan Feng, Jukka T. Niiranen, and Lev N. Krasnoperov. A special thanks is given to Irene R. Slagle for her support, advice, and valuable assistance.

JB wishes to especially recognize the work of Branko Ruscic, whose labors are reflected in many of the photoionization studies reported here. We also acknowledge support by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

Table I

Second- and Third-Law Determinations of Radical Heats of Formation Based on Studies of the Kinetics of $Br + RH \rightleftharpoons R + HBr$ Equilibria

	ΔH_{f298}^{0} (kcal/mol)			
Radical	Second Law	Third Law	$DH_{0,298K}(R\text{-}H)$	Reference
CH_3	34.8 ± 0.3	34.7 ± 0.6	104.7 ± 0.3	144,32,33
CH_3CH_2	29.1 ± 0.4	29.2 ± 0.4	101.0 ± 0.4	25
$CH(CH_3)_2$	21.3 ± 0.3	21.6 ± 0.5	98.6 ± 0.4	25
$CH_3CHCH_2CH_3$	16.2 ± 0.7	16.1 ± 0.5	98.2 ± 0.5	25
$C(CH_3)_3$	12.3 ± 0.4	12.3 ± 0.4	96.5 ± 0.4	25
CH_2OH	—	-2.9 ± 0.4	97.2 ± 0.4	1, 145
CH_3CO	-2.5 ± 0.4	-2.4 ± 0.3	89.4 ± 0.3	146
SiH_3	48.0 ± 0.7	47.8 ± 0.6	91.8 ± 0.8	21
SH	34.0 ± 0.7	34.4 ± 0.7	91.2 ± 0.7	26
CH_3S	29.9 ± 0.4	29.7 ± 0.4	87.4 ± 0.4	26

TABLE II

Molecular Acidities & Electron Affinities

Above the solid line, ΔH_{acid}(RH) is computed from EA(R) and D_0(RH). Below the line, D(RH) is determined by EA(R) and ΔH_{acid}(RH). All values are in kcal/mol; see text for further details.

Molecule (RH)		$\Delta H_{acid,298K}$(R-H)	Electron Affinity(R)	$DH_{0,298K}$(R-H)	D_0(R-H)	Reference
H_2	≡	400.353 ± 0.002	17.392 ± 0.002	104.174 ± 0.002	103.267 ± 0.002	147
HF	≡	371.4 ± 0.2	78.433 ± 0.0001	136.3 ± 0.2	135.2 ± 0.2	148
HCl	≡	333.5 ± 0.1	83.311 ± 0.001	103.2 ± 0.1	102.2 ± 0.1	149
HBr	≡	323.5 ± 0.1	77.599 ± 0.069	87.5 ± 0.1	86.7 ± 0.1	149
HI	≡	314.3 ± 0.1	70.545 ± 0.002	71.3 ± 0.1	70.4 ± 0.1	149
H_2O	≡	390.5 ± 0.3	42.1471 ± 0.0005	119.1 ± 0.2	117.9 ± 0.3	150
CH_2O	≡	394.4 ± 0.3	7.2 ± 0.1	88.0 ± 0.2	86.6 ± 0.2	151
NH_3	≡	404.0 ± 0.3	17.8 ± 0.1	108.0 ± 0.3	106.7 ± 0.3	152
CH_4	≡	416.4 ± 0.7	1.8 ± 0.7	104.7 ± 0.2	103.2 ± 0.1	153
HCN		351.1 ± 0.5	89.1 ± 0.1	127.0 ± 0.6	125.5 ± 0.5	154
H_2S		351.1 ± 2.0	53.43 ± 0.05	90.7± 2.0	89.8 ± 2.0	155
H_2Se		350.5 ± 4.6	51.0 ± 0.7	87.9 ± 4.7	86.4 ± 4.7	156

PH_3	370.8 ± 2.0	29.3 ± 0.2	86.5 ± 2.0	85.0 ± 2.1	157
AsH_3	357.7 ± 2.0	29.3 ± 0.7	73.4 ± 2.1	72.0 ± 2.1	158
SiH_4	372.2 ± 2.0	32.4 ± 0.3	91.1 ± 2.0	89.6 ± 2.0	159
GeH_4	355.9 ± 3.6	≤ 40.1 ± 0.9	≤ 82.5 ± 3.7	≤ 81.0 ± 3.7	160
HCCH	377.8 ± 0.6	68.5 ± 0.2	132.8 ± 0.6	131.3 ± 0.6	37
CH_2CH_2	409.4 ± 0.6	15.4 ± 0.6	111.2 ± 0.8	109.7 ± 0.8	37
C_6H_6	399.4 ± 2.1	25.3 ± 0.1	111.1 ± 2.1	109.6 ± 2.1	161
CH_2CHCH_2-H	390.8 ± 2.1	10.9 ± 0.2	88.2 ± 2.1	86.7 ± 2.1	162
$C_6H_5CH_2$-H	380.8 ± 2.0	21.0 ± 0.1	88.2 ± 2.0	86.8 ± 2.1	163
H-CH_2CHO	365.8 ± 2.2	42.08 ± 0.01	94.3 ± 2.2	92.8 ± 2.2	164
CH_3CO-H	391.1 ± 2.1	9.8 ± 0.9	87.2 ± 2.3	85.7 ± 2.3	165
CH_2CO	364.8 ± 2.1	54.2 ± 0.5	105.4 ± 2.1	104.0 ± 2.2	166
CH_3O-H	381.5 ± 0.4	36.2 ± 0.5	104.2 ± 0.7	102.7 ± 0.8	167
CH_3CH_2O-H	377.4 ± 2.0	39.5 ± 0.2	103.3 ± 2.0	101.8 ± 2.1	168
CH_3S-H	356.9 ± 2.2	43.1 ± 0.3	86.4 ± 2.2	84.9 ± 2.2	169
H-CH_2SH	394 ± 3	$HSCH_2^-$ has never been photodetached			170
CH_3CN	372.9 ± 2.1	35.6 ± 0.3	94.8 ± 2.1	93.3 ± 2.1	171

CH_3NC	380.0 ± 2.0	24.4 ± 0.6	91.0 ± 2.1	89.5 ± 2.1	172
HCOO-H	345.3 ± 2.2	$HCOO^-$ has never been photodetached			173
H-COOH	^-COOH acidity could not be determined				174
CH_3COO-H	341.5 ± 3.0	CH_3COO^- has never been photodetached			175
H-CH_2COOH	368.1 ± 3.1	$HOOCCH_2^-$ has never been photodetached			176
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				

Table III

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

Molecule	Ion-pair Threshold/eV	$\Delta H_{acid\ 0K}$(RH)/kcal mol^{-1}	$\Delta H_{acid\ 298K}$(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

Table IV

Photoionization Appearance Potentials and Radical Ionization Potentials

Molecule	$AP[R^+ \leftarrow (RH)]$ /eV	IP(R) /eV	D_0(R-H) /kcal mol^{-1}	Ref.
HF	$H^+ = 19.42 \pm 0.01$	13.5985	134.8 ± 0.2	177
HO-H	$OH^+ = 18.11 \pm 0.01$	13.01 ± 0.01	117.6 ± 0.3	178, 179
H_2N-H	$NH_2^+ = 15.768 \pm 0.004$	11.14 ± 0.01	106.7 ± 0.3	180, 181
HN-H	$NH^+ = 17.440 \pm 0.005$	13.49 ± 0.01	91.0 ± 0.5	178, 182
H_3C-H	$CH_3^+ = 14.320 \pm 0.004.$	9.843 ± 0.002	103.2 ± 0.1	183, 184
H_2C-H	$CH_2^+ = 15.09 \pm 0.03$	10.396 ± 0.003	108.2 ± 0.7	185, 181
C_2H_5-H	$\Delta H_{f0}°(C_2H_5^+) = 218.8 \pm 0.5$ kcal/mol	8.117 ± 0.008	99.5 ± 0.5	186, 187
C_2H_3-H	$C_2H_3^+ = 13.22 \pm 0.02$	$\leq 8.59 \pm 0.3$	≥ 106.8	188, 189
	$\Delta H_{f0}°(C_2H_3^+) = 256^{+1}_{-2}$ kcal/mol	$8.25^{+0.20}_{-0.05}$	$111.8^{+1.1}_{-4.6}$	190, 191
$HOCH_2$-H	$CH_2OH^+ = 11.67 \pm 0.03$	7.549 ± 0.006	95.0 ± 0.7	192, 193
H-CO_2H	$^+COOH = 12.30 \pm 0.02$	$\leq 8.48 \pm 0.012$ (8.20)	≥ 88 (94.5)	194,195

