Bond Dissociation Energies of Organic Molecules

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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, $\Delta_{rxn}H_{298}(1)$, which is by definition[2] the bond dissociation enthalpy of the molecule AB, $DH_{298}(AB)$:

$$AB \rightarrow A + B \quad (1)$$

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:
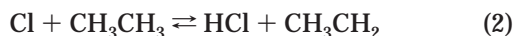
$$Cl + CH_3CH_3 \rightleftharpoons HCl + CH_3CH_2 \quad (2)$$

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

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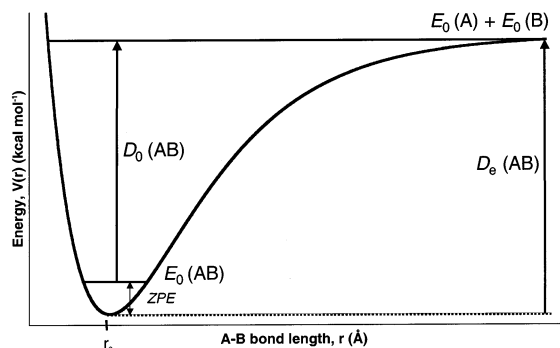
enthalpy of ethane, $DH_{298}(CH_3CH_2-H) = 101.1 \pm 0.4$ kcal mol^{-1}, and the bond enthalpy of hydrochloric acid, $DH_{298}(HCl) = 103.15 \pm 0.03$ kcal mol^{-1}, the forward reaction is determined to be exothermic since $\Delta_{rxn}H_{298}(2) = DH_{298}(CH_3CH_2-H) - DH_{298}(HCl) = -2.1 \pm 0.4$ kcal mol^{-1}; the reverse reaction is endothermic, $\Delta_{rxn}H_{298}(-2) = +2.1 \pm 0.4$ 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, $\Delta_{rxn}H_{298}(1)$, and thus depends exclusively on the relative enthalpies of formation of reactant and product states:

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

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 spectroscopists[3] 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, $D_0(AB) = D_e(AB) - ZPE$ (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).

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Table 1. Molecular Bond Dissociation Energies for RH → 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	$OH^- \rightarrow O^- + H$	110.21 ± 0.07	-33.23 ± 0.07	34
HF	136.25 ± 0.01	18.83 ± 0.17	6	$OH^+ \rightarrow O + H^+$	115.2 ± 0.1	59.55 ± 0.02	34
HCl	103.15 ± 0.03	29.03 ± 0.04	9	H_2S	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_2O	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_2CH-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_6H_5-H	112.9 ± 0.5	80.5 ± 0.5	6
CH	80.9 ± 0.2	171.3 ± 0.1	9	$C_6H_5 \rightarrow o\text{-}C_6H_4 + H$	78 ± 3	106 ± 3	37
CH_3CH_2-H	101.1 ± 0.4	29.0 ± 0.4	10	$C_6H_5 \rightarrow m\text{-}C_6H_4 + H$	94 ± 3	122 ± 3	37
$(CH_3)_2CH-H$	98.6 ± 0.4	21.5 ± 0.4	10	$C_6H_5 \rightarrow p\text{-}C_6H_4 + H$	109 ± 3	138 ± 3	37
$CH_3CH_2(CH_3)CH-H$	98.2 ± 0.5	16.1 ± 0.5	10	CH_2CHCH_2-H	88.8 ± 0.4	41.4 ± 0.4	38
$(CH_3)_3C-H$	96.5 ± 0.4	12.3 ± 0.4	10	$C_6H_5CH_2-H$	89.8 ± 0.6	49.7 ± 0.6	38
				Alcohols			
$H-CH_2OH$	96.1 ± 0.2	-4.08 ± 0.2	16	CH_3CH_2O-H	104.7 ± 0.8	-3.6 ± 0.8	6
CH_3O-H	104.6 ± 0.7	4.3 ± 0.7	6	$(CH_3)_2CHO-H$	105.7 ± 0.7	-11.5 ± 0.7	6
CH_3S-H	87.4 ± 0.5	29.8 ± 0.4	39,40	$(CH_3)_3CO-H$	106.3 ± 0.7	-20.5 ± 0.7	6
$H-CH_2SH$	94 ± 2	36 ± 2	39, 40	C_6H_5O-H	90 ± 3	-58 ± 3	41
				Peroxides			
$HOO-H$	87.8 ± 0.5	3.2 ± 0.5	14	CH_3CH_2OO-H	85 ± 2	-6.8 ± 2.3	42
CH_3OO-H	88 ± 1	4.8 ± 1.2	42	$(CH_3)_3COO-H$	84 ± 2	-25.2 ± 2.3	42
				Carbonyls			
$H-CHO$	88.144 ± 0.008	10.1 ± 0.1	6	$H-COOH$ is $\geq$	96 ± 1	-46.5 ± 0.7	45
$CH_3C(O)-H$	89.4 ± 0.3	-2.4 ± 0.3	43	CH_3COO-H	112 ± 3	-43 ± 3	44
$H-CH_2CHO$	94 ± 2	2.5 ± 2.2	9	C_6H_5COO-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 → 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, $\int_0^{298} C_p(H)\, dT = 1.48$ kcal mol^{-1}, so $D_0(RH) \cong DH_{298}(RH) - 1.5$ 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 ± 3 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 $T \rightarrow 0$ 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 $T = 0$ 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, $U \cong E_0 = E_{elec} + ZPE$ (Figure 1). Therefore, at 0 K, the homolytic bond dissociation energy can be given in terms of eq 5:

