

Bond Dissociation Energies of Organic Molecules

STEPHEN J. BLANKSBY*[†] AND
G. BARNEY ELLISON*[‡]

Department of Chemistry, University of Wollongong,
NSW, 2522, Australia, and Department of Chemistry &
Biochemistry, University of Colorado,
Boulder, Colorado 80309-0215

Received August 6, 2002

ABSTRACT

In this Account we have compiled a list of reliable bond energies that are based on a set of critically evaluated experiments. A brief description of the three most important experimental techniques for measuring bond energies is provided. We demonstrate how these experimental data can be applied to yield the heats of formation of organic radicals and the bond enthalpies of more than 100 representative organic molecules.

Introduction

The making and breaking of bonds is the basis of all chemical transformation. A sound knowledge of the energies required to break bonds and the energies released upon their formation is fundamental to understanding chemical processes.¹ The energy required for *homolytic* bond cleavage at 298 K corresponds to the enthalpy of reaction 1, $\Delta_{\text{rxn}}H_{298}(1)$, which is by definition² the bond dissociation enthalpy of the molecule AB, $DH_{298}(AB)$:



Conversely, if the radicals A and B recombine to form the molecule AB, then thermal energy equivalent to the bond dissociation enthalpy is released, according to the first law of thermodynamics. Using these ideas, it is possible to determine the energetics of a wide range of simple but important reactions involving the exchange of a single bond. This is achieved by subtracting the energy gained from the bond formed from the energy required to break the initial bond. For example, consider the energetics of reaction 2, where a single carbon–hydrogen bond is broken and a hydrogen–chlorine bond is formed:

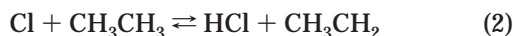


Table 1 provides a set of experimentally determined bond enthalpies: typical values range from 60 to 130 kcal mol⁻¹. Using the tabulated values for the carbon–hydrogen bond

enthalpy of ethane, $DH_{298}(\text{CH}_3\text{CH}_2\text{--H}) = 101.1 \pm 0.4$ kcal mol⁻¹, and the bond enthalpy of hydrochloric acid, $DH_{298}(\text{HCl}) = 103.15 \pm 0.03$ kcal mol⁻¹, the forward reaction is determined to be exothermic since $\Delta_{\text{rxn}}H_{298}(2) = DH_{298}(\text{CH}_3\text{CH}_2\text{--H}) - DH_{298}(\text{HCl}) = -2.1 \pm 0.4$ kcal mol⁻¹; the reverse reaction is endothermic, $\Delta_{\text{rxn}}H_{298}(-2) = +2.1 \pm 0.4$ kcal mol⁻¹. This simple scheme allows the elucidation of precise thermochemistry for a broad range of chemical reactions for which experimental bond enthalpies are available. One must be cautious, however. In reactions where multiple bonds are broken, the bond enthalpy of a particular bond can be changed dramatically by the cleavage of ancillary bonds within the molecule. That is, once the first bond is broken, the remaining bond enthalpies are often altered. Several examples of this behavior will be discussed.

Thermochemistry

The bond dissociation energy for a species, AB, at room temperature is the *bond enthalpy*, $DH_{298}(AB)$. By definition, it is the reaction enthalpy of the bond homolysis reaction 1, $\Delta_{\text{rxn}}H_{298}(1)$, and thus depends exclusively on the relative enthalpies of formation of reactant and product states:

$$\Delta_{\text{rxn}}H_{298}(1) = \Delta_{\text{f}}H_{298}(A) + \Delta_{\text{f}}H_{298}(B) - \Delta_{\text{f}}H_{298}(AB) = DH_{298}(AB) \quad (3)$$

By computing heat capacity corrections, one can adjust the bond enthalpies to any reaction temperature. For example, correcting $DH_{298}(AB)$ to 0 K using eq 4 yields $D_0(AB)$, which is strictly defined by spectroscopists³ as the *bond dissociation energy* and is shown schematically in Figure 1. The bond dissociation energy is related to the depth of the potential well, $D_e(AB)$, by the zero-point energy, $D_0(AB) = D_e(AB) - \text{ZPE}$ (Figure 1):

$$D_0(AB) = DH_{298}(AB) - \int_0^{298} [C_p(A) + C_p(B) - C_p(AB)] dT \quad (4)$$

Adjusting $DH_{298}(AB)$ to obtain $D_0(AB)$, or vice versa, requires the evaluation of the integrated heat capacity term shown in eq 4. It should be noted that the integrated heat capacity of a molecule, AB, from 0 to 298 K is equal to the heat content, $H_{298}(AB) - H_0(AB) = \int_0^{298} C_p(H) dT$. For some common molecules, values for heat content have been evaluated and tabulated over a range of temperatures.⁴ In most cases, however, heat content is calculated using equilibrium statistical mechanics with harmonic oscillator and rigid rotor approximations.³ In such calculations, the contributions to the heat content arising from translation, rotation, and vibration (electronic contributions are generally zero) are treated as independent and are calculated using vibrational frequencies obtained from experiment or ab initio calculation (for examples of such calculations, see refs 5 and 6).

Stephen Blanksby obtained his Ph.D. from the University of Adelaide in 1999 under the supervision of John Bowie. He then worked as a postdoctoral researcher at the University of Colorado from 2000 to 2002, and has recently taken up a faculty position in the Department of Chemistry at the University of Wollongong.

Barney Ellison studied at Trinity College (Hartford, CT) and then earned a Ph.D. in chemistry at Yale University under the supervision of K. B. Wiberg. Ellison teaches organic chemistry at the University of Colorado and studies the chemical physics of organic molecules.

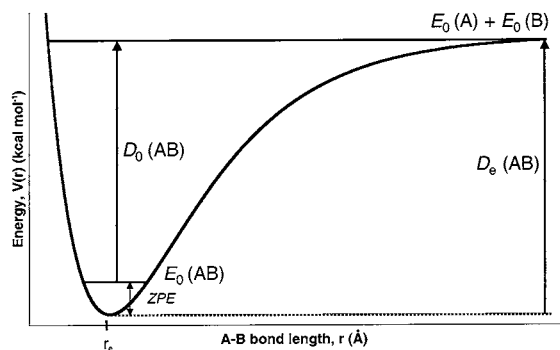
* Address correspondence to either author. E-mail: blanksby@uow.edu.au and barney@jila.colorado.edu.

[†] University of Wollongong.

[‡] University of Colorado.

Table 1. Molecular Bond Dissociation Energies for $RH \rightarrow R + H$: Experimental Bond Enthalpies and Radical Heats of Formation at 298 K