$HSCH_2$-H	$CH_2SH^+ = 11.611 \pm 0.005$	7.536 ± 0.003	93.97 ± 0.14	196, 197
H-CHO	$HCO^+ = 11.92 \pm 0.01$	8.14 ± 0.04	87.2 ± 0.9	198, 199
H-CHS	$HCS^+ = 11.46 \pm 0.016$	$\leq 7.499 \pm 0.005$	$\geq 91.3 \pm 0.4$	200
		(7.412 ± 0.007)	(93.3 ± 0.4)	
H-C_6H_5	$C_6H_5{}^+ = 12.90_6$	8.1 ± 0.1	110.8 - 115.6	201, 202
	$= 13.01 \pm 0.10$	8.0 ± 0.1		203, 204
$C_6H_5CH_2$-H	$C_6H_5CH_2{}^+ = 11.17 \pm 0.10$	7.2487 ± 0.006	90.4 ± 2.3	205, 206
	$\Delta H_{f0}{}^{\circ}(C_6H_5CH_2{}^+) = 219.\ 6 \pm 1.2$		86.6 ± 1.2	207
H_2P-H	$PH_2{}^+ = 13.40 \pm 0.02$	9.824 ± 0.002	82.46 ± 0.46	208
HP-H	$PH^+ (PH_3) = 12.492 \pm 0.005$	10.149 ± 0.008	74.8 ± 0.5	202, 209
H_2As-H	$AsH_2{}^+ = 12.69 \pm 0.01$	9.443 ± 0.007	74.9 ± 0.2	210
HAs-H	$AsH^+ (AsH_3) = 11.295 \pm 0.005$	9.641 ± 0.008	66.5 ± 0.3	210
HSe-H	$SeH^+ = 13.266 \pm 0.007$	9.845 ± 0.003	78.89 ± 0.18	211
Se-H	$Se^+ (H_2Se) = 11.916 \pm 0.006$	9.7525	74.27 ± 0.23	211,212
H_3Si-H	$SiH_3{}^+ \leq 12.086 \pm 0.020$	$8.135^{+0.005}_{-0.002}$	$\leq 91.1 \pm 0.05$	213,214
H_2Si-H	$SiH_2{}^+ (SiH_4) = 11.54 \pm 0.01$	9.15 ± 0.02	$\geq 67.3 \pm 0.5$	214, 215

HSi-H			75.6 ± 1.4	214
Si-H			68.7 ± 0.7	214
H_3Ge-H	$GeH_3^+ \leq 11.657 \pm 0.01$	$\leq 7.94_8 \pm 0.005$	< 85.5 (82 ± 2)	216
B_2H_5-H	$B_2H_5^+ \leq 11.40 \pm 0.05$	$(\geq 6.94_5)$	≤ 102.7	217
B_2H_4-H	$B_2H_4^+$ (H2) $\leq 11.415 \pm 0.04$	9.70 ± 0.02	≅ 40.1	218
Si_2H_5-H	$Si_2H_5^+ \leq 11.59 \pm 0.02$ (11.41 ± 0.03)	7.60 ± 0.05	< 92.0 (87.9 ± 1.3)	219, 220
Si_2H_4-H	$Si_2H_4^+$ (Si_2H_6) $\leq 10.04 \pm 0.02$	8.09 ± 0.03	(60.4 ± 1.5)	212,213
N_2H_3-H	$N_2H_3^+ = 11.112 \pm 0.01_0$	7.61 ± 0.01	80.8 ± 0.3	181, 221
N_2H_2-H			43.8 ± 1.1	221

TABLE V

Recommended Bond Energies & Heats of Formation/kcal mol^{-1}

Molecule (RH)	$\Delta H_{f298}{}^{o}(R)$	$DH_{298}(R\text{-}H)$	$\Delta H_{f0}{}^{o}(R)$	$D_o(R\text{-}H)$	Ref
H_2	52.103 ± 0.001	104.174 ± 0.002	51.634 ± 0.001	103.267 ± 0.002	147
HF	18.97 ± 0.07	136.3 ± 0.2	18.47 ± 0.07	135.2 ± 0.2	148
HCl	28.992 ± 0.001	103.2 ± 0.1	28.590 ± 0.001	102.2 ± 0.1	149
HBr	26.74 ± 0.01	87.5 ± 0.1	28.19 ± 0.01	86.7 ± 0.1	149
HI	25.52 ± 0.01	71.3 ± 0.1	25.61 ± 0.01	70.4 ± 0.1	149
H_2O	9.3 ± 0.3	119.1 ± 0.3	9.2 ± 0.3	117.9 ± 0.3	150
H_2CO	10.0 ± 0.2	88.04 ± 0.22	9.99 ± 0.19	86.57 ± 0.16	151
NH_3	45.5 ± 1.5	108.0 ± 0.3	46.2 ± 1.5	106.7 ± 0.3	152
CH_4	34.7 ± 0.3	104.7 ± 0.3	35.7 ± 0.1	103.24 ± 0.12	153
HCN	107.2 ± 2.1	127.0 ± 0.6	106.3 ± 2.1	125.5 ± 0.5	154
H_2S	34.18 ± 0.68	91.2 ± 0.7	34.07 ± 0.72	89.9 ± 0.7	26
H_2Se	35.4 ± 0.4	80.4 ± 0.4	34.8 ± 0.3	78.89 ± 0.18	178

PH_3	37.3 ± 0.6	83.9 ± 0.5	37.7 ± 0.6	82.46 ± 0.46	205
AsH_3	40.2 ± 0.4	76.4 ± 0.4	40.5 ± 0.2	74.9 ± 0.2	207
SiH_4	47.9 ± 0.6	91.8 ± 0.8	≤ 49.5 ± 0.5	≤ 91.1 ± 0.05	21,132,209,110
GeH_4	< 56.6 ± 5	< 87.0 ± 0.5	< 52.5 ± 0.3	< 85.5 ± 0.3	212
H_2CS		≥ 92.8 ± 0.6	≤ 73.3 ± 1.0	≥ 91.3 ± 0.4	197
HCCH	135.2 ± 0.6	132.8 ± 0.6	134.3 ± 0.6	131.3 ± 0.6	37,132
H_2CCH_2	71.6 ± 0.8	111.2 ± 0.8	72.6 ± 0.8	109.7 ± 0.8	37,132
C_6H_6	78.7 ± 2.1	111.1 ± 2.1	81.9 ± 2.1	109.6 ± 2.1	132,161
CH_2CHCH_2-H	40.9 ± 2.1	88.2 ± 2.1	43.5 ± 2.1	86.7 ± 2.1	132,162
$C_6H_5CH_2$-H	48.1 ± 2.0	88.2 ± 2.0	52.5 ± 2.1	86.8 ± 2.1	132,163
H-CH_2CHO	2.5 ± 2.2	94.3 ± 2.2	3.6 ± 2.2	92.8 ± 2.2	132,164
CH_3CO-H	- 2.4 ± 0.3	89.4 ± 0.3	- 1.4 ± 0.5	87.9 ± 0.5	132,146
CH_2CO	41.9 ± 2.1	105.4 ± 2.1	41.8 ± 2.2	104.0 ± 2.2	132,166
H-CH_2OH	- 2.9 ± 0.4	97.2 ± 0.4	- 2.1 ± 0.7	95.0 ± 0.7	1,145
CH_3O-H	4.1 ± 0.7	104.2 ± 0.7	5.6 ± 0.7	102.7 ± 0.8	132,167
CH_3CH_2O-H	- 5.0 ± 2.0	103.3 ± 2.0	- 2.3 ± 2.1	101.8 ± 2.1	132,168
CH_3S-H	29.78 ± 0.44	87.35 ± 0.58	31.44 ± 0.54	86.1 ± 0.6	26