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

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 [$K_{eq}(2) = k_2/k_{-2}$], which is related to the Gibbs free energy of the reaction, $\Delta_{rxn}G_{298}(2)$, at constant pressure by eq 6, where $R = 1.987$ cal mol^{-1} K^{-1} is the gas constant and $T = 298$ K is the equilibrium standard-state temperature.

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

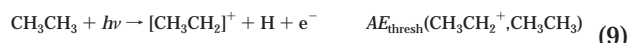$$\Delta_{rxn}H_{298}(2) = \Delta_{rxn}G_{298}(2) + (298)\,\Delta_{rxn}S_{298}(2) \quad (7)$$

The Gibbs free energy of reaction is related to the enthalpy of reaction, $\Delta_{rxn}H_{298}(2)$, by eq 7. The reaction entropy, $\Delta_{rxn}S_{298}(2)$, can be obtained from a statistical mechanics analysis[3] but is typically small for a simple hydrogen abstraction such as reaction 2 (e.g., $\Delta_{rxn}S_{298} \cong 26$ cal mol^{-1} K^{-1}). The experimentally determined $\Delta_{rxn}H_{298}(2)$ 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}(HCl), the carbon−hydrogen bond enthalpy of ethane can be extracted via eq 8:

$$DH_{298}(CH_3CH_2-H) = \Delta_{rxn}H_{298}(2) + DH_{298}(HCl) \quad (8)$$

Halogen atom kinetic studies[10] of ethane reveal that $DH_{298}(CH_3CH_2-H) = 101.1 \pm 0.4$ 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$_3$CH$_3$ in reaction 9.

$$CH_3CH_3 + h\nu \rightarrow [CH_3CH_2]^+ + H + e^- \qquad AE_{thresh}(CH_3CH_2^+, CH_3CH_3) \quad (9)$$

$$[CH_3CH_2]^+ + e^- \rightarrow CH_3CH_2 + h\nu \qquad -IE_0(CH_3CH_2) \quad (10)$$

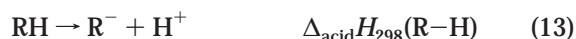$$CH_3CH_3 \rightarrow CH_3CH_2 + H \qquad D_0(CH_3CH_2-H) \quad (11)$$