	DH_{298} (kcal mol ⁻¹)	$\Delta_f H_{298}(R)$ (kcal mol ⁻¹)	ref		DH_{298} (kcal mol ⁻¹)	$\Delta_f H_{298}(R)$ (kcal mol ⁻¹)	ref
Inorganics							
H ₂	104.206 ± 0.003	52.103 ± 0.003	4	OH ⁻ → O ⁻ + H	110.21 ± 0.07	-33.23 ± 0.07	34
HF	136.25 ± 0.01	18.83 ± 0.17	6	OH ⁺ → O + H ⁺	115.2 ± 0.1	59.55 ± 0.02	34
HCl	103.15 ± 0.03	29.03 ± 0.04	9	H ₂ S	91.2 ± 0.1	34.2 ± 0.2	6
HBr	87.54 ± 0.05	28.62 ± 0.06	9	SH	84.1 ± 0.2	66.2 ± 0.3	6
HI	71.32 ± 0.06	26.04 ± 0.08	9	H-NO	49.5 ± 0.7	21.8 ± 0.1	4
H-CN	126.3 ± 0.2	105.0 ± 0.7	6	H-ONO (trans)	79.1 ± 0.2	8.2 ± 0.1	4
NH ₃	107.6 ± 0.1	44.5 ± 0.1	6	H-ONO ₂	101.7 ± 0.4	17.6 ± 0.3	35
H ₂ O	118.82 ± 0.07	8.86 ± 0.07	34	SiH ₄	91.7 ± 0.5	47.9 ± 0.6	9
OH	101.76 ± 0.07	59.55 ± 0.02	34	GeH ₄	83 ± 2	53 ± 2	9
Hydrocarbons							
CH ₄	104.99 ± 0.03	35.05 ± 0.07	31	CH ₂ CH-H	110.7 ± 0.6	71.1 ± 0.7	6
CH ₃	110.4 ± 0.2	93.3 ± 0.2	31	HCC-H	133.32 ± 0.07	135.6 ± 0.2	36
CH ₂	101.3 ± 0.3	142.5 ± 0.2	9	C ₆ H ₅ -H	112.9 ± 0.5	80.5 ± 0.5	6
CH	80.9 ± 0.2	171.3 ± 0.1	9	C ₆ H ₅ → <i>o</i> -C ₆ H ₄ + H	78 ± 3	106 ± 3	37
CH ₃ CH ₂ -H	101.1 ± 0.4	29.0 ± 0.4	10	C ₆ H ₅ → <i>m</i> -C ₆ H ₄ + H	94 ± 3	122 ± 3	37
(CH ₃) ₂ CH-H	98.6 ± 0.4	21.5 ± 0.4	10	C ₆ H ₅ → <i>p</i> -C ₆ H ₄ + H	109 ± 3	138 ± 3	37
CH ₃ CH ₂ (CH ₃)CH-H	98.2 ± 0.5	16.1 ± 0.5	10	CH ₂ CHCH ₂ -H	88.8 ± 0.4	41.4 ± 0.4	38
(CH ₃) ₃ C-H	96.5 ± 0.4	12.3 ± 0.4	10	C ₆ H ₅ CH ₂ -H	89.8 ± 0.6	49.7 ± 0.6	38
Alcohols							
H-CH ₂ OH	96.1 ± 0.2	-4.08 ± 0.2	16	CH ₃ CH ₂ O-H	104.7 ± 0.8	-3.6 ± 0.8	6
CH ₃ O-H	104.6 ± 0.7	4.3 ± 0.7	6	(CH ₃) ₂ CHO-H	105.7 ± 0.7	-11.5 ± 0.7	6
CH ₃ S-H	87.4 ± 0.5	29.8 ± 0.4	39,40	(CH ₃) ₃ CO-H	106.3 ± 0.7	-20.5 ± 0.7	6
H-CH ₂ SH	94 ± 2	36 ± 2	39,40	C ₆ H ₅ O-H	90 ± 3	-58 ± 3	41
Peroxides							
HOO-H	87.8 ± 0.5	3.2 ± 0.5	14	CH ₃ CH ₂ OO-H	85 ± 2	-6.8 ± 2.3	42
CH ₃ OO-H	88 ± 1	4.8 ± 1.2	42	(CH ₃) ₃ COO-H	84 ± 2	-25.2 ± 2.3	42
Carbonyls							
H-CHO	88.144 ± 0.008	10.1 ± 0.1	6	H-COOH is ≥	96 ± 1	-46.5 ± 0.7	45
CH ₃ C(O)-H	89.4 ± 0.3	-2.4 ± 0.3	43	CH ₃ COO-H	112 ± 3	-43 ± 3	44
H-CH ₂ CHO	94 ± 2	2.5 ± 2.2	9	C ₆ H ₅ COO-H	111 ± 4	-12 ± 4	44
HCOO-H	112 ± 3	-30 ± 3	44				

**FIGURE 1.** The energy required to fragment the molecule AB in its ground state (i.e., the lowest energy electronic, vibrational, and rotational eigenstate) to ground-state fragments A and B is by definition the bond dissociation energy, $D_0(AB)$.

For some systems, however, eq 4 can be approximated. Consider the dissociation of a hydride, R-H, where R is an organic radical: $R-H \rightarrow R + H$. For large RH molecules, it is common that $\int C_p(R) dT \cong \int C_p(RH) dT$. Thus, one can simplify eq 4 to $D_0(RH) \cong DH_{298}(RH) - \int C_p(H) dT$. At 298 K, the heat capacity integral for an atom can be calculated exactly, $\int_0^{298} C_p(H) dT = 1.48 \text{ kcal mol}^{-1}$, so $D_0(RH) \cong DH_{298}(RH) - 1.5 \text{ kcal mol}^{-1}$. For many organics, $D_0(RH)$ and $DH_{298}(RH)$ are almost numerically equivalent, and as a consequence the terms “bond dissociation energy” (BDE) and “bond dissociation enthalpy” often appear interchangeably in the literature (and indeed in this Account). For the most part this is innocuous, but if a

precision of better than $\pm 3 \text{ kcal mol}^{-1}$ is required, then it is crucial to specify the appropriate $D_0(RH)$ or $DH_T(RH)$.

By definition,³ the enthalpy of a system (H) is equal to its internal energy (U) and its ability to do pressure-volume work (pV): $H = U + pV$. For 1 mol of an ideal gas, $pV = RT$; therefore, as an approximation, as $T \rightarrow 0 \text{ K}$, $H \rightarrow U$. From statistical mechanics it is possible to approximate the internal energy of a system as independent contributions from electronic (E_{elec}), vibrational (E_{vib}), rotational (E_{rot}), and translational (E_{trans}) energy. At $T = 0 \text{ K}$, all molecules will be in their ground vibrational and rotational states (written as $|v' = 0, J'' = 0\rangle$, where the double primes indicate the ground electronic state) and will have ceased translation; thus, $U \cong E_0 = E_{\text{elec}} + \text{ZPE}$ (Figure 1). Therefore, at 0 K, the homolytic bond dissociation energy can be given in terms of eq 5:

$$D_0(AB) = E_0(A) + E_0(B) - E_0(AB) \quad (5)$$

Electronic structure calculations (such as those provided by the GAUSSIAN suite of codes)⁷ can derive E_0 by a range of ab initio and semiempirical methods. Thus, $D_0(AB)$ values provide a useful comparison between experimental and theoretical thermochemistry. While this is outside the scope of this Account, these theoretical methods show excellent agreement with experimental bond dissociation energies.⁸

Measuring Bond Energies

The experimental measurement of BDEs is not easy and requires a great deal of care. Three broadly applicable techniques exist for the experimental determination of R–H bond energies in polyatomic molecules: (1) the study of radical kinetics, (2) photoionization mass spectrometry (PIMS), and (3) the acidity/electron affinity cycle. These three techniques have provided the bulk of the data listed in Table 1. Each of these methods requires a pair of very difficult measurements conducted using advanced instrumentation. A brief description of each technique is given below, but a more detailed discussion is provided elsewhere.⁹

(1) Radical Kinetics. Consider the abstraction of a hydrogen atom by chlorine from the ethane molecule (reaction 2). By careful independent experiments, the forward (k_2) and reverse (k_{-2}) rate coefficients for reaction 2 can be measured. The ratio of the rate coefficients gives the equilibrium constant [$K_{\text{eq}}(2) = k_2/k_{-2}$], which is related to the Gibbs free energy of the reaction, $\Delta_{\text{rxn}}G_{298}(2)$, at constant pressure by eq 6, where $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$ is the gas constant and $T = 298 \text{ K}$ is the equilibrium standard-state temperature.

$$\Delta_{\text{rxn}}G_{298}(2) = -RT \ln K_{\text{eq}}(2) = -R(298) \ln K_{\text{eq}}(2) \quad (6)$$

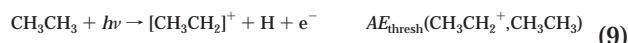
$$\Delta_{\text{rxn}}H_{298}(2) = \Delta_{\text{rxn}}G_{298}(2) + (298) \Delta_{\text{rxn}}S_{298}(2) \quad (7)$$

The Gibbs free energy of reaction is related to the enthalpy of reaction, $\Delta_{\text{rxn}}H_{298}(2)$, by eq 7. The reaction entropy, $\Delta_{\text{rxn}}S_{298}(2)$, can be obtained from a statistical mechanics analysis³ but is typically small for a simple hydrogen abstraction such as reaction 2 (e.g., $\Delta_{\text{rxn}}S_{298} \cong 26 \text{ cal mol}^{-1} \text{ K}^{-1}$). The experimentally determined $\Delta_{\text{rxn}}H_{298}(2)$ relates directly to the difference in the R–H bond energies of ethane and hydrochloric acid. Therefore, given the precisely known value of the reference bond enthalpy, $DH_{298}(\text{HCl})$, the carbon–hydrogen bond enthalpy of ethane can be extracted via eq 8:

$$DH_{298}(\text{CH}_3\text{CH}_2\text{-H}) = \Delta_{\text{rxn}}H_{298}(2) + DH_{298}(\text{HCl}) \quad (8)$$

Halogen atom kinetic studies¹⁰ of ethane reveal that $DH_{298}(\text{CH}_3\text{CH}_2\text{-H}) = 101.1 \pm 0.4 \text{ kcal mol}^{-1}$.

(2) Photoionization Mass Spectrometry. Mass spectrometry is a powerful tool for the study of molecular thermochemistry. Photoionization mass spectrometry uses a tunable light source, $h\nu$, to dissociatively ionize a target species. Consider CH_3CH_3 in reaction 9.



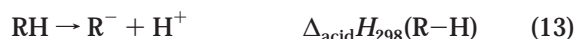
For the case of photoionization mass spectrometry, the bond dissociation energy of ethane (reaction 11) is determined by the sum of the two individual reactions 9 and 10.