H-CH_2SH		≤ 95.4 ± 0.4	≤ 29.9 ± 0.9	≤ 94.0 ± 0.1	134,194
CH_3CN	58.1 ± 2.7	94.8 ± 2.1	58.7 ± 2.7	93.3 ± 2.1	132,171
CH_3NC	78.0 ± 2.7	91.0 ± 2.1	78.5 ± 2.7	89.5 ± 2.1	132,172
H-COOH	≥	—	≥ - 54.1 ± 0.5	≥ 88	134,136
CH_3CH_2-H	28.9 ± 0.4	101.0 ± 0.4	30.9 ± 0.5	99.5 ± 0.5	25,186,187
$CH_3CH_2CH(CH_3)$-H	16.1 ± 0.5	98.2 ± 0.5	21.9 ± 0.6	96.7 ± 0.6	25,132
$(CH_3)_2CH$-H	21.5 ± 0.4	98.6 ± 0.4	25.6 ± 0.6	97.1 ± 0.6	25,132
$(CH_3)_3C$-H	12.3 ± 0.4	96.5 ± 0.4		95.0 ± 0.6	25,132

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V, for a complete discussion of these issues. The connection between the energy at 0 K and the enthalpy at some temperature, T, is provided by equilibrium statistical mechanics. The total energy of one mole of gas (including translational as well as internal degrees of freedom) consists of the zero point energy of the gas, E_0, and $n_1, n_2, n_3, \ldots$ molecules populating levels $\varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots$ above the lowest energy.

$$E = E_0 + n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + n_4\varepsilon_4 + \ldots$$

The population, (n_i), is described by the Maxwell-Boltzmann law and one can use the partition function, Q, to write the molecular energy.

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

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

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

Assuming symmetric tops and harmonic vibrations but ignoring internal rotations, Herzberg derives explicit formulae 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})
$HC{\equiv}C\ \tilde{X}\ ^2\Sigma^+$	2.5	49.6	3600, 1840, 370, 370	1.46
$HC{\equiv}C^-\ \tilde{X}\ ^1\Sigma^+$	2.4	48.8	3200, 1800, 520, 520	1.39
$HC{\equiv}CH\ \tilde{X}\ ^1\Sigma_g^+$	2.4	48.0	3374, 1974, 3289, 612, 612, 730, 730	1.1766

55 Notice that if one just replaces $\Delta S_{acid298K}(HCC\text{-}H) \equiv [S_{298K}(HC{\equiv}C^-) + S_{298K}(H^+) - S_{298K}(HCCH)]$ by $S_{298K}(H^+)$, the approximation is reasonable. By

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explicit calculation, $\Delta S_{acid298K}(HCC\text{-}H) = 26.8$ cal/mol•K while $S_{298K}(H^+) = 26.0$ cal/mol•K.

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60 In the earlier versions of Ref. 45, the uncertainties were simply added; consequently errors of the order of ± [0.2 + 2 + 0.6] or ± 2.8 kcal/mol are listed. In later editions, the final uncertainty listed will be the smaller RMS error. Privately communicated by Prof. J.E. Bartmess (December, 1992).

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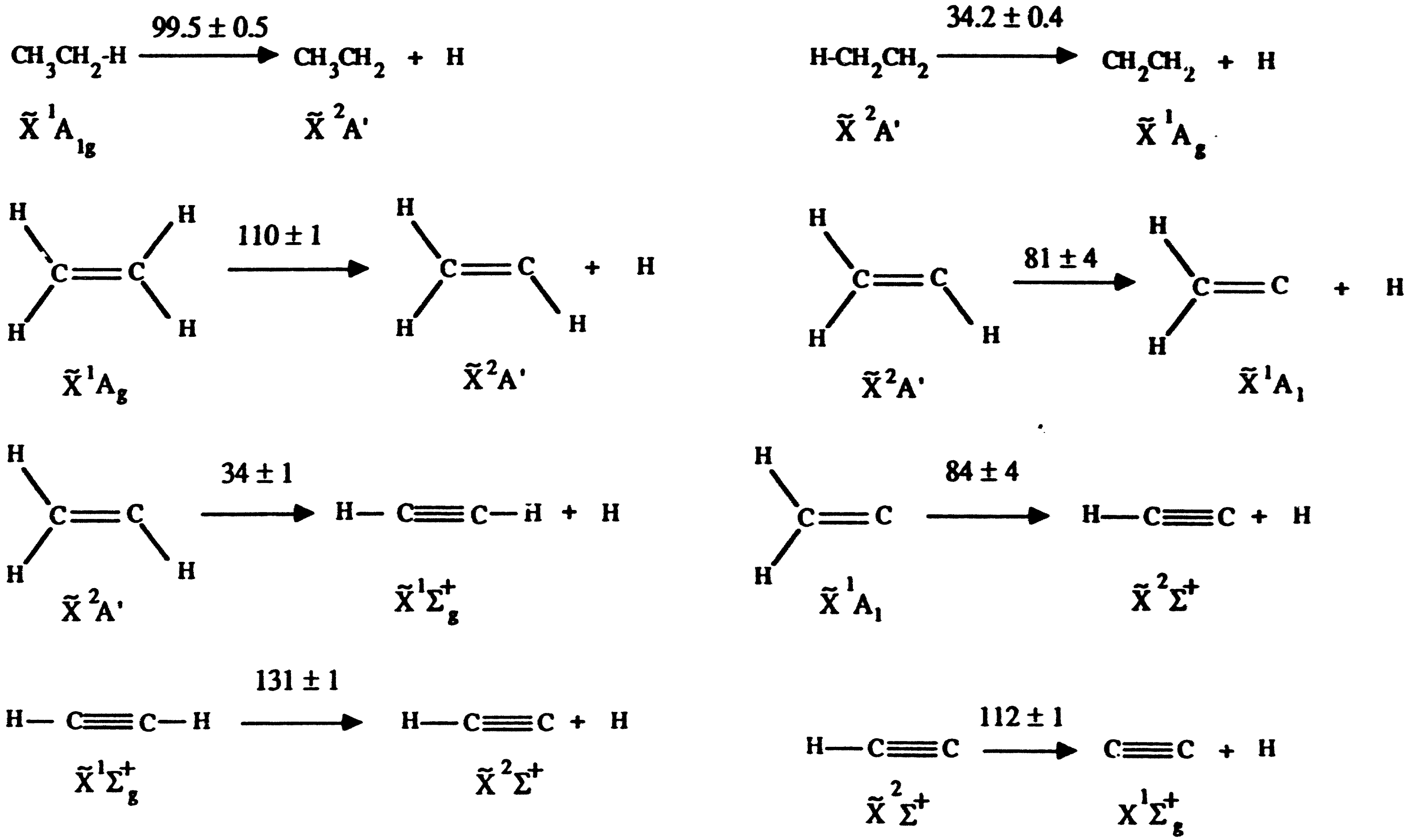
Chart I

Ethane Experimental Bond Strengths (D_o in kcal mol^{-1})