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, $AE_{thresh}(CH_3CH_2^+, CH_3CH_3)$. This quantity can be directly measured by scanning the energy of a light beam passing through a sample of ethane until the appearance of [CH$_3$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, $IE_0(CH_3CH_2)$, is measured. Combining reactions 9 and 10 gives reaction 11, and thus the bond dissociation energy can be calculated via eq 12. PIMS studies[11] of

$$D_0(CH_3CH_2-H) = AE_{thresh}(CH_3CH_2^+, CH_3CH_3) - IE_0(CH_3CH_2) \quad (12)$$

ethane and ethyl iodide imply that $D_0(CH_3CH_2-H) = 99.5 \pm 0.5$ kcal mol^{-1}. When the $D_0(CH_3CH_2-H)$ value is corrected to 298 K via eq 4, it matches the radical kinetics value, $DH_{298}(CH_3CH_2-H) = 101.1 \pm 0.4$ 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, $\Delta_{acid}H_{298}$ (reaction 13).

$$RH \rightarrow R^- + H^+ \qquad \Delta_{acid}H_{298}(R-H) \quad (13)$$

$$R^- + h\nu \rightarrow R + e^- \qquad EA_0(R) \quad (14)$$

$$H^+ + e^- \rightarrow H + h\nu \qquad -IE_0(H) \quad (15)$$

Summing reactions 13−15 gives[12] the homolytic bond enthalpy in eq 16.

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

In eq 16, "[thermal correction]" is a set of heat capacity integrals, $\int[C_p(R) - C_p(R^-) + C_p(H) - C_p(H^+)]\,dT$, which may be evaluated as previously described, but their value is generally less than 0.3 kcal mol^{-1}. By rearranging eq 16, one can estimate typical values for $\Delta_{acid}H_{298}(RH)$; since $DH_{298}(RH)$ for many organics is approximately 100 kcal mol^{-1}, the $IE_0(H)$ is 313.6 kcal mol^{-1}, and the electron affinities[13] of most radicals are about 23 kcal mol^{-1}, $\Delta_{acid}H_{298}(R-H)$ is [100 + 313 − 23], or roughly 390 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, $\Delta_{acid}H_{298}(R-H) \gg DH_{298}(RH)$. 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$_3$CH$_3$ since the [CH$_3$CH$_2$]$^-$ carbanion cannot be prepared in the gas phase. But H$_2$O$_2$ is a nice example of the negative ion cycle. Experiments conducted by Ramond et al.[14] measured the enthalpy of deprotonation of hydrogen peroxide, $\Delta_{acid}H_{298}(HOO-H) = 376.5$ kcal mol^{-1}, and the electron affinity of the hydroperoxyl radical, EA_0(HOO) = 24.86 kcal mol^{-1}. Using these values in eq 16 gives $DH_{298}(HOO-H) = 376.5 - 313.58 + 24.86 = 87.8 \pm 0.5$ 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$_3$)$_2$	*tert*-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}(C$_6$H$_5$–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 CH$_3$F or C$_6$H$_5$CH$_2$F) where $\Delta_f H_{298}$(parent) is not provided by Pedley et al., so we have adopted the value recommended by the NIST Web site[46] (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, CH$_2$CH–OCH$_3$), 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}(C$_6$H$_5$–CH$_3$) = DH_{298}(CH$_3$–C$_6$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 CH$_2$OH 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}(H–CH$_2$OH) = 97.2 $\pm$ 1.0 kcal mol^{-1}.

$$X + CH_3OH \rightleftharpoons HX + CH_2OH \qquad (17)$$
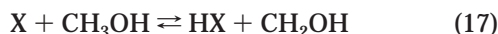
PIMS studies of methanol[16] yielded a threshold for the appearance of the hydroxymethyl cation (reaction 18), AE_{thresh}(CH$_2$OH$^+$, CH$_3$OH) = 11.649 $\pm$ 0.003 eV. Combining

$$CH_3OH + h\nu_{thresh} \rightarrow {}^+[CH_2OH] + H \qquad (18)$$

AE_{thresh}(CH$_2$OH$^+$,CH$_3$OH) with the measured[9] ionization energy of the hydroxymethyl radical, IE_0(CH$_2$OH) = 7.553 $\pm$ 0.006 eV, gives the bond energy of methanol as D_0(H–CH$_2$OH) = 94.55 $\pm$ 0.14 kcal mol^{-1}, which corrects to room temperature as DH_{298}(H–CH$_2$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 [CH$_3$O]$^-$. Gas-phase acidity studies[6,17] reveal $\Delta_{acid}H_{298}$(CH$_3$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(CH$_3$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}(CH$_3$O–H) = 104.6