The energy required for reaction 9 is defined as the appearance energy threshold, $AE_{\text{thresh}}(\text{CH}_3\text{CH}_2^+, \text{CH}_3\text{CH}_3)$. This quantity can be directly measured by scanning the energy of a light beam passing through a sample of ethane until the appearance of $[\text{CH}_3\text{CH}_2]^+$ is detected at m/z 29 by a mass spectrometer. In a similar experiment (the reverse of reaction 10), the ionization energy of ethyl radical, $IE_0(\text{CH}_3\text{CH}_2)$, is measured. Combining reactions 9 and 10 gives reaction 11, and thus the bond dissociation energy can be calculated via eq 12. PIMS studies¹¹ of

$$D_0(\text{CH}_3\text{CH}_2\text{-H}) = AE_{\text{thresh}}(\text{CH}_3\text{CH}_2^+, \text{CH}_3\text{CH}_3) - IE_0(\text{CH}_3\text{CH}_2) \quad (12)$$

ethane and ethyl iodide imply that $D_0(\text{CH}_3\text{CH}_2\text{-H}) = 99.5 \pm 0.5 \text{ kcal mol}^{-1}$. When the $D_0(\text{CH}_3\text{CH}_2\text{-H})$ value is corrected to 298 K via eq 4, it matches the radical kinetics value, $DH_{298}(\text{CH}_3\text{CH}_2\text{-H}) = 101.1 \pm 0.4 \text{ kcal mol}^{-1}$.

(3) Acidity/Electron Affinity Cycle. Gas-phase acidity studies use *heterolytic* bond cleavages to extract molecular thermochemistry. In the case of an R–H bond at 298 K, the heterolytic bond enthalpy is known as the enthalpy of deprotonation, $\Delta_{\text{acid}}H_{298}$ (reaction 13).



Summing reactions 13–15 gives¹² the homolytic bond enthalpy in eq 16.

$$DH_{298}(\text{RH}) = \Delta_{\text{acid}}H_{298}(\text{RH}) + EA_0(\text{R}) - IE_0(\text{H}) + [\text{thermal correction}] \quad (16)$$

In eq 16, “[thermal correction]” is a set of heat capacity integrals, $\int [C_p(\text{R}) - C_p(\text{R}^-) + C_p(\text{H}) - C_p(\text{H}^+)] dT$, which may be evaluated as previously described, but their value is generally less than $0.3 \text{ kcal mol}^{-1}$. By rearranging eq 16, one can estimate typical values for $\Delta_{\text{acid}}H_{298}(\text{RH})$; since $DH_{298}(\text{RH})$ for many organics is approximately $100 \text{ kcal mol}^{-1}$, the $IE_0(\text{H})$ is $313.6 \text{ kcal mol}^{-1}$, and the electron affinities¹³ of most radicals are about 23 kcal mol^{-1} , $\Delta_{\text{acid}}H_{298}(\text{R-H})$ is $[100 + 313 - 23]$, or roughly $390 \text{ kcal mol}^{-1}$. Notice that heterolytic dissociation of a molecule into isolated positive and negative ions (reaction 13) requires a great deal more energy than does homolytic cleavage, $\Delta_{\text{acid}}H_{298}(\text{R-H}) \gg DH_{298}(\text{RH})$. The additional energy required for heterolytic bond cleavage arises from the need to overcome the Coulombic attraction between the positive and negative fragments formed in this process.

The acidity/electron affinity cycle cannot be applied to CH_3CH_3 since the $[\text{CH}_3\text{CH}_2]^-$ carbanion cannot be prepared in the gas phase. But H_2O_2 is a nice example of the negative ion cycle. Experiments conducted by Ramond et al.¹⁴ measured the enthalpy of deprotonation of hydrogen peroxide, $\Delta_{\text{acid}}H_{298}(\text{HOO-H}) = 376.5 \text{ kcal mol}^{-1}$, and the electron affinity of the hydroperoxyl radical, $EA_0(\text{HOO}) = 24.86 \text{ kcal mol}^{-1}$. Using these values in eq 16 gives $DH_{298}(\text{HOO-H}) = 376.5 - 313.58 + 24.86 = 87.8 \pm 0.5 \text{ kcal mol}^{-1}$.

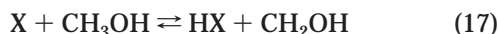
Table 2. Experimental Bond Enthalpies, DH_{298} (kcal mol⁻¹)^a

	methyl CH ₃	ethyl CH ₂ CH ₃	isopropyl CH(CH ₃) ₂	<i>tert</i> -butyl C(CH ₃) ₃	vinyl CHCH ₂	allyl CH ₂ CHCH ₂	phenyl C ₆ H ₅	benzyl CH ₂ C ₆ H ₅	methoxy CH ₃ O	formyl HC(O)	acetyl CH ₃ C(O)
H	104.9(0.1)	101.1(0.4)	98.6(0.4)	96.5(0.4)	110.7(0.7)	88.8(0.4)	112.9(0.6)	89.7(0.6)	104.6(0.7)	88.1(0.2)	89.4(0.3)
F	115(4) ^a	—	110.6(0.5)	—	123.3(0.8)	—	127.2(0.7)	98.7(0.7) ^a	—	—	122.2(0.9)
Cl	83.7(0.1)	84.8(0.5)	85.2(0.5)	84.9(0.7)	91.2(0.7)	—	97.1(0.6)	74(1)	—	—	84.7(0.4)
Br	72.1(0.3)	72.4(0.6)	73.9(0.7)	72.6(0.6)	80.8(0.8)	59(1)	84(1)	63(1)	—	—	71.7(0.3)
I	57.6(0.4)	56.9(0.7)	57(1)	55.6(0.9)	—	45.6(0.9)	67(2)	51(2)	—	—	53.8(0.7)
HO	92.1(0.1)	94.0(0.4)	95.5(0.4)	95.8(0.4)	—	80.1(0.6)	112.4(0.6)	82.6(0.7)	—	109.5(0.2)	109.9(0.7)
CH ₃ O	83.2(0.9)	85(1)	85.8(0.5)	84(1)	—	—	101(1)	—	38(1)	99.6(0.9)	100(1)
NH ₂	85.2(0.3)	84.8(0.4)	86.0(0.4)	85.7(0.5)	—	—	104.2(0.6)	71.7(0.7)	—	—	99.1(0.4)
CN	122.4(0.7)	121.6(0.8)	120.9(0.5)	117.8(0.8)	133(1)	108.7(0.9)	134(1)	—	—	—	—
NO ₂	61.0(0.2)	61.6(0.4)	62.9(0.5)	62.8(0.9)	—	—	72.5(0.6)	50.5(0.9)	42(1)	—	—
CH ₃	90.1(0.1)	89.0(0.4)	88.6(0.4)	87.5(0.4)	101.4(0.7)	76.5(0.5)	103.5(0.6)	77.6(0.6)	R	84.8(0.2)	84.5(0.4)
CH ₃ CH ₂	R	87.9(0.6)	87.1(0.5)	85.6(0.6)	100.0(0.8)	75.4(0.6)	102.2(0.7)	76.7(0.7)	R	83.3(0.5)	83.5(0.5)
(CH ₃) ₂ CH	R	R	85.6(0.5)	82.7(0.6)	99.2(0.8)	75.2(0.7)	101.0(0.7)	76.4(0.8)	R	83.1(0.5)	81.9(0.5)
(CH ₃) ₃ C	R	R	R	78.6(0.7)	97.8(0.8)	73.2(0.7)	98.3(0.8)	—	R	—	79.4(0.6)
CH ₂ CH	R	R	R	R	116(1)	87.3(0.8)	116(1)	—	—	—	41(3) ^a
CH ₂ CHCH ₂	R	R	R	R	R	62.7(0.6)	—	—	—	—	—
HCC	126.5(0.3)	125.1(0.5)	124.5(0.6) ^a	122.3(0.5) ^a	—	—	—	—	—	—	—
HCC-CH ₂	78(3)	77(3) ^a	—	—	—	—	—	—	—	—	—
C ₆ H ₅	R	R	R	R	R	—	118(1)	R	R	99.3(0.9)	98.8(0.8)
C ₆ H ₅ CH ₂	R	R	R	—	—	—	97(1)	65.2(0.9)	—	—	71.4(0.9)

^a Bond enthalpies of stable organic molecules are tabulated along with their uncertainties. For example, $DH_{298}(\text{C}_6\text{H}_5\text{-OH}) = 112.4 \pm 0.6$ kcal mol⁻¹. These bond enthalpies are calculated from the radical heats of formation from Table 1 and the parent $\Delta_f H_{298}$ values tabulated by Pedley et al.^{19,20} There are a few entries (such as CH₃F or C₆H₅CH₂F) where $\Delta_f H_{298}(\text{parent})$ is not provided by Pedley et al., so we have adopted the value recommended by the NIST Web site⁴⁶ (<http://webbook.nist.gov>); we have marked these parent compounds with an "a". In some cases the heat of formation of the parent species is not available (e.g., vinylmethyl ether, CH₂CH-OCH₃), so the bond enthalpy cannot be computed, and this is marked with a dash. There are a number of redundant entries in this table [e.g., $DH_{298}(\text{C}_6\text{H}_5\text{-CH}_3) = DH_{298}(\text{CH}_3\text{-C}_6\text{H}_5)$], so the second entry is marked with an "R". The uncertainties have been added in quadrature.