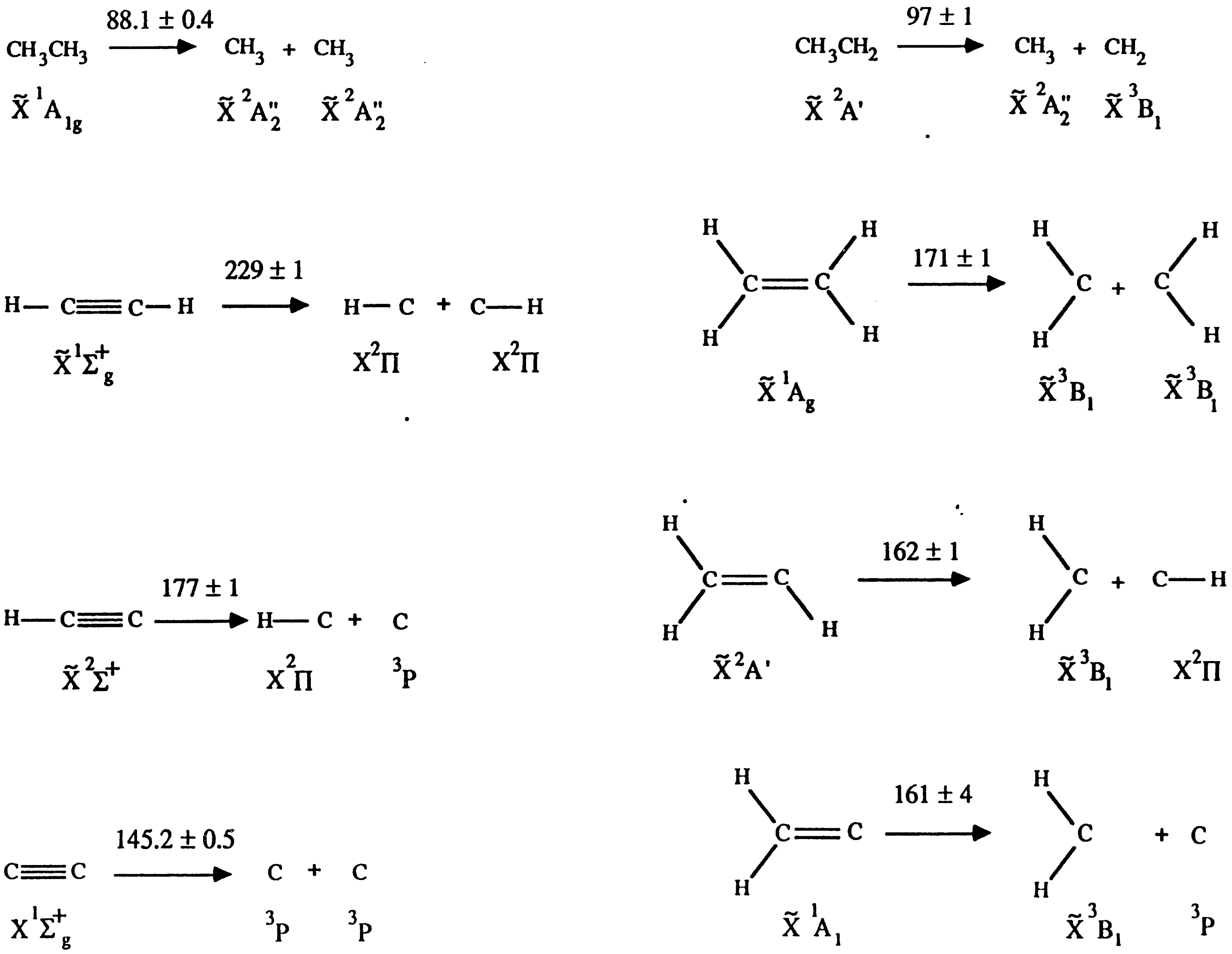
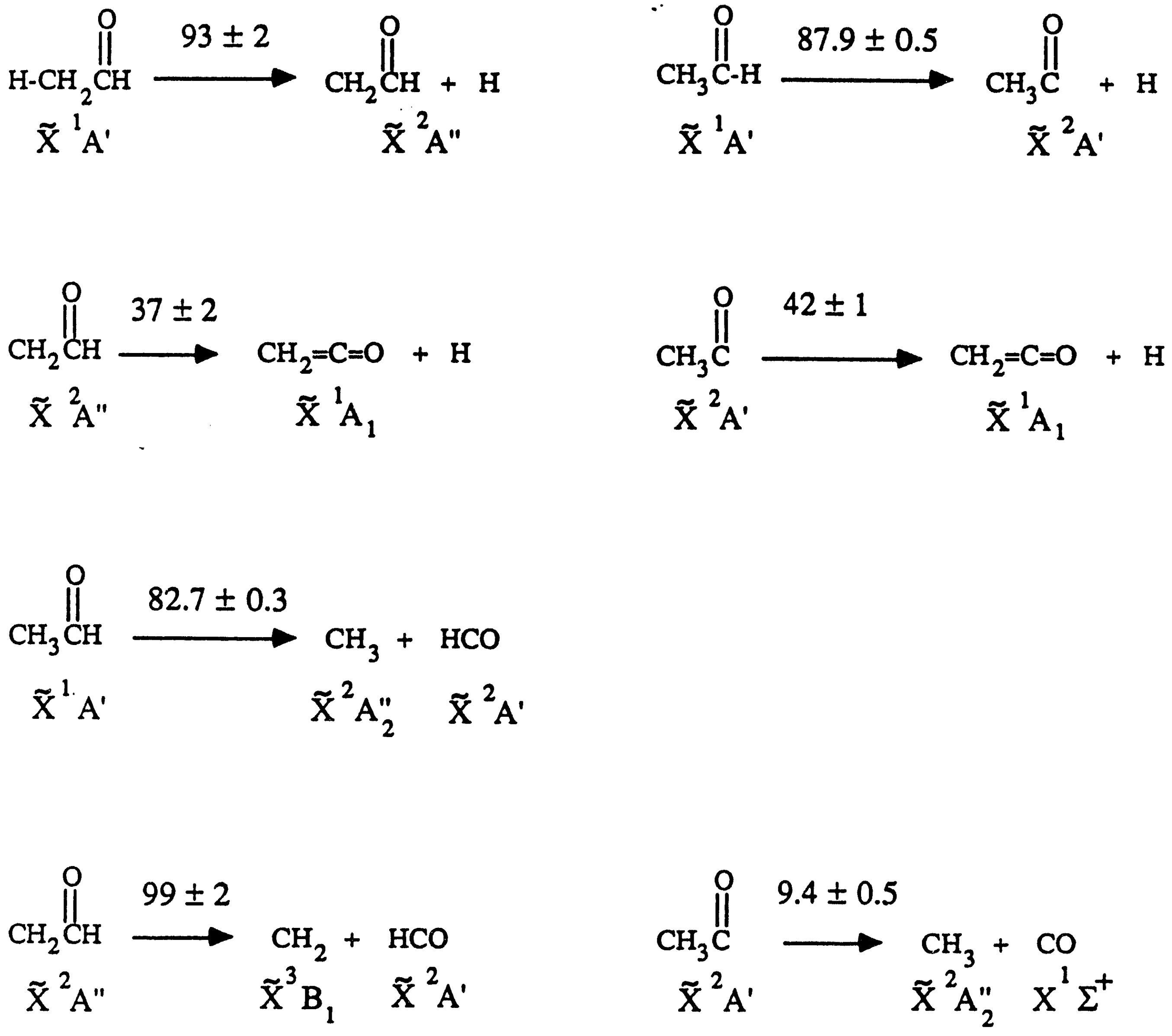

CH3CH3 → CH3 + CH3
88.1 ± 0.4
X̃ 1A1g   X̃ 2A2"   X̃ 2A2"
CH3CH2 → CH3 + CH2
97 ± 1
X̃ 2A'   X̃ 2A2"   X̃ 3B1
H—C≡C—H → H—C + C—H
229 ± 1
X̃ 1Σg+   X 2Π   X 2Π
H2C=CH2 → H2C + CH2
171 ± 1
X̃ 1Ag   X̃ 3B1   X̃ 3B1
H—C≡C → H—C + C
177 ± 1
X̃ 2Σ+   X 2Π   3P
H2C=CH → H2C + C—H
162 ± 1
X̃ 2A'   X̃ 3B1   X 2Π
C≡C → C + C
145.2 ± 0.5
X 1Σg+   3P   3P
H2C=C → H2C + C
161 ± 4
X̃ 1A1   X̃ 3B1   3P