$\pm$ 0.7 kcal mol^{-1}. Notice that the weakest bond in methanol is, unexpectedly, the C–O bond, where DH_{298}(CH$_3$–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}(R–H) values is the determination of the heats of formation of the corresponding radicals, $\Delta_f H_{298}$(R). For the R–H bond enthalpies, eq 3 can be rewritten as eq 19, where the heat of formation of hydrogen atom, $\Delta_f H_{298}$(H) is known, 52.103 $\pm$ 0.003 kcal mol^{-1} (Table 1), and the heats of formation of over 3000 parent compounds, $\Delta_f H_{298}$(RH), have been measured by standard calorimetry techniques. This ex-

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

pression has been used to compile the heats of formation of the radicals listed in Table 1. There are several compendia available for $\Delta_f H_{298}$(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 compendium[20] 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

$$CH_3-CH_2CH_3 \rightarrow CH_3 + CH_2CH_3 \qquad (20)$$
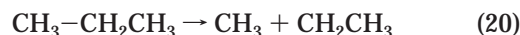
reaction can be found by combining $\Delta_f H_{298}$(CH$_3$) = 35.05 $\pm$ 0.07 kcal mol^{-1} and $\Delta_f H_{298}$(CH$_2$CH$_3$) = 29.0 $\pm$ 0.4 kcal

mol^{-1} from Table 1 and $\Delta_f H_{298}(CH_3CH_2CH_3) = -25.0 \pm 0.1$ kcal mol^{-1} from Pedley.[20] Equation 21 gives the bond

$$DH_{298}(CH_3-CH_2CH_3) = \Delta_f H_{298}(CH_3) + \Delta_f H_{298}(CH_2CH_3) - \Delta_f H_{298}(CH_3CH_2CH_3) \quad (21)$$