A Comparison of the Techniques

Methanol is a nice example of the power and the complementarity of these three experimental methods. The reactions of CH₂OH with HBr and HI were studied over a range of temperatures.¹⁵ Measurement of the forward and reverse rate coefficients (where X = Br or I) for the reactions 17 provides the value of the C-H bond enthalpy of methanol, $DH_{298}(\text{H-CH}_2\text{OH}) = 97.2 \pm 1.0$ kcal mol⁻¹.



PIMS studies of methanol¹⁶ yielded a threshold for the appearance of the hydroxymethyl cation (reaction 18), $AE_{\text{thresh}}(\text{CH}_2\text{OH}^+, \text{CH}_3\text{OH}) = 11.649 \pm 0.003$ eV. Combining



$AE_{\text{thresh}}(\text{CH}_2\text{OH}^+, \text{CH}_3\text{OH})$ with the measured⁹ ionization energy of the hydroxymethyl radical, $IE_0(\text{CH}_2\text{OH}) = 7.553 \pm 0.006$ eV, gives the bond energy of methanol as $D_0(\text{H-CH}_2\text{OH}) = 94.55 \pm 0.14$ kcal mol⁻¹, which corrects to room temperature as $DH_{298}(\text{H-CH}_2\text{OH}) = 96.15 \pm 0.14$ kcal mol⁻¹. As in the earlier case of ethane, the kinetics studies and the PIMS measurements on methanol arrive at values for the C-H bond energy which are in agreement with each other.

Acidity/electron affinity experiments are negative ion techniques, so methanol is studied through $[\text{CH}_3\text{O}]^-$. Gas-phase acidity studies^{6,17} reveal $\Delta_{\text{acid}} H_{298}(\text{CH}_3\text{O-H}) = 381.9 \pm 0.5$ kcal mol⁻¹, and photoelectron spectroscopy has been used^{13,18} to measure the electron affinity of the methoxyl radical, $EA_0(\text{CH}_3\text{O}) = 1.570 \pm 0.006$ eV. Consequently, the acidity/electron affinity cycle in eq 16 provides the BDE of the O-H bond, $DH_{298}(\text{CH}_3\text{O-H}) = 104.6$

± 0.7 kcal mol⁻¹. Notice that the weakest bond in methanol is, unexpectedly, the C-O bond, where $DH_{298}(\text{CH}_3\text{-OH}) = 92.1 \pm 0.1$ kcal mol⁻¹ (Chart 2, below).

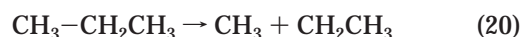
Heats of Formation of Organic Radicals

An important extension of the measured $DH_{298}(\text{R-H})$ values is the determination of the heats of formation of the corresponding radicals, $\Delta_f H_{298}(\text{R}\cdot)$. For the R-H bond enthalpies, eq 3 can be rewritten as eq 19, where the heat of formation of hydrogen atom, $\Delta_f H_{298}(\text{H})$ is known, 52.103 ± 0.003 kcal mol⁻¹ (Table 1), and the heats of formation of over 3000 parent compounds, $\Delta_f H_{298}(\text{RH})$, have been measured by standard calorimetry techniques. This ex-

$$\Delta_f H_{298}(\text{R}\cdot) = DH_{298}(\text{R-H}) + \Delta_f H_{298}(\text{RH}) - \Delta_f H_{298}(\text{H}) \quad (19)$$

pression has been used to compile the heats of formation of the radicals listed in Table 1. There are several compendia available for $\Delta_f H_{298}(\text{RH})$ values, but we believe that the tables of Gurvich et al.⁴ and Pedley et al.^{19,20} are exceptionally reliable and internally consistent. Due to its broader coverage of organic compounds, we use the most recent Pedley compendium²⁰ for the derivations in this Account.

The radical heats of formation listed in Table 1 have been used to determine the bond enthalpies of numerous types of bonds in several common organic molecules (Table 2). For an example of this simple arithmetic, consider the homolytic cleavage of the carbon-carbon bond in propane (reaction 20). The enthalpy of this



reaction can be found by combining $\Delta_f H_{298}(\text{CH}_3\cdot) = 35.05 \pm 0.07$ kcal mol⁻¹ and $\Delta_f H_{298}(\text{CH}_2\text{CH}_3\cdot) = 29.0 \pm 0.4$ kcal

mol^{-1} from Table 1 and $\Delta_f H_{298}(\text{CH}_3\text{CH}_2\text{CH}_3) = -25.0 \pm 0.1 \text{ kcal mol}^{-1}$ from Pedley.²⁰ Equation 21 gives the bond

$$DH_{298}(\text{CH}_3-\text{CH}_2\text{CH}_3) = \Delta_f H_{298}(\text{CH}_3) + \Delta_f H_{298}(\text{CH}_2\text{CH}_3) - \Delta_f H_{298}(\text{CH}_3\text{CH}_2\text{CH}_3) \quad (21)$$

energy of the carbon-carbon bond in propane, $DH_{298}(\text{CH}_3-\text{CH}_2\text{CH}_3) = 89.0 \pm 0.4 \text{ kcal mol}^{-1}$, where the uncertainties have been added in quadrature.

Bond Enthalpies of Organic Molecules

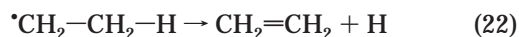
The bond enthalpies listed in Tables 1 and 2 serve to quantify some familiar relationships used by chemists. As expected, the C-H bond energies of alkanes decrease with increasing substitution with the familiar trend of $\text{CH}_4 > 1^\circ > 2^\circ > 3^\circ$; Table 1 reveals this trend as $105 > 101 > 99 > 97 \text{ kcal mol}^{-1}$. Similarly, increased hybridization of the carbon center increases the C-H bond energy as $\text{sp} > \text{sp}^2 > \text{sp}^3$: $DH_{298}(\text{HCC-H}) = 133 > DH_{298}(\text{CH}_2\text{CH-H}) = 111 > DH_{298}(\text{CH}_3\text{CH}_2\text{-H}) = 101 \text{ kcal mol}^{-1}$. The C-H bond energy of C_6H_6 ($113 \text{ kcal mol}^{-1}$) is close to that of CH_2CH_2 ($111 \text{ kcal mol}^{-1}$), while the values for toluene and propene are much lower, $DH_{298}(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) \cong DH_{298}(\text{CH}_2\text{CHCH}_2\text{-H}) \cong 89 \text{ kcal mol}^{-1}$, on account of the extended conjugation in the subsequently formed benzyl and allyl radicals. The bonding of halogen acids also reflects expected trends of decreasing bond enthalpy down the periodic column: $DH_{298}(\text{HF}) = 136.4 > DH_{298}(\text{HCl}) = 103.15 > DH_{298}(\text{HBr}) = 87.54 > DH_{298}(\text{HI}) = 71.32 \text{ kcal mol}^{-1}$. An analogous trend is observed for the halogen-carbon bonds, where the bond enthalpies decrease, $\text{C-F} > \text{C-Cl} > \text{C-Br} > \text{C-I}$.

In contrast to the examples discussed thus far, there are also a number of surprises in the values listed in Tables 1 and 2. For example, it might be expected that the bond energy for water, $DH_{298}(\text{HO-H}) = 119 \text{ kcal mol}^{-1}$, would provide a useful approximation for other O-H bonds.²¹ However, the O-H bond energies of the aliphatic alcohols (RO-H) are both nearly 14 kcal mol^{-1} lower than that of water,²² and those of the hydroperoxides (ROO-H) are some 30 kcal mol^{-1} lower. Further, the bond energies of carboxylic acids, $DH_{298}(\text{RCOO-H}) \cong 112 \text{ kcal mol}^{-1}$, are greater than those of the alcohols but less than that of water. This is somewhat surprising, as one is used to considering the low heterolytic bond enthalpy of the O-H bond in carboxylic acids (i.e., $\text{RCOOH} \rightarrow \text{RCO}_2^- + \text{H}^+$).