Chart II

Acetaldehyde Experimental Bond Strengths (D_0 in kcal mol^{-1})



$$\underset{\tilde{X}\,{}^1A'}{\mathrm{H\text{-}CH_2\overset{\overset{O}{\|}}{C}H}} \xrightarrow{93 \pm 2} \underset{\tilde{X}\,{}^2A''}{\mathrm{CH_2\overset{\overset{O}{\|}}{C}H}} + \mathrm{H}$$

$$\underset{\tilde{X}\,{}^1A'}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}\text{-}H}} \xrightarrow{87.9 \pm 0.5} \underset{\tilde{X}\,{}^2A'}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}}} + \mathrm{H}$$

$$\underset{\tilde{X}\,{}^2A''}{\mathrm{CH_2\overset{\overset{O}{\|}}{C}H}} \xrightarrow{37 \pm 2} \underset{\tilde{X}\,{}^1A_1}{\mathrm{CH_2{=}C{=}O}} + \mathrm{H}$$

$$\underset{\tilde{X}\,{}^2A'}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}}} \xrightarrow{42 \pm 1} \underset{\tilde{X}\,{}^1A_1}{\mathrm{CH_2{=}C{=}O}} + \mathrm{H}$$

$$\underset{\tilde{X}\,{}^1A'}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}H}} \xrightarrow{82.7 \pm 0.3} \underset{\tilde{X}\,{}^2A_2''}{\mathrm{CH_3}} + \underset{\tilde{X}\,{}^2A'}{\mathrm{HCO}}$$

$$\underset{\tilde{X}\,{}^2A''}{\mathrm{CH_2\overset{\overset{O}{\|}}{C}H}} \xrightarrow{99 \pm 2} \underset{\tilde{X}\,{}^3B_1}{\mathrm{CH_2}} + \underset{\tilde{X}\,{}^2A'}{\mathrm{HCO}}$$

$$\underset{\tilde{X}\,{}^2A'}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}}} \xrightarrow{9.4 \pm 0.5} \underset{\tilde{X}\,{}^2A_2''}{\mathrm{CH_3}} + \underset{X\,{}^1\Sigma^+}{\mathrm{CO}}$$

Chart III

Methanol Experimental Bond Strengths (D_o in kcal mol^{-1})

$$\underset{\tilde{X}\ {}^{1}A}{CH_3OH} \xrightarrow{103 \pm 1} \underset{\tilde{X}\ {}^{2}E}{CH_3O} + H$$

$$\underset{\tilde{X}\ {}^{1}A}{CH_3SH} \xrightarrow{86.1 \pm 0.6} \underset{\tilde{X}\ {}^{2}E}{CH_3S} + H$$

$$\underset{\tilde{X}\ {}^{1}A}{H\text{-}CH_2OH} \xrightarrow{95 \pm 1} H + \underset{\tilde{X}\ {}^{2}A''}{CH_2OH}$$

$$\underset{\tilde{X}\ {}^{1}A}{H\text{-}CH_2SH} \xrightarrow{93.9 \pm 0.2} H + \underset{\tilde{X}\ {}^{2}A''}{CH_2SH}$$

$$\underset{\tilde{X}\ {}^{2}E}{CH_3O} \xrightarrow{21 \pm 1} \underset{\tilde{X}\ {}^{1}A_1}{CH_2O} + H$$

$$\underset{\tilde{X}\ {}^{2}E}{CH_3S} \xrightarrow{50 \pm 1} \underset{\tilde{X}\ {}^{1}A_1}{CH_2S} + H$$

$$\underset{\tilde{X}\,^2A''}{CH_2OH} \xrightarrow{29 \pm 1} \underset{\tilde{X}\,^1A_1}{CH_2O} + H$$

$$\underset{\tilde{X}\,^2A''}{CH_2SH} \xrightarrow{42 \pm 1} \underset{\tilde{X}\,^1A_1}{CH_2S} + H$$

$$\underset{\tilde{X}\,^1A}{CH_3OH} \xrightarrow{90.3 \pm 0.4} \underset{\tilde{X}\,^2A_2''}{CH_3} + \underset{X\,^2\Pi}{OH}$$

$$\underset{\tilde{X}\,^1A}{CH_3SH} \xrightarrow{73 \pm 1} \underset{\tilde{X}\,^2A_2''}{CH_3} + \underset{X\,^2\Pi}{SH}$$

$$\underset{\tilde{X}\,^2E}{CH_3O} \xrightarrow{89 \pm 1} \underset{\tilde{X}\,^2A_2''}{CH_3} + \underset{^3P}{O}$$

$$\underset{\tilde{X}\,^2E}{CH_3S} \xrightarrow{70 \pm 1} \underset{\tilde{X}\,^2A_2''}{CH_3} + \underset{^3P}{S}$$

$$\underset{\tilde{X}\,^2A''}{CH_2OH} \xrightarrow{104 \pm 1} \underset{\tilde{X}\,^3B_1}{CH_2} + \underset{X\,^2\Pi}{OH}$$

$$\underset{\tilde{X}\,^2A''}{CH_2SH} \xrightarrow{88 \pm 1} \underset{\tilde{X}\,^3B_1}{CH_2} + \underset{X\,^2\Pi}{SH}$$

	A	B	C	D	E	F	G	H
1								
2	H2	JANAF						
3								
4	HF	JANAF						
5								
6	HCl	JANAF						
7								
8	HBr	JANAF						
9								
10	HI	JANAF						
11								
12	H2O	JANAF						
13								
14	H2CO	M.-C. Chuang, M.F. Foltz, and C.B. Moore, J. Chem. Phys. 87, 3855 (1987) report Do(H-CHO) =						
15		86.57 ± 0.16 kcal/mol and DH298(H-CHO) = 88.0 ± 0.2 kcal/mol, & deltaHf298o(CH2O) is						
16		-25.95 ± 0.11 kcal/mol; D.L. Baulch, R.A. Cox, P.J. Crutzen, R.F. Hampson Jr., J. Troe, and						
17		R.T. Watson, J. Phys. Chem. Ref Data 11, 493 (1982). To compute deltaHf0(CH2O), I used H2CO						
18		vibrational Harmonic frequencies from T. Shimanouchi, "Tables of Vibrational Frequencies," Consolidated						
19		Vol. I NSRDS-NBS 39 (1972).						
20								
21	NH3	JANAF; S.T. Gibson, J.P. Greene, and J. Berkowitz, J. Chem. Phys. 83, 4319 (1985)						
22								
23	CH4	JANAF; deltaHf298(CH3) from Table I & deltaHf0(CH3) from W.A. Chupka, J. Chem. Phys. 48, 2337 (						
24								
25	HCN	The threshold for photoion-pair formation is reported in Table III as 15.18 ± 0.02 eV or 350.1 ± 0.5						
26								
27	H2S	J. M. Nicovich, K.D. Kreutter, C.A. van Dijk, and P.H. Wine, J. Phys. Chem. 96, 2518 (1992).						
28								
29	H2Se	H.M. Rosenstock, K. Draxl, B.W. Steiner, and J.T. Herron, J. Phys. and Chem. Ref Data 6, (1977) Supple						
30		S.T. Gibson, J.P. Greene and J. Berkowitz, J. Chem. Phys. 85, 4815 (1986).						
31								
32	PH3	JANAF,J. Berkowitz, L.A. Curtiss, S.T. Gibson, J.P. Greene, G.L. Hillhouse and J. A. Pople, J. Chem. Phy						
33		84, 375 (1986).						