energy of the carbon−carbon bond in propane, $DH_{298}(CH_3-CH_2CH_3) = 89.0 \pm 0.4$ 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 CH$_4$ > 1° > 2° > 3°; Table 1 reveals this trend as 105 > 101 > 99 > 97 kcal mol^{-1}. Similarly, increased hybridization of the carbon center increases the C−H bond energy as sp > sp^2 > sp^3: $DH_{298}(HCC-H) = 133 > DH_{298}(CH_2CH-H) = 111 > DH_{298}(CH_3CH_2-H) = 101$ kcal mol^{-1}. The C−H bond energy of C$_6$H$_6$ (113 kcal mol^{-1}) is close to that of CH$_2$CH$_2$ (111 kcal mol^{-1}), while the values for toluene and propene are much lower, $DH_{298}(C_6H_5CH_2-H) \cong DH_{298}(CH_2CHCH_2-H) \cong 89$ 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: $DH_{298}(HF) = 136.4 > DH_{298}(HCl) = 103.15 > DH_{298}(HBr) = 87.54 > DH_{298}(HI) = 71.32$ kcal mol^{-1}. An analogous trend is observed for the halogen−carbon bonds, where the bond enthalpies decrease, C−F > C−Cl > C−Br > 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, $DH_{298}(HO-H) = 119$ 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, $DH_{298}(RCOO-H) \cong 112$ 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., RCOOH → RCO$_2^-$ + 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
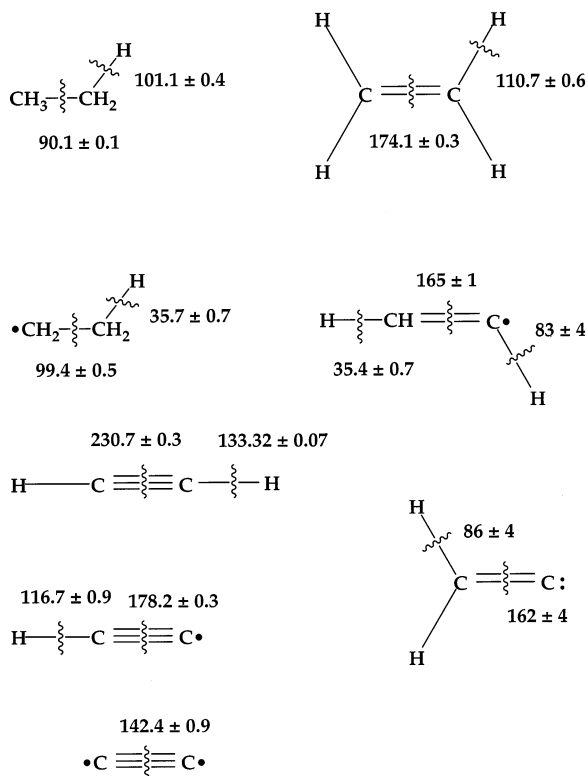
$$\bullet CH_2-CH_2-H \rightarrow CH_2=CH_2 + H \quad (22)$$
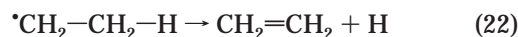
the heat of formation of the ethyl radical, $\Delta_f H_{298}(CH_2CH_3) = 29.0 \pm 0.4$ kcal mol^{-1}. Therefore, using the heat of formation of ethylene, $\Delta_f H_{298}(CH_2CH_2) = 12.5 \pm 0.1$ kcal mol^{-1}, from Pedley's compendium,[20] one can extract the bond energy of the C−H bond β to the radical center, $DH_{298}(CH_2CH_2-H) = 35.7 \pm 0.4$ kcal mol^{-1}. The bond energy in the ethyl radical is nearly a factor of 3 smaller than that of ethane, $DH_{298}(CH_3CH_2-H) = 101$ kcal mol^{-1}, because fragmentation of the former leads to formation of a new π-bond, producing a stable alkene, CH$_2$=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: $DH_{298}(CH_3-CH_3) = 90 < DH_{298}(CH_2=CH_2) = 174 < DH_{298}(HC\equiv CH) = 231$ kcal mol^{-1}. But compare these values with those for the corresponding radicals: $DH_{298}(CH_3-CH_2) = 99 < DH_{298}(CH_2=CH) = 165 < DH_{298}(HC\equiv C) = 178$ kcal mol^{-1}. In going from ethane to ethyl radical, $DH_{298}(C-C)$ 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 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$_3$OH have already been discussed. The C−H bond energy in CH$_3$O falls to 22 kcal mol^{-1}, and the O−H bond energy in CH$_2$OH is only 30 kcal mol^{-1}. In both cases, loss of an H atom produces a very stable product, namely formaldehyde: CH$_3$O → CH$_2$=O + H and CH$_2$OH → CH$_2$=O + H. It is interesting to observe that $DH_{298}(CH_3-OH) \cong DH_{298}(CH_3-O) \cong 91$ kcal mol^{-1}, but the bond energy goes up in the hydroxymethyl radical, $DH_{298}(CH_2-OH) = 106$ kcal mol^{-1}.