Bond Enthalpies of Organic Radicals

In addition to the familiar bond energies of the stable, closed-shell molecules in Tables 1 and 2, it is fun to examine the bond energies of organic radicals, which contain many non-intuitive results (Charts 1-3). While it is beyond the scope of this Account, molecular quantum mechanics can provide a rationale for all of these interesting data.^{8,23-25}

How can one determine the energetics of complex organic radicals? Consider ethyl radical as an example (reaction 22).⁵ Table 1 lists the bond energy of ethane and

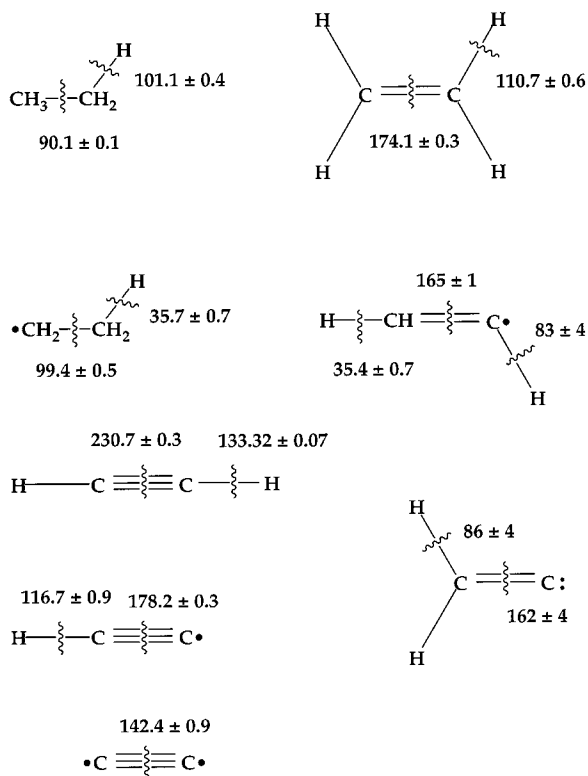


the heat of formation of the ethyl radical, $\Delta_f H_{298}(\text{CH}_2\text{CH}_3) = 29.0 \pm 0.4 \text{ kcal mol}^{-1}$. Therefore, using the heat of formation of ethylene, $\Delta_f H_{298}(\text{CH}_2\text{CH}_2) = 12.5 \pm 0.1 \text{ kcal mol}^{-1}$, from Pedley's compendium,²⁰ one can extract the bond energy of the C-H bond β to the radical center, $DH_{298}(\text{CH}_2\text{CH}_2-\text{H}) = 35.7 \pm 0.4 \text{ kcal mol}^{-1}$. The bond energy in the ethyl radical is nearly a factor of 3 smaller than that of ethane, $DH_{298}(\text{CH}_3\text{CH}_2-\text{H}) = 101 \text{ kcal mol}^{-1}$, because fragmentation of the former leads to formation of a new π -bond, producing a stable alkene, $\text{CH}_2=\text{CH}_2$ (reaction 22). This serves as a good illustration of the definition of bond enthalpy (eq 3), whereby the stability of the dissociated state results in a low bond energy. Further, reaction 22 is an example of how dramatically bond energies can be altered within a molecule following homolysis of the first bond.

Chart 1 shows single bond energies for several important hydrocarbons and hydrocarbon radicals. As expected, the carbon-carbon bond energies increase with increasing bond order: $DH_{298}(\text{CH}_3-\text{CH}_3) = 90 < DH_{298}(\text{CH}_2=\text{CH}_2) = 174 < DH_{298}(\text{HC}\equiv\text{CH}) = 231 \text{ kcal mol}^{-1}$. But compare these values with those for the corresponding radicals: $DH_{298}(\text{CH}_3-\text{CH}_2) = 99 < DH_{298}(\text{CH}_2=\text{CH}) = 165 < DH_{298}(\text{HC}\equiv\text{C}) = 178 \text{ kcal mol}^{-1}$. In going from ethane to ethyl radical, $DH_{298}(\text{C-C})$ has increased by 9 kcal mol^{-1} . The C=C bond energy in the vinyl radical is roughly that of ethylene, but the C=C bond energy in the ethynyl radical falls to 178 from $231 \text{ kcal mol}^{-1}$ in acetylene. The C=C bond energy in C_2 is less than the bond energy of a typical carbon-carbon double bond. These surprising trends can be understood in terms of structural and/or electronic stabilization in the dissociated states. These effects are well described by modern electronic structure theory.^{23,25,26}

Chart 2 shows the bond enthalpies of some oxygen-containing hydrocarbons. The bond enthalpies of CH_3OH have already been discussed. The C-H bond energy in CH_3O falls to 22 kcal mol^{-1} , and the O-H bond energy in CH_2OH is only 30 kcal mol^{-1} . In both cases, loss of an H atom produces a very stable product, namely formaldehyde: $\text{CH}_3\text{O} \rightarrow \text{CH}_2=\text{O} + \text{H}$ and $\text{CH}_2\text{OH} \rightarrow \text{CH}_2=\text{O} + \text{H}$. It is interesting to observe that $DH_{298}(\text{CH}_3-\text{OH}) \cong DH_{298}(\text{CH}_3-\text{O}) \cong 91 \text{ kcal mol}^{-1}$, but the bond energy goes up in the hydroxymethyl radical, $DH_{298}(\text{CH}_2-\text{OH}) = 106 \text{ kcal mol}^{-1}$.

Organic peroxy radicals are important atmospheric and combustion intermediates. The bond energies of *tert*-butyl hydroperoxide are shown in Chart 2. As expected, the weakest bond is the $(\text{CH}_3)_3\text{CO-OH}$ bond (47 kcal mol^{-1}), but this increases in the peroxy radical to $DH_{298}[(\text{CH}_3)_3\text{CO-O}] = 65 \text{ kcal mol}^{-1}$. Conversely, the C-O bond energy drops from 74 kcal mol^{-1} in $(\text{CH}_3)_3\text{C-OOH}$ to 38 kcal mol^{-1} in $(\text{CH}_3)_3\text{C-OO}$, since fragmentation of the latter produces $(\text{CH}_3)_3\text{C}$ and the very stable O_2 molecule, which has formed a new π -bond not present in the reactants. Such stabilization of the product state is

Chart 1. Experimental Bond Enthalpies, DH_{298} , for Several Important Hydrocarbons and Hydrocarbon Radicals^a

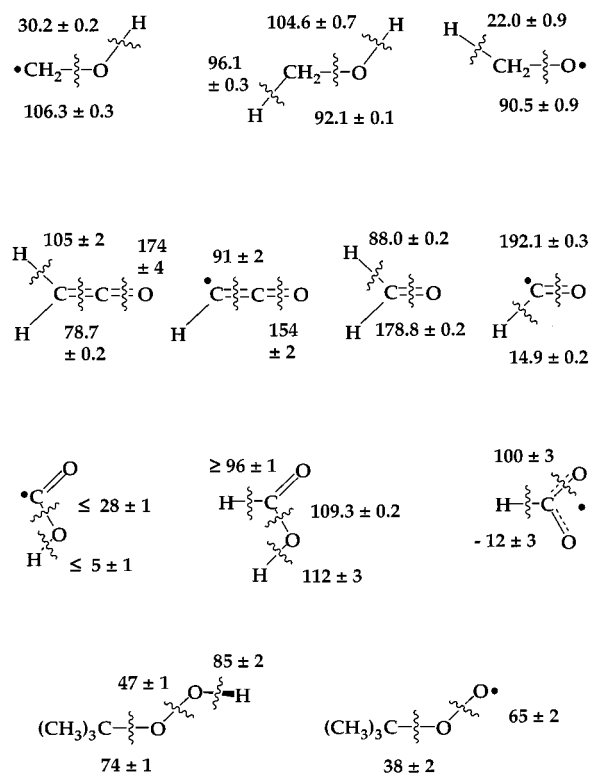
^a Values are in kcal mol⁻¹ and represent the energy required to break only the single bond indicated. Thus, $DH_{298}(\text{HC}\equiv\text{CH} \rightarrow \text{HC} + \text{CH}) = 230.7 \pm 0.2$ kcal mol⁻¹ but $DH_{298}(\text{HCC}-\text{H} \rightarrow \text{HCC} + \text{H}) = 133.32 \pm 0.07$ kcal mol⁻¹.

unavailable in the dissociation of the hydroperoxide, $(\text{CH}_3)_3\text{C}-\text{OOH}$.

Chart 3 shows a comparison of the C-H bond energies of benzene and the phenyl radical. These experimental values are available from the ingenious negative ion studies of Squires and co-workers^{27,28} and demonstrate the increasing bond strengths at the ortho < meta < para positions, quantifying the increasing stability of the resulting benzyne as *o*- > *m*- > *p*-benzyne.

What Are Bond Strengths?