	A	B	C	D	E	F	G	H
34								
35	AsH3	H.M. Rosenstock, K. Draxl, B.W. Steiner, and J.T. Herron, J. Phys. and Chem. Ref Data 6, (1977) Supple						
36		J. Berkowitz, J. Chem. Phys. 89, 7065 (1988).						
37								
38	SiH4	Table I; JANAF						
39		J. Berkowitz, J.P. Greene, H. Cho and B. Ruscic, J. Chem. Phys. 86, 1235 (1987).						
40								
41	GeH4	H.M. Rosenstock, K. Draxl, B.W. Steiner, and J.T. Herron, J. Phys. and Chem. Ref Data 6, (1977) Supple						
42		B. Ruscic, M. Schwarz and J. Berkowitz, J. Chem. Phys. 92, 1865 (1990).						
43								
44	H2CS							
45								
46	HCCH	J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed. (Chapm						
47		K.M. Ervin, S. Gronert, S.E. Barlow, M.K. Gilles, A.G. Harrison, V.M. Bierbaum, C.H. DePuy, W.C. Lineberg						
48		and G.B. Ellison, J. Am. Chem. Soc. 112, 5750 (1990).						
49								
50	CH2CH2	JANAF						
51		K.M. Ervin, S. Gronert, S.E. Barlow, M.K. Gilles, A.G. Harrison, V.M. Bierbaum, C.H. DePuy, W.C. Lineberg						
52		and G.B. Ellison, J. Am. Chem. Soc. 112, 5750 (1990).						
53								
54	C6H6	J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed. (Chapm						
55		& Hall, London New York, 1986). To compute deltaHf0(C6H6), I used C6H6 vibrational Harmonic						
56		frequencies from T. Shimanouchi, "Tables of Vibrational Frequencies," Consolidated Vol. I NSRDS-NBS						
57		39 (1972).						
58								
59	CH2CHCH2-H	J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed. (Chapm						
60		& Hall, London New York, 1986). To compute deltaHf0(C3H6), I used C3H6 vibrational frequencies fr						
61		Herzberg III						
62		G.I. McKay, M.H. Lien, A.C. Hopkinson, and D.K. Bohme, Can. J. Chem. 56, 131 (1978); J.M. Oakes and						
63		G.B. Ellison, J. Am. Chem. Soc. 106, 7734 (1984); M.L. Polak and W.C. Lineberger (unpublished, 1992)						
64								
65	C6H5CH2-H	J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed. (Chapm						
66		& Hall, London New York, 1986). To compute deltaHf0(C7H8), I used C7H8 harmonic vibrational freq						

	A	B	C	D	E	F	G	H
67		calc by Weisshaar & Weinhold: MP/2; 4-31G						
68		32.9, 206.5, 348.0, 413.1, 465.1, 537.5, 658.6, 665.9, 724.1, 794.8, 840.5, 874.7, 920.0,						
69		923.7, 1024.3, 1030.3, 1060.4, 1118.7, 1132.6, 1226.0, 1239.9, 1251.9, 1321.6, 1401.0,						
70		1486.9, 1497.8, 1542.5, 1580.3, 1588.1, 1609.2, 1610.5, 3077.8, 3143.4, 3153.2						
71								
72	H-CH2CHO	H.M. Rosenstock, K. Draxl, B.W. Steiner, and J.T. Herron, J. Phys. and Chem. Ref Data 6, (1977) Supple						
73		J.E. Bartmess, J.A. Scott, and R.T. McIver Jr., J. Am. Chem. Soc. 101, 6047 (1979)						
74		R.D. Mead, K.R. Lykke, W.C. Lineberger, J. Marks, and J.I. Brauman, J. Chem. Phys. 81, 4883 (1984).						
75								
76	CH3CO-H	H.M. Rosenstock, K. Draxl, B.W. Steiner, and J.T. Herron, J. Phys. and Chem. Ref Data 6, (1977) Supple						
77		Table I,J.K. Niiranen, D. Gutman, and L.N.Krasnoperov, J. Phys. Chem. 96, 5881 (1992).						
78								
79	CH2CO	J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed. (Chapm						
80		To compute deltaHf0(CH2CO), I used CH2CO vibrational frequencies from Herzberg III						
81		J.M. Oakes, M.E. Jones, V.M. Bierbaum, and G.B. Ellison, J. Phys. Chem. 87, 4810 (1983).						
82								
83	H-CH2OH	V.P. Glushko, L.V. Gurvich, G.A. Bergman, I.V. Veits, V.A. Medvedev, G.A. Khachkuruzov, and V.S. Yur						
84		Termodinamicheskie Svoistva Individual'nikh Veshchestv, vol 2 (Nauka, Moscow, 1979).						
85		deltaHf298(CH2OH) = -2 9 ± 0.4 kcal/mol; see text & ref 41						
86		B. Ruscic and J. Berkowitz, J. Chem. Phys. 95, 4033 (1991).						
87								
88	CH3O-H	V.P. Glushko, L.V. Gurvich, G.A. Bergman, I.V. Veits, V.A. Medvedev, G.A. Khachkuruzov, and V.S. Yur						
89		Termodinamicheskie Svoistva Individual'nikh Veshchestv, vol 2 (Nauka, Moscow, 1979).						
90		M. Meot-Ner and L.W. Sieck, J. Phys. Chem. 90, 6687 (1986).						
91		P.C. Engelking, G.B. Ellison, W.C. Lineberger, J. Chem. Phys. 69, 1826 (1978).						
92								
93	CH3CH2O-H	H.M. Rosenstock, K. Draxl, B.W. Steiner, and J.T. Herron, J. Phys. and Chem. Ref Data 6, (1977) Supple						
94		J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed. (Chapm						
95		T.T. Dang, E.L. Motell, M.J. Travers, E.P. Clifford, G.B. Ellison, C.H. DePuy, and V.M. Bierbaum,						
96		Int. J. Mass Spectrom. Ion Proc. 123, 171 (1993).						
97								
98	CH3S-H	J. M. Nicovich, K.D. Kreutter, C.A. van Dijk, and P.H. Wine, J. Phys. Chem. 96, 2518 (1992).						
99								

	A	B	C	D	E	F	G	H
100	H-CH2SH	B. Ruscic and J. Berkowitz, J. Chem. Phys. 97, 1818 (1992).						
101								
102	CH3CN	J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed. (Chapm						
103		To compute deltaHf0(CH3CN), I used CH3CN Harmonic frequencies from T. Shimanouchi, "Tables of						
104		Consolidated Vol. I NSRDS-NBS 39 (1972).						
105		J.E. Bartmess, J.A. Scott, and R.T. McIver Jr. J. Am. Chem. Soc. 101, 6047 (1979)						
106		S. Moran, H.B. Ellis Jr., D.J. DeFrees, A.D. McLean, and G.B. Ellison, J. Am. Chem. Soc. 109, 5996 (1987						
107								
108	CH3NC	J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed. (Chapm						
109		To compute deltaHf0(CH3CN), I used CH3CN Harmonic frequencies from T. Shimanouchi, "Tables of						
110		Consolidated Vol. I NSRDS-NBS 39 (1972). R.A.L. Peerboom,						
111		S. Ingemann, N.M.M. Nibbering, and J.F. Liebman, J. Chem. Soc. Perkin Trans. II 1825 (1990); S. Moran,						
112		H.B. Ellis Jr., D.J. DeFrees, A.D. McLean, S.E. Paulson, and G.B. Ellison, J. Am. Chem. Soc. 109, 6004 (						
113								
114	H-COOH	J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed. (Chapm						
115		B. Ruscic, M. Schwarz and J. Berkowitz, J. Chem. Phys. 91, 6780 (1989).						
116								
117								
118	CH3CH2-H	Table I, B. Ruscic, J. Berkowitz, L.A. Curtiss and J.A. Pople, J. Chem Phys. 91, 114 (1989).						
119		JANAF						
120								
121	CH3CH2CH2CH(CH3)-H	Table I, J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed						
122		To compute deltaHf0(C4H10), I used C4H10 Harmonic frequencies from T. Shimanouchi, "Tables of						
123		Consolidated Vol. I NSRDS-NBS 39 (1972).						
124								
125	(CH3)2CH-H	Table I, J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed						
126		To compute deltaHf0(C3H8), I used C3H8 Harmonic frequencies from T. Shimanouchi, "Tables of Vi						
127		Consolidated Vol. I NSRDS-NBS 39 (1972).						
128								
129	(CH3)3C-H	Table I, J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed						