Organic peroxyl 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 (CH$_3$)$_3$CO−OH bond (47 kcal mol^{-1}), but this increases in the peroxyl radical to $DH_{298}[(CH_3)_3CO-O] = 65$ kcal mol^{-1}. Conversely, the C−O bond energy drops from 74 kcal mol^{-1} in (CH$_3$)$_3$C−OOH to 38 kcal mol^{-1} in (CH$_3$)$_3$C−OO, since fragmentation of the latter produces (CH$_3$)$_3$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
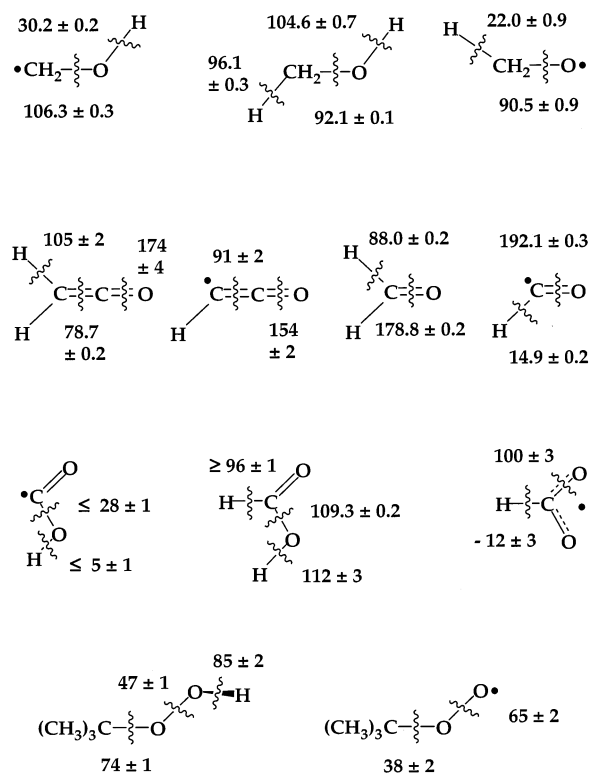
$CH_3 \text{-} CH_2$ H 101.1 ± 0.4

90.1 ± 0.1

$C = C$ 110.7 ± 0.6 174.1 ± 0.3

•$CH_2 \text{-} CH_2$ H 35.7 ± 0.7

99.4 ± 0.5

$H \text{-} CH = C•$ 165 ± 1 83 ± 4 35.4 ± 0.7

230.7 ± 0.3   133.32 ± 0.07

$H \text{---} C \equiv C \text{-} H$

$C = C:$ 86 ± 4 162 ± 4

116.7 ± 0.9   178.2 ± 0.3

$H \text{-} C \equiv C•$

142.4 ± 0.9

•$C \equiv C•$

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

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

•$CH_2 \text{-} O$ H 30.2 ± 0.2

106.3 ± 0.3

$CH_2 \text{-} O$ H 104.6 ± 0.7 96.1 ± 0.3 92.1 ± 0.1

$CH_2 \text{-} O•$ H 22.0 ± 0.9 90.5 ± 0.9

$C = C = O$ H 105 ± 2 174 ± 4 78.7 ± 0.2

•$C = C = O$ H 91 ± 2 154 ± 2

$C = O$ H 88.0 ± 0.2 178.8 ± 0.2

•$C = O$ H 192.1 ± 0.3 14.9 ± 0.2

•C O O H ≤ 28 ± 1 ≤ 5 ± 1

$H \text{-} C$ O O H ≥ 96 ± 1 109.3 ± 0.2 112 ± 3

$H \text{-} C$ O O 100 ± 3 - 12 ± 3

$(CH_3)_3C \text{-} O \text{-} H$ 47 ± 1 85 ± 2 74 ± 1

$(CH_3)_3C \text{-} O•$ O• 65 ± 2 38 ± 2

^{a} Values are in kcal mol^{-1} and represent the energy required to break only the single bond indicated. Thus, $DH_{298}(CH_3O\text{-}H \rightarrow CH_3O + H) = 104.6 \pm 0.7$ kcal mol^{-1} but $DH_{298}(H\text{-}CH_2OH \rightarrow H + CH_2OH) = 96.1 \pm 0.3$ kcal mol^{-1} and $DH_{298}(CH_3\text{-}OH \rightarrow CH_3 + OH) = 92.1 \pm 0.1$ kcal mol^{-1}.

unavailable in the dissociation of the hydroperoxide, $(CH_3)_3C\text{-}OOH$.