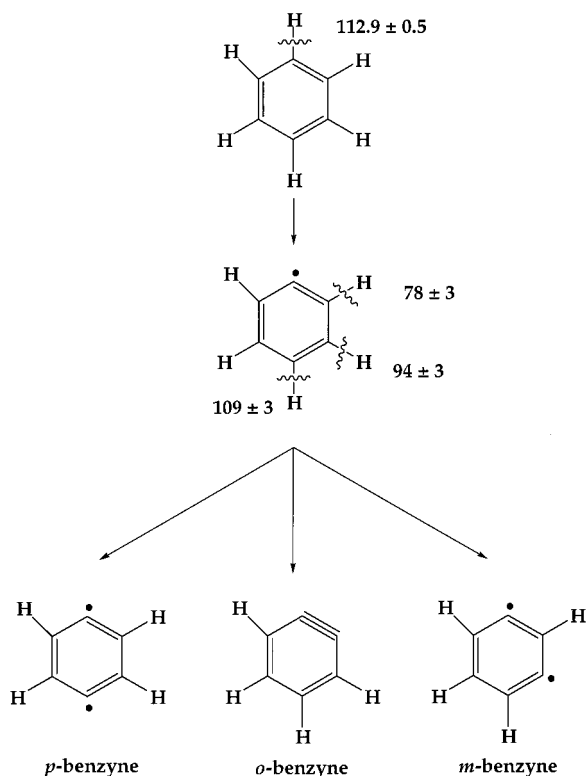
A common term which often appears in the literature is the *average bond energy*. This is defined as the energy required to break all the bonds in a given molecule at 298 K, divided by the number of bonds. For example, consider the *atomization* of methane, which is the dissociation of CH_4 to carbon and four hydrogens ($\text{CH}_4 \rightarrow \text{C} + 4\text{H}$). The enthalpy of atomization is known from the experimental heats of formation of methane, carbon, and hydrogen, $\Delta_{\text{atom}}H_{298}(\text{CH}_4) = \Delta_fH_{298}(\text{C}) + 4\Delta_fH_{298}(\text{H}) - \Delta_fH_{298}(\text{CH}_4) = 397.5$ kcal mol⁻¹. This implies that the methane molecule contains 397.5 kcal mol⁻¹ of energy that is partitioned among four bonds; thus, $D_{\text{av}}H_{298} = 99.4$ kcal mol⁻¹. In Table 1, we list the separate experimental bond enthalpies of methane and its constituent radicals CH_3 , CH_2 , and CH : $DH_{298}(\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}) = 104.99$ kcal mol⁻¹, $DH_{298}(\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}) = 110.4$ kcal mol⁻¹, $DH_{298}(\text{CH}_2 \rightarrow$

Chart 2. Experimental Bond Enthalpies, DH_{298} , for Several Important Oxycarbons and OxyCarbon Radicals^a

^a Values are in kcal mol⁻¹ and represent the energy required to break only the single bond indicated. Thus, $DH_{298}(\text{CH}_3\text{O}-\text{H} \rightarrow \text{CH}_3\text{O} + \text{H}) = 104.6 \pm 0.7$ kcal mol⁻¹ but $DH_{298}(\text{H}-\text{CH}_2\text{OH} \rightarrow \text{H} + \text{CH}_2\text{OH}) = 96.1 \pm 0.3$ kcal mol⁻¹ and $DH_{298}(\text{CH}_3-\text{OH} \rightarrow \text{CH}_3 + \text{OH}) = 92.1 \pm 0.1$ kcal mol⁻¹.

$\text{CH} + \text{H}) = 101.3$ kcal mol⁻¹, and $DH_{298}(\text{CH} \rightarrow \text{C} + \text{H}) = 80.9$ kcal mol⁻¹. Notice that *not one* of these bond enthalpies is equal to the average bond energy of methane. Therefore, one should be cautious when interpreting the significance of the average bond enthalpy of a molecule. It is important to note that if these four independently measured bond enthalpies are combined, they give $\Delta_{\text{rxn}}H_{298}(\text{CH}_4 \rightarrow \text{C} + 4\text{H}) = 397.5 \pm 0.6$ kcal mol⁻¹, as required by the first law of thermodynamics.

One should also be careful about the term *bond strength* and the tendency to treat these energetic quantities as transferable objects between different molecules. Equation 3 shows that the bond dissociation energy is the energy of a *fragmentation reaction* rather than any intrinsic property of a chemical bond. Acetylene is a good example (Chart 1). One could say that the $\text{HC}\equiv\text{CH}$ bond strength is 231 kcal mol⁻¹ [$\text{HC}\equiv\text{CH} \rightarrow \text{HC} + \text{CH}$] and that both C-H bonds are equivalent, with bond strengths of 81 kcal mol⁻¹ [$\text{HC} \rightarrow \text{C} + \text{H}$, see Table 1]. However, one could equally well claim that the first CH bond strength is 133 kcal mol⁻¹ [$\text{HC}\equiv\text{CH} \rightarrow \text{HC}\equiv\text{C} + \text{H}$], which is different from the second CH bond strength of 117 kcal mol⁻¹ [$\text{HC}\equiv\text{C} \rightarrow \text{C}\equiv\text{C} + \text{H}$], while the CC bond strength [$\text{C}\equiv\text{C} \rightarrow \text{C} + \text{C}$] is only 142 kcal mol⁻¹. Or alternatively, the first CH bond strength is 133 kcal mol⁻¹, while the CC bond strength [$\text{HC}\equiv\text{C} \rightarrow \text{HC} + \text{C}$] is 178 kcal mol⁻¹, and the second CH bond strength [$\text{HC} \rightarrow \text{H} + \text{C}$] is only 81 kcal mol⁻¹. Clearly, one arrives at different bond

Chart 3. Experimental Bond Enthalpies, DH_{298} , for Benzene and Phenyl Radical^a

^a Values are in kcal mol⁻¹ and represent the energy required to break only the single bond indicated. Thus, $DH_{298}(\text{C}_6\text{H}_5\text{-H} \rightarrow \text{C}_6\text{H}_5 + \text{H}) = 112.9 \pm 0.5$ kcal mol⁻¹ but $DH_{298}(\text{C}_6\text{H}_4\text{-H} \rightarrow \text{H} + \textit{o}\text{-C}_6\text{H}_4) = 78 \pm 3$ kcal mol⁻¹, $DH_{298}(\text{C}_6\text{H}_4\text{-H} \rightarrow \text{H} + \textit{m}\text{-C}_6\text{H}_4) = 94 \pm 3$ kcal mol⁻¹, and $DH_{298}(\text{C}_6\text{H}_4\text{-H} \rightarrow \text{H} + \textit{p}\text{-C}_6\text{H}_4) = 109 \pm 3$ kcal mol⁻¹.

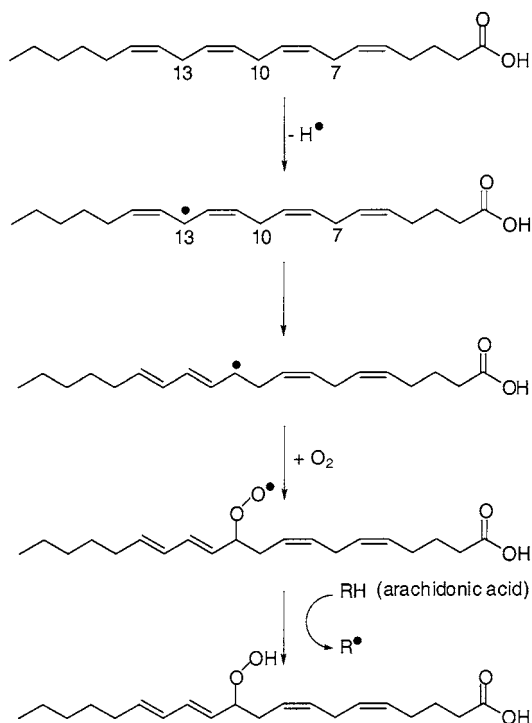
strengths by breaking the bonds in different orders. Rigorous quantum mechanical discussions of these trends are available elsewhere,²⁶ along with other provocative discussions of bond strengths.^{23,24,29}

The example of HCCH serves to reiterate that the bond enthalpy is the enthalpy of a homolysis reaction (eq 3) and thus depends exclusively on the relative stability of reactant and product states. More generally, creation of new bonds in the products, or otherwise stabilized products, always decreases the bond enthalpy. As an example, consider ketene in Chart 2. The carbon-carbon bond enthalpy^{30,31} of ketene, $DH_{298}(\text{CH}_2=\text{CO}) = 78.7 \pm 0.2$ kcal mol⁻¹, is almost 100 kcal mol⁻¹ less than that of ethylene, $DH_{298}(\text{CH}_2=\text{CH}_2) = 174$ kcal mol⁻¹, because one of the products of the ketene fragmentation is an extremely stable molecule, namely carbon monoxide. This example illustrates that not all double bonds are created equal^{24,26} and that extrapolations of bond energies from one molecular species to another must be conducted carefully.