Heats of Formation

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1		Constants from Cohen & Taylor/1986													
2	Temp =	298.15	K	so	207.226	cm-1									
3	R =	1.987216	cal/mol I	and	0.59249	kcal/mol									
4	k =	1.38E-16	erg/K												
5	c =	3E+10	cm/sec												
6	h =	6.63E-27	erg sec	so	0.69504	cm-1/K									
7	1 atm =	1013250	dyne/cm2												
8	Avogadro no.	6.02E+23	atoms/m	4.184											
9	H mass (amu)	1.00783	O mass (	15.99	F mass =	18.998									
10	C mass (amu)	12	N mass (	14											
11	Cl mass (amu)	34.96885	Br(79) =	78.92											

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
12															
13	ΔHf0(H)/kJ mol-1	216.035	0.006												
14	ΔHf298(H)/kJ mol-1	217.999	0.006												
15			**R-H → R + H so**			**D(R-H) = ΔHf(R) + ΔHf(H) - ΔHf(RH)**									
16			**And: ΔHf(R) =**			**D(RH) - ΔHf(H) + ΔHf(RH)**									
17	J.B. Pedley, R.D. Naylor, and S.P. Kirby,"Thermochemical Data of Organic Compounds", 2nd Ed. (Chapman & Hall, London New York, 19														
18															
19	H2 + 2 C → HCCH so:		ΔHf(HCCH) ≡ ΔHf(HCCH) - 2 ΔHf(C) - ΔHf(H2)												
20			ΔHf298(HCCH) = ΔHf0(HCCH) +⟨Cp(HCCH) - 2Cp(C) - Cp(H2)⟩												
21	molecule	ΔHf298(RH)	± kJ/mol	{H(298)-	DH298(RH	± kcal/mo	ΔHf298(	± kcal/	Do(R-H)	±kcal/mol	⟨Cp⟩	ΔHf0(RH)	±kJ/mol	ΔHf0(R)	± kcal/
22	CH4	-74.87	0.70	2.396	104.8	0.3	34.8	0.2	103.24	0.12	-1.903	-66.6	0.3	35.7	0.1
23							*34.80*	*0.30*							
24	HC≡CH	228.20	0.79	2.391	132.80	0.60	135.2	0.6	131.30	0.60	-0.135	228.8	0.8	134.3	0.6
25															
26	CH2=CH2	52.47	0.29	2.511	111.20	0.80	71.6	0.8	109.70	0.80	-2.039	61.0	0.3	72.6	0.8
27															
28	C6H6	82.60	0.70	3.393	111.10	2.10	78.7	2.1	109.60	2.10	-4.185	100.1	0.7	81.9	2.1
29															
30	CH2=CHCH3	20.00	0.80	3.188	88.20	2.10	40.9	2.1	86.70	2.10	-3.636	35.2	0.8	43.5	2.1
31															
32	C6H5CH3	50.40	0.60	4.520	88.20	2.00	48.1	2.0	86.80	2.10	-5.333	72.7	0.6	52.5	2.1
33															
34	CH2CO	-47.50	1.60	2.823	105.40	2.10	41.9	2.1	104.00	2.20	-0.741	-44.4	1.6	41.8	2.2
35															
36	CH3CN	64.30	7.20	2.888	94.80	2.10	58.1	2.7	93.30	2.10	-1.686	71.4	7.2	58.7	2.7
37															
38	CH3NC	163.50	7.20	3.023	91.00	2.10	78.0	2.7	89.50	2.10	-1.551	170.0	7.2	78.5	2.7
39															
40	CH3CH2CH3	-104.70	0.50	3.725	98.6	0.4	21.5	0.4	97.10	0.60	-5.124	-83.3	0.5	25.6	0.6
41															
42	CH3(CH2)2CH3	-125.60	0.70	4.316	98.2	0.5	16.1	0.5	96.70	0.60	-6.807	-97.1	0.7	21.9	0.6
43															
44	CH2=O	-108.57	0.46	2.393	88.04	0.22	10.0	0.2	86.57	0.16	-0.920	-104.7	0.5	9.9	0.2

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
45															
46	H-CH2OH	-201.00	0.59		97.2	0.4	**-2.9**	**0.4**	95.00	0.70		-190.04	0.59	-2.1	0.7
47															
48	CH3O-H	-201.00	0.59		104.2	0.7	4.1	0.7	102.70	0.80		-190.04	0.59	5.6	0.8
49															
50	CH2=O	-108.57	0.46		88.04	0.22	10.0	0.2			D.L. Baulch, R.A. Cox, P.J. Crutzen, R.F				
51	CH3CO-H	-166.10	0.50		89.40	0.30	-2.4	0.3			H.M. Rosenstock, K. Draxl, B.W. Steiner				
52	ΔHf0(CH3CO-H)	-155.39	0.50		87.88	0.50	-0.9	0.5			H.M. Rosenstock, K. Draxl, B.W. Steiner				
53	CH3CH2OH	-235.20	0.40		103.30	2.00	-5.0	2.0							
54	ΔHf0(CH3CH2OH)	-217.44	0.40		101.80	2.10	-1.8	2.1			H.M. Rosenstock, K. Draxl, B.W. Steiner				
55	HCOOH	-378.70	0.60		≥ 88.5	0.50	-54.1	0.5							
56	CH3CH3	-83.80	0.40		101.0	0.4	28.9	0.4							
57	CH(CH3)3	-134.2	0.7		96.5	0.4	12.3	0.4	95.0	0.4					
58	ΔHf0(CH3CH3)	-69.13	0.60		99.50	0.50	31.3	0.5							
59	SiH4	34.31	2.10		91.8	0.8	47.9	0.6			JANAF				
60	ΔHf0(SiH4)	43.92	2.10		≤ 91.1	0.05	50.0	0.5			JANAF				
61	H-CH2CHO	-166.10	0.50		94.30	2.20	2.5	2.2			H.M. Rosenstock, K. Draxl, B.W. Steiner				
62	ΔHf0(H-CH2CHO)	-155.39	0.50		92.80	2.20	4.0	2.2			H.M. Rosenstock, K. Draxl, B.W. Steiner				
63	PH3	22.89	1.70		83.94	0.5016	37.3	0.6			JANAF				
64	ΔHf0(PH3)	30.81	1.70		82.46	0.46	38.2	0.6			JANAF				
65	AsH3	66.44	0.30		76.38	0.40	40.2	0.4			H.M. Rosenstock, K. Draxl, B.W. Steiner				
66	ΔHf0(AsH3)	74.06	0.30		74.90	0.20	41.0	0.2			H.M. Rosenstock, K. Draxl, B.W. Steiner				
67	H2Se	29.70	0.80		80.37	0.40	35.4	0.4			H.M. Rosenstock, K. Draxl, B.W. Steiner				
68	ΔHf0(H2Se)	33.68	0.80		78.89	0.18	35.3	0.3			H.M. Rosenstock, K. Draxl, B.W. Steiner				
69	GeH4	90.80	0.50		< 87	0.50	56.6	0.5			H.M. Rosenstock, K. Draxl, B.W. Steiner				
70	ΔHf0(GeH4)	79.96	0.50		< 85.5	0.30	53.0	0.3			H.M. Rosenstock, K. Draxl, B.W. Steiner				