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 benzynes 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 ($CH_4 \rightarrow C + 4H$). The enthalpy of atomization is known from the experimental heats of formation of methane, carbon, and hydrogen, $\Delta_{atom}H_{298}(CH_4) = \Delta_f H_{298}(C) + 4\Delta_f H_{298}(H) - \Delta_f H_{298}(CH_4) = 397.5$ kcal mol^{-1}. This implies that the methane molecule contains 397.5 kcal mol^{-1} of energy that is partitioned among four bonds; thus, $D_{av}H_{298} = 99.4$ 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: $DH_{298}(CH_4 \rightarrow CH_3 + H) = 104.99$ kcal mol^{-1}, $DH_{298}(CH_3 \rightarrow CH_2 + H) = 110.4$ kcal mol^{-1}, $DH_{298}(CH_2 \rightarrow$

CH + H) = 101.3 kcal mol^{-1}, and $DH_{298}(CH \rightarrow C + H) = 80.9$ 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 $\Delta_{rxn}H_{298}(CH_4 \rightarrow C + 4H) = 397.5 \pm 0.6$ 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 HC≡CH bond strength is 231 kcal mol^{-1} [HC≡CH → HC + CH] and that both C–H bonds are equivalent, with bond strengths of 81 kcal mol^{-1} [HC → C + H, see Table 1]. However, one could equally well claim that the first CH bond strength is 133 kcal mol^{-1} [HC≡CH → HC≡C + H], which is different from the second CH bond strength of 117 kcal mol^{-1} [HC≡C → C≡C + H], while the CC bond strength [C≡C → C + C] is only 142 kcal mol^{-1}. Or alternatively, the first CH bond strength is 133 kcal mol^{-1}, while the CC bond strength [HC≡C → HC + C] is 178 kcal mol^{-1}, and the second CH bond strength [HC → H + 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]
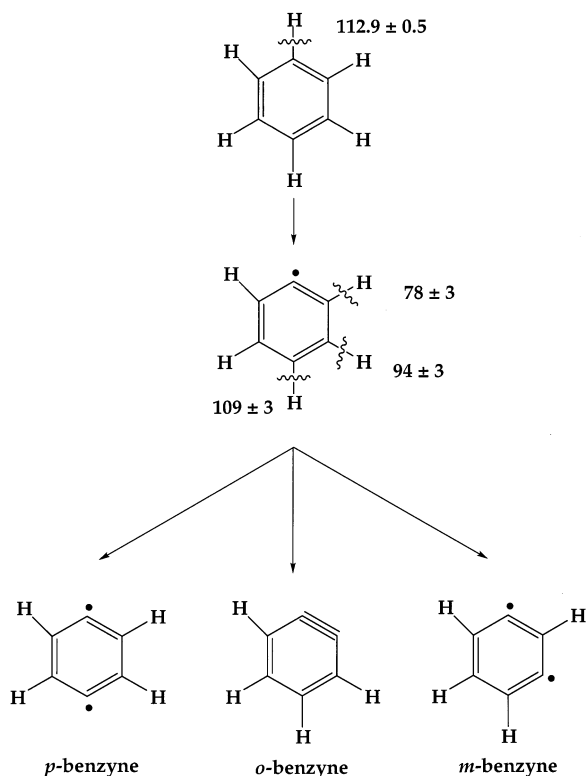
[a] Values are in kcal mol^{-1} and represent the energy required to break only the single bond indicated. Thus, $DH_{298}(C_6H_5-H \rightarrow C_6H_5 + H) = 112.9 \pm 0.5$ kcal mol^{-1} but $DH_{298}(C_6H_4-H \rightarrow H + o\text{-}C_6H_4) = 78 \pm 3$ kcal mol^{-1}, $DH_{298}(C_6H_4-H \rightarrow H + m\text{-}C_6H_4) = 94 \pm 3$ kcal mol^{-1}, and $DH_{298}(C_6H_4-H \rightarrow H + p\text{-}C_6H_4) = 109 \pm 3$ 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, $DH_{298}(CH_2=CO) = 78.7 \pm 0.2$ kcal mol^{-1}, is almost 100 kcal mol^{-1} less than that of ethylene, $DH_{298}(CH_2=CH_2) = 174$ 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, $D_{soln}H_{298}(R-H)$,
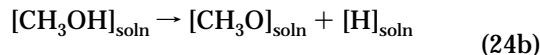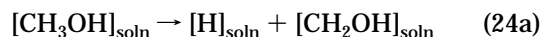
Scheme 1
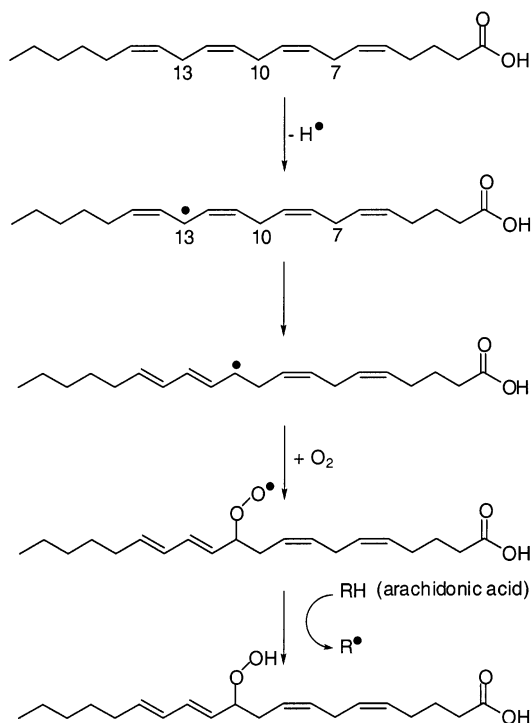
depends on the difference in the enthalpy of solvation, $\Delta_{soln}H_{298}$, of the two radicals and the parent compound, as expressed in terms of eq 23. There are not many