Bond Enthalpies in Solution

The bond enthalpies tabulated in this Account are exclusively gas-phase values. This raises the question of how to relate gas-phase bond enthalpies to chemical problems occurring in solution? The difference between a gas-phase bond enthalpy and that in solution, $D_{\text{soln}}H_{298}(\text{R-H})$,

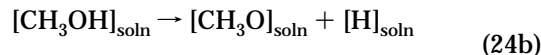
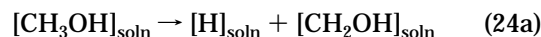
Scheme 1



depends on the difference in the enthalpy of solvation, $\Delta_{\text{soln}}H_{298}$, of the two radicals and the parent compound, as expressed in terms of eq 23. There are not many

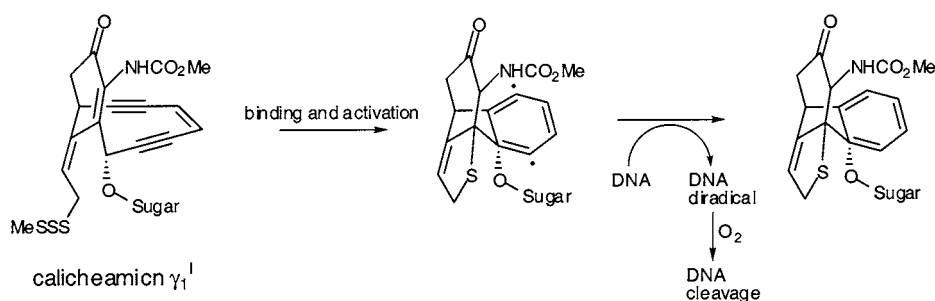
$$D_{\text{soln}}H_{298}(\text{R-H}) = DH_{298}(\text{R-H}) - [\Delta_{\text{soln}}H_{298}(\text{R}) + \Delta_{\text{soln}}H_{298}(\text{H}) - \Delta_{\text{soln}}H_{298}(\text{RH})] \quad (23)$$

accurate measurements available for the enthalpy of solvation of radical species, and we can only estimate the effects of solvation on organic BDEs. The solvation energy of a hydrogen atom is likely to be negligible in most solvents, and therefore the correction to an R-H gas-phase bond enthalpy can be approximated as $[\Delta_{\text{soln}}H_{298}(\text{R}) - \Delta_{\text{soln}}H_{298}(\text{RH})]$. As both the radical and the parent are neutral, the solvation energies are likely to be small and similar in most cases, particularly in nonpolar solvents. The small effect on bond enthalpy is likely to be most noticeable in protic polar solvents, where hydrogen bonding may play a key role in preferentially stabilizing the radical or parent in solution. Consider, for example, the C-H and O-H bond enthalpies of CH₃OH in a polar protic solvent (reactions 24).



While in reaction 24a both methanol and the hydroxymethyl radical can hydrogen bond to the surrounding solvent, such stabilization may be less prevalent for the methoxyl radical in reaction 24b due to the absence of the highly polarized O-H bond. Therefore, one might surmise that the H-CH₂OH bond energy of methanol in a protic solvent would be largely unchanged from the gas phase, while the CH₃O-H value could be slightly higher in solution. There is clearly much work to be done in this area.

Scheme 2



Bond Enthalpies in Chemistry

The bond enthalpies tabulated in this Account serve as models for common molecular motifs. Careful consideration of these values can provide useful thermochemical estimates for complex chemical problems, provided that only a single bond-breaking or -forming event is considered at a time.

Oxidation of poly-unsaturated fatty acids is a crucial aspect of oxidative stress in biological systems.³² Consider the thermochemistry of peroxidation of arachidonic acid as shown in simplified form in Scheme 1. We can estimate the relative bond strengths of the various R–H bonds in arachidonic acid by comparing them to model systems from Table 1: $DH_{298}(\text{carboxylic acid, O–H}) \cong 112 > DH_{298}(\text{vinyl, C–H}) \cong 111 > DH_{298}(\text{methylene, C–H}) \cong 99 > DH_{298}(\alpha\text{-carbonyl, C–H}) \cong 94 > DH_{298}(\text{allylic, C–H}) \cong 88 \text{ kcal mol}^{-1} > DH_{298}(\text{bisallylic, C–H})$. Given these estimates, the hydrogens most susceptible to radical abstraction will be those in the allylic positions. While there is at present no direct data for doubly allylic C–H bond enthalpies, one might conjecture that the bond energy will be roughly 80 kcal mol⁻¹, given that the difference between a typical methylenic C–H (e.g., $DH_{298}(\text{CH}_2\text{CH}_2\text{–H}) \cong 98.6 \text{ kcal mol}^{-1}$) and a singly allylic C–H (e.g., $DH_{298}(\text{H}_2\text{C}=\text{CHCH}_2\text{–H}) \cong 88.8 \text{ kcal mol}^{-1}$) is about 10 kcal mol⁻¹. Thus, the bisallylic hydrogens at carbons 7, 10, and 13 represent the most labile hydrogens in the molecule. Once a carbon-centered radical is produced and rearranged to its most stable form, it will readily add O₂ to form a peroxy radical: Chart 2 indicates that the OO–CMe₃ bond enthalpy is 38 kcal mol⁻¹. Given that the O–H bond enthalpy of a hydroperoxide is approximately 85 kcal mol⁻¹, a radical chain reaction will be exothermic.

The biological activity of the enediyne anticancer antibiotic agents is thought to be due to their ability to form reactive diradicals *in situ*.³³ Molecules such as calicheamicin γ_1^I possess an extended sugar residue which serves to deliver the enediyne moiety, the active part of the molecule, to a sequence-specific position on the DNA double-helix. Upon delivery to the target, the enediyne functionality is activated to undergo a Bergman cycloaromatization, which yields a substituted *p*-benzynes (Scheme 2). From Chart 3 we can estimate that the diradical can abstract all hydrogens bound by $\leq 109 \text{ kcal mol}^{-1}$. This makes the *p*-benzynes a quite powerful hydrogen abstraction reagent, and further, once one hydrogen has been

abstracted, a substituted phenyl radical results, which can abstract all hydrogens bound by $\leq 113 \text{ kcal mol}^{-1}$. Thus, two exothermic hydrogen abstractions by the reactive *p*-benzynes moiety can lead to selective cutting of double-stranded DNA.

Summary

The critically evaluated bond enthalpies listed in Tables 1 and 2 should serve as an important resource for the organic chemist. The values listed may be used to calculate rigorous experimental thermochemistry for many common reactions, and further, with appropriate care, instructive estimations of reaction thermochemistry can be made for complex chemical problems.

This work was supported by grants from the Chemical Physics Program, United States Department of Energy (DE-FG02-87ER13695), and the National Science Foundation (CHE-0201848). We are grateful for the sustained advice and criticism from our Colorado colleagues: Carl Lineberger, Veronica Bierbaum, Shuji Kato, Mark Nimlos, Xu Zhang, Bob Damrauer, Charles H. DePuy, Geoff Tyndall, and Veronica Vaida. We are also continually educated by our friends: Emily Carter, George Petersson, Larry Harding, Kent Ervin, Richard O'Hair, and Branko Ruscic. Finally G.B.E. would like to thank Joseph Berkowitz, now retired, for 25 years of friendship and physics.

References

- (1) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.
- (2) Mills, I.; Cvitas, T.; Homann, K.; Kallay, N.; Kuchitsu, K. *Quantities, Units, and Symbols in Physical Chemistry*; Blackwell Scientific Publications: Oxford, 1988. This reference lists the IUPAC's guidelines concerning thermochemical symbols, which we adopt. Instead of the more common expressions $\Delta G_{\text{rxn}}^{298}(1)$, $\Delta H_f^\circ(\text{R})$, or $\Delta H_f^{298}(\text{RH})$, the use of $\Delta_{\text{rxn}}G_{298}(1)$, $\Delta_f H_0(\text{R})$, or $\Delta_f H_{298}(\text{RH})$ is recommended. See p 46.
- (3) Herzberg, G. H. *Molecular Spectra and Molecular Structure: Infrared and Raman Spectra of Polyatomic Molecules*; D. Van Nostrand: Princeton, NJ, 1945; Vol. II, see Chapter V.
- (4) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B.; Iorish, V. S. *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere: New York, 1991; Vol. 2.
- (5) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; Charles H. DePuy; Lineberger, W. C.; Ellison, G. B. Bond Strengths of Ethylene and Acetylene. *J. Am. Chem. Soc.* **1990**, *112*, 5750–5759.
- (6) Ervin, K. M.; DeTuri, V. F. Anchoring the Gas-Phase Acidity Scale: Experiment and Theory. *J. Phys. Chem. A* **2002**, *106*, 9947–9956.
- (7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.;

- Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (8) Petersson, G. A. In *Computational Thermochemistry*; Irikura, K. K., Frurip, D. J., Eds.; ACS Symposium Series 677; American Chemical Society: Washington, DC, 1998; pp 237–266.
- (9) Berkowitz, J.; Ellison, G. B.; Gutman, D. Three Methods to Measure RH Bond Energies. *J. Phys. Chem.* **1994**, *98*, 2744–2765.
- (10) Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. Kinetics and Thermochemistry of $R + HBr \leftrightarrow RH + Br$ Reactions—Determinations of the Heat of Formation of C_2H_5 , $i-C_3H_7$, $sec-C_4H_9$, and $tert-C_4H_9$. *J. Phys. Chem.* **1992**, *96*, 9847–9855.
- (11) Ruscic, B.; Berkowitz, J.; Curtiss, L. A.; Pople, J. A. The Ethyl Radical—Photoionization and Theoretical Studies. *J. Chem. Phys.* **1989**, *91*, 114–121.
- (12) Ervin, K. M. Experimental techniques in gas-phase ion thermochemistry. *Chem. Rev.* **2001**, *101*, 391–444.
- (13) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F., III; Nandi, S.; Ellison, G. B. Atomic and Molecular Electron Affinities: Photoelectron Experiments and Theoretical Computations. *Chem. Rev.* **2002**, *102*, 231–282.
- (14) Ramond, T. M.; Blanksby, S. J.; Kato, S.; Bierbaum, V. M.; Davico, G. E.; Schwartz, R. L.; Lineberger, W. C.; Ellison, G. B. The Heat of Formation of the Hydroperoxyl Radical HOO via Negative Ion Studies. *J. Phys. Chem. A* **2002**, *106*, 9641–9647.
- (15) Seetula, J. A.; Gutman, D. Kinetics of the $CH_2OH + HBr$ and $CH_2OH + HI$ Reactions and Determination of the Heat of Formation of CH_2OH . *J. Phys. Chem.* **1992**, *96*, 5401–5405.
- (16) Ruscic, B.; Berkowitz, J. Heat of Formation of CH_2OH and $D_0(H-CH_2OH)$. *J. Phys. Chem.* **1993**, *97*, 11451–11455.
- (17) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1), 1.
- (18) Ramond, T. M.; Davico, G. E.; Schwartz, R. L.; Lineberger, W. C. Vibronic structure of alkoxy radicals via photoelectron spectroscopy. *J. Chem. Phys.* **2000**, *112*, 1158–1169.
- (19) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemistry of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986.
- (20) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994.
- (21) The huge value of $DH_{298}(H_2O)$ is the reason that the OH radical is such an important species in atmospheric chemistry. Hydroxyl radicals result from solar photodissociation of O_3 , and they react with all organic species pumped into the atmosphere.
- (22) Ingold, K. U.; Wright, J. S. Understanding trends in C–H, N–H, and O–H bond dissociation enthalpies. *J. Chem. Educ.* **2000**, *77*, 1062–1064.
- (23) Goddard, W. A., III; Harding, L. B. The Description of Chemical Bonding from Ab Initio Calculations. *Annu. Rev. Phys. Chem.* **1978**, *29*, 363–396.
- (24) Carter, E. A.; Goddard, W. A. Relation between Singlet Triplet Gaps and Bond-Energies. *J. Phys. Chem.* **1986**, *90*, 998–1001.
- (25) Dunning, T. H., Jr. A Road Map for the Calculation of Molecular Binding Energies. *J. Phys. Chem. A* **2000**, *104*, 9062–9080.
- (26) Wu, C. J.; Carter, E. A. *Ab Initio* Thermochemistry for Unsaturated C_2 Hydrocarbons. *J. Phys. Chem.* **1991**, *95*, 8352–8363.
- (27) Wenthold, P. G.; Squires, R. R. Gas-phase acidities of *o*-, *m*- and *p*-dehydrobenzoic acid radicals. Determination of the substituent constants for a phenyl radical site. *Int. J. Mass Spectrom.* **1998**, *175*, 215–224.
- (28) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. Ultraviolet photoelectron spectroscopy of the *o*-, *m*-, and *p*-benzynes negative ions. Electron affinities and singlet–triplet splittings for *o*-, *m*-, and *p*-benzyne. *J. Am. Chem. Soc.* **1998**, *120*, 5279–5290.
- (29) Chen, P. In *Unimolecular and Bimolecular Reaction Dynamics*; Ng, C. Y., Baer, T., Powis, I., Eds.; John Wiley & Sons: New York, 1994; Vol. 3, pp 372–425.
- (30) Oakes, J. M.; Jones, M. E.; Bierbaum, V. M.; Ellison, G. B. Photoelectron Spectroscopy of CCO^- and $HCCO^-$. *J. Phys. Chem.* **1983**, *87*, 4810–4815.
- (31) Ruscic, B.; Litorja, M.; Asher, R. L. Ionization energy of methylene revisited: Improved values for the enthalpy of formation of CH_2 and the bond dissociation energy of CH_3 via simultaneous solution of the local thermochemical network. *J. Phys. Chem. A* **1999**, *103*, 8625–8633.
- (32) Halliwell, B.; Gutteridge, J. M. C. *Free Radicals in Biology and Medicine*, 3rd ed.; Oxford University Press Inc.: New York, 1999.
- (33) Nicolaou, K. C.; Smith, A. L.; Yue, E. W. Chemistry and Biology of Natural and Designed Eneidyne. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 5881–5888.
- (34) Ruscic, B.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Harding, L. B.; Asher, R. L.; Wagner, A. F. Evidence for a lower enthalpy of formation of hydroxyl radical and a lower gas-phase bond dissociation energy of water. *J. Phys. Chem. A* **2001**, *105*, 1–4.
- (35) Davis, H. F.; Kim, B. S.; Johnston, H. S.; Lee, Y. T. Dissociation-Energy and Photochemistry of NO_3 . *J. Phys. Chem.* **1993**, *97*, 2172–2180.
- (36) Mordaunt, D. H.; Ashfold, M. N. R. Near-Ultraviolet Photolysis of C_2H_2 —a Precise Determination of $D_0(HCC-H)$. *J. Chem. Phys.* **1994**, *101*, 2630–2631.
- (37) Wenthold, P. G.; Squires, R. R. Biradical Thermochemistry from Collision-Induced Dissociation Threshold Energy Measurements. Absolute Heats of Formation of *ortho*-, *meta*-, and *para*-Benzyne. *J. Am. Chem. Soc.* **1994**, *116*, 6401–6412.
- (38) Ellison, G. B.; Davico, G. E.; Bierbaum, V. M.; DePuy, C. H. The Thermochemistry of the Benzyl and Allyl Radicals and Ions. *Int. J. Mass Spectrom. Ion Processes* **1996**, *156*, 109–131.
- (39) Nicovich, J. M.; Kreutter, K. D.; Vandijk, C. A.; Wine, P. H. Temperature-Dependent Kinetics Studies of the Reactions $Br(^2P_{3/2}) + H^2S$ Reversible $SH + HBr$ and $Br(^2P_{3/2}) + CH_3SH$ Reversible $CH_3S + HBr$ —Heats of Formation of SH and CH_3S Radicals. *J. Phys. Chem.* **1992**, *96*, 2518–2528.
- (40) Ruscic, B.; Berkowitz, J. Photoionization Mass-Spectrometric Studies of the Isomeric Transient Species CH_2SH and CH_3S . *J. Chem. Phys.* **1992**, *97*, 1818–1823.
- (41) DeTuri, V. F.; Ervin, K. M. Proton transfer between Cl^- and C_6H_5OH . O–H bond energy of phenol. *Int. J. Mass Spectrom.* **1998**, *175*, 123–132.
- (42) Blanksby, S. J.; Ramond, T. M.; Davico, G. E.; Nimlos, M. R.; Kato, S.; Bierbaum, V. M.; Lineberger, W. C.; Ellison, G. B.; Okumura, M. Negative Ion Photoelectron Spectroscopy, Gas-Phase Acidity, and Thermochemistry of the Peroxyl Radicals CH_3OO and CH_3CH_2OO . *J. Am. Chem. Soc.* **2001**, *123*, 9585–9596.
- (43) Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. Kinetics and Thermochemistry of the CH_3CO Radical—Study of the $CH_3CO + HBr \rightarrow CH_3CHO + Br$ Reaction. *J. Phys. Chem.* **1992**, *96*, 5881–5886.
- (44) Thermochemistry evaluated via the “acidity/EA cycle” described by Berkowitz et al. Wang et al. report $EA(CH_3CO_2) = 3.35 \pm 0.08$ eV [*Phys. Rev. Lett.* **1998**, *81*, 2667]; Kim et al. report $EA(HCO_2) = 3.498 \pm 0.015$ eV [*J. Chem. Phys.* **1995**, *103*, 7801]; Wang et al. report $EA(C_6H_5CO_2) = 3.7 \pm 0.1$ eV [*J. Chem. Phys.* **2000**, *113*, 653]. Gas-phase acidities are measured by Cumming and Kebarle [*Can. J. Chem.* **1978**, *56*, 1]; $\Delta_{acid}H_{298}(HCOO-H) = 345 \pm 3$ kcal mol⁻¹, $\Delta_{acid}H_{298}(CH_3CO_2-H) = 349 \pm 3$ kcal mol⁻¹, $\Delta_{acid}H_{298}(C_6H_5CO_2-H) = 339 \pm 3$ kcal mol⁻¹.
- (45) Ruscic, B.; Litorja, M. Photoionization of HOCO revisited: a new upper limit to the adiabatic ionization energy and lower limit to the enthalpy of formation. *Chem. Phys. Lett.* **2000**, *316*, 45–50.
- (46) Linstrom, P. J.; Mallard, W. G. *NIST Chemistry WebBook*; NIST Standard Reference Database No. 69; National Institute of Standards and Technology: Gaithersburg MD, 2001; <http://webbook.nist.gov>.

AR020230D