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
71		**************************************													
72			Linear Molecule					ΔHf(HCCH) = ΔHf(HCCH) - 2 ΔHf(C) - ΔHf(H2)							
73			H2				ΔHf298(HCCH) = ΔHf0(HCCH) +⟨Cp(HCCH) - 2Cp(C) - Cp(H2)⟩								
74	Constants from Huber & Herzberg									ΔHf298/kJ			⟨Cp[RH-	calc ΔHf	expt'l Δ
75		Symmetry no.		2					CH4	-74.873	0.70	2.396	-1.9	-66.91	-66.91
76	B (cm-1) =	60.853	Mol wt (amu) =		2.01566										
77									HC≡CH	228.20	0.79	2.39	-0.1	228.76	235.76
78		freqs in c	ω/k	H vib	Cp vib	S vib									
79	v1 =	4158.541	20.068	2.3E-08	1.54E-06	8.06E-08			CH2=CH2	52.47	0.29	2.511	-2.0	61.00	60.99
80	Cp vib	1.54E-06	cal/mol•K												
81	vibrational H	2.29E-08	kcal/mol	8E-08	cal/mol•K				C6H6	82.60	0.70	3.393	-4.2	100.11	
82	rotational H = RT	0.592508	kcal/mol	1.987	cal/mol•K										
83	translation H =(5/	1.48127	kcal/mol	4.968	cal/mol•K				CH2=CHC	20.00	0.80	3.188	-3.6	35.21	
84	"thermal enthalpy" H(T) - H(0K			2.074	kcal/mol	2.0237/JANAF									
85									C6H5CH3	50.40	0.60	4.520	-5.3	72.71	
86	**In the single case of H2, the high temp approximation is not good**														
87	**enough. You also need to explicitly count ortho & para states. JANAF**								CH2CO	-47.50	1.60	2.823	-0.7	-44.40	
88	**calc's "thermal enthalpy", H(298.15) - H(0K) =**				**2.024**	**kcal/mol**									
89		**************************************							CH3CN	64.30	7.20	2.888	-1.7	71.36	
90	C atom reference state is C atom/solid - must use JANAF p. 535														
91	JANAF lists H298K(C) - H0K(C) =			1.051	kJ/mol				CH3NC	163.50	7.20	3.023	-1.6	169.99	
92				0.251	kcal/mol										
93		**************************************							CH3CH2C	-104.70	0.50	3.725	-5.1	-83.26	
94	O2 reference state - use JANAF p. 1667														
95	JANAF lists H298K(O2) - H0K(O2) =			8.683	kJ/mol				CH3(CH2)	-125.60	0.70	4.316	-6.8	-97.12	
96				2.075	kcal/mol										
97		**************************************							CH2=O	-108.57	0.46	2.393	-0.9	-104.73	
98	N2 reference state - use JANAF p. 1551														
99	JANAF lists H298K(N2) - H0K(N2) =			8.670	kJ/mol										
100				2.072	kcal/mol										
101		**************************************													
102		ΔHf298(HX) kJ/mol			ΔHf0(HX) kJ/mol										
103	C	716.677	0.46024		711.19632	0.46024	JANF								

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
104	CH	596.513	1.50624		593.04016	1.50624	H. Helm, P.C. Cosby, M.M. Graff, and J.T. Mosley, Phys. Rev. A25, 304 (1982).								
105	CH2	388.694	2.5104		388.2752	2.5104	Leopold/WCL								
106															
107	CO	-100.530	0.17		-113.81	0.17	JANF								
108	CHO	41.798	0.79496				M.-C. Chuang, M.F. Foltz, and C.B. Moore, JCP 87, 3855 (1987).								
109	OH	38.987	1.21		38.39	1.21	JANF								
110	O	249.170	0.1		246.79	0.1	JANF								
111	CH3SH	-23.012	0.4184		-12.552	0.4184	B. Ruscic and J. Berkowitz, J. Chem. Phys. 98, 2568 (1993).								
112	CH2S				100.416	12.552	S.W. Benson and L.G.S. Shum, Int. J. Chem. Kinetics 17, 749 (1985).								
113					125.1016	3.7656	B. Ruscic and J. Berkowitz, J. Chem. Phys. 98, 2568 (1993).								
114	SH	143.009	2.84512		142.54888	3.01248	J.M. Nicovich, K.D. Kreutter, C.A. van Dijk, and P.H. Wine, J. Phys. Chem. 96,								34.2
115	SH	143.093	2.9288				Gutman section/Jan 93								
116	S	276.980	0.25		274.73	0.25	JANF								
117	H2S	-20.502	0.799144		-17.58535	0.79914	J.M. Nicovich, K.D. Kreutter, C.A. van Dijk, and P.H. Wine, J. Phys. Chem. 96, 2518 (1								
118	SiH4	34.310	2.1		43.92	2.1	JANF								
119	H2O	-241.826	0.042		-238.921	0.042	JANAF								
120	CH4	-74.4	0.4				J.B. Pedley, R.D. Naylor, S.P. Kirby, "Thermochemistry of organic Compounds," 2nd Ed								
121	CH2=O	-108.6	0.5				J.B. Pedley, R.D. Naylor, S.P. Kirby, "Thermochemistry of organic Compounds," 2nd Ed								
122	CH2=O	-108.5748	0.46024				D.L. Baulch, R.A. Cox, P.J. Crutzen, R.F. Hampson Jr., J. Troe, and R.T. Watson, J. Phy								
123					-104.726	0.5	⟨Cp⟩ correction to Pedley								
124	CH3OH	-201.5	0.3		-190.2694	0.09649	J.B. Pedley, R.D. Naylor, S.P. Kirby, "Thermochemistry of organic Compounds," 2nd Ed								
125		-200.99936	0.58576		-190.0373	0.58576	V.P. Glushko, L.V. Gurvich, G.A. Bergman, I.V. Veits, V.A. Medvedev, G.A. Khachkur								
126							Termodinamicheskie Svoistva Individual'nikh Veshchestv, vol 2 (Nauka, Moscow, 1979)								
127							K.M.A. Refaey and W.A. Chupka, J. Chem. Phys. 48, 5205 (1968). ΔHf0K(CH3OH) = -								
128	CH2=C=O	-47.5	1.6				J.B. Pedley, R.D. Naylor, S.P. Kirby, "Thermochemistry of organic Compounds," 2nd Ed								
129		-61.1					H.M. Rosenstock, K. Draxl, B.W. Steiner, and J.T. Herron, J. Phys. and CHem. Ref Data								
130		-47.6976	1.6736				J. Vogt, A.D. Williamson, and J.L. Beauchamp, JACS, 100, 3478 (1978).								
131	CH2CHO	10.31355	9.2178		16.880259	9.25574	acidity/EA cycle								
132	CH3S	124.5995	1.841		131.54496	2.25936	J.M. Nicovich, K.D. Kreutter, C.A. van Dijk, and P.H. Wine, J. Phys. Cher								
133	CH2SH				164.4312	0.8368	B. Ruscic and J. Berkowitz, J. Chem. Phys. 98, 2568 (1993).								
134															

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
135					DH298/kcal	± kcal/mol			Do/kcal	± kcal/mol					
136	CH3CHO → CH3CO + H				89.4	0.3			87.9	0.5					
137	CH3CHO → CH2CHO + H				94.3	2.2			92.8	2.2					
138	CH3CO → CH2CO + H				43.2	0.5			41.9	0.6					
139	CH2CHO → CH2CO + H				38.3	2.2			37.0	2.2					
140	CH3CHO → CH3 + CHO				84.5	0.3			82.7	0.3					
141	CH3CO → CH3 + CO				13.2	0.4			9.4	0.5					
142	CH2CHO → CH2 + CHO				100.4	2.3			98.7	2.3					
143															
144	CH3OH → CH3O + H				104.2	0.7			102.7	0.8					
145	CH3OH → CH2OH + H				97.2	0.4			95.0	0.7					
146	CH3O → CH2O + H				22.1	0.7			21.0	0.8					
147	CH2OH → CH2O + H				29.1	0.4			28.7	0.8					
148	CH3OH → CH3 + OH				92.2	0.4			90.3	0.4					
149	CH3O → CH3 + O				90.3	0.7			89.0	0.8					
150	CH2OH → CH2 + OH				105.1	0.8			104.0	1.0					
151															
152	CH3SH → CH3S + H				87.4	0.5			86.1	0.5					
153	CH3SH → CH2SH + H								93.9	0.2					
154	CH3S → CH2S + H								50.1	1.0					
155	CH2SH → CH2S + H								42.2	0.9					
156	CH3SH → CH3 + SH				74.5	0.7			72.8	0.7					
157	CH3S → CH3 + S				71.2	0.6			69.9	0.6					
158	CH2SH → CH2 + SH								87.6	1.0					

END DATE
1-14-94