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

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 can be approximated as $[\Delta_{soln}H_{298}(R) - \Delta_{soln}H_{298}(RH)]$. 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 is 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 CH_3OH in a polar protic solvent (reactions 24).

$$[CH_3OH]_{soln} \rightarrow [H]_{soln} + [CH_2OH]_{soln} \quad (24a)$$

$$[CH_3OH]_{soln} \rightarrow [CH_3O]_{soln} + [H]_{soln} \quad (24b)$$

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–CH_2OH bond energy of methanol in a protic solvent would be largely unchanged from the gas phase, while the CH_3O–H value could be slightly higher in solution. There is clearly much work to be done in this area.

Scheme 2

calicheamicin γ_1^I
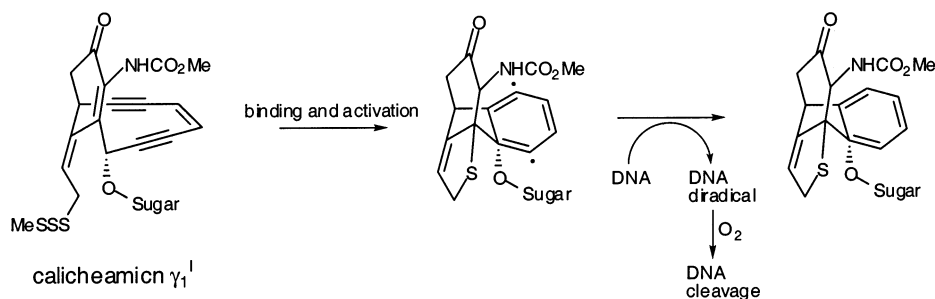
Bond Enthalpies in Chemistry

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}(carboxylic acid,O—H) $\cong$ 112 > DH_{298}(vinyl,C—H) $\cong$ 111 > DH_{298}(methylene,C—H) $\cong$ 99 > DH_{298}(α-carbonyl,C—H) $\cong$ 94 > DH_{298}(allylic,C—H) $\cong$ 88 kcal mol^{-1} > DH_{298}(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}((CH$_3$)$_2$CH—H) $\cong$ 98.6 kcal mol^{-1}) and a singly allylic C—H (e.g., DH_{298}(H$_2$C=CHCH$_2$—H) $\cong$ 88.8 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 O$_2$ to form a peroxyl radical: Chart 2 indicates that the OO—CMe$_3$ 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*-benzyne (Scheme 2). From Chart 3 we can estimate that the diradical can abstract all hydrogens bound by $\leq$109 kcal mol^{-1}. This makes the *p*-benzyne 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 kcal mol^{-1}. Thus, two exothermic hydrogen abstractions by the reactive *p*-benzyne 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.

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