

Understanding Trends in C–H, N–H, and O–H Bond Dissociation Enthalpies

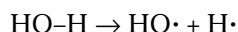
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The gas-phase bond dissociation enthalpy (BDE) of water corresponds to the enthalpy change for the reaction



where the indicated bond is broken and the products are radicals (\cdot). Gas-phase BDE data are usually tabulated at 298 K and denoted ΔH_{298}° . This quantity is also referred to in the *CRC Handbook of Chemistry and Physics* as “bond strength” and denoted $D_{298}^\circ(I)$; thus the two terms are synonymous. To make matters more confusing, sometimes the terms “bond dissociation energy” and “bond energy” are used interchangeably, but there is a difference: the BDE is a true thermodynamic quantity, since reactants and products are well-defined chemical species in standard states, whereas the bond energy is not. For example, one could define the O–H bond energy in water as the average value of the BDE for $\text{HO-H} \rightarrow \text{HO}\cdot + \text{H}\cdot$, and $\text{HO}\cdot \rightarrow \cdot\text{O}\cdot + \text{H}\cdot$, where the atoms are in their ground electronic states (^3P state for oxygen, ^2S for hydrogen).

Extensive tabulations of BDE data exist, for example, in the *CRC Handbook of Chemistry and Physics* (1), the *NIST Database* (2), and several recent compilations (3). The data span a wide variety of simple inorganic (gas-phase) species, hydrocarbons, and other organic molecules. The reported uncertainties associated with these data are usually 4–10 kJ/mol and occasionally less, although for many species the uncertainties can be larger. To complicate the interpretation of trends, reported BDE values are sometimes in disagreement by as much as 12 kJ/mol or more, even for important chemical species (such as phenol).

Table 1. Gas-Phase Bond Dissociation Enthalpies

Bond	BDE/ ΔH_{298}°			
	Experimental	Calculated		
		G2 [†]	DFT	
		Ref 5b	Lit.	
HO-H	499.2 ± 0.2 (3a)	498.7	495.0	—
H ₂ N-H	452.7 ± 0.1 (3a)	451.5	450.2	—
H ₃ C-H	438.9 ± 0.4 (3a)	442.7	442.7	—
H ₃ CO-H	436.0 ± 3.8 (3a)	444.8	431.4	—
H ₃ CNH-H	429.3; 418.4 ± 10.5 (2)	421.3	413.8	—
H ₃ CCH ₂ -H	423.0 ± 1.7 (3a)	429.3	422.6	423.0 (1a)
F ₃ CO-H	521.7 ± 15; 456.1 ± 10 (3g, 6b)	499.6 (5e)	492.5	493.7 (5e)
F ₃ CNH-H	—	—	448.5	—
F ₃ CCH ₂ -H	446.4 ± 4.6 (1b)	—	—	436.4 (5f)
PhO-H	356.9; 365.3 ± 6.3 (2, 3c)	—	363.2	—
PhNH-H	375.3 ± 6.3; 372.8 ± 4.2 (3e, 3f)	—	382.0	—
PhCH ₂ -H	370.7 ± 6.3; 373.6 (3a, 2)	—	375.3	—

The growing body of experimental BDE's has stimulated the development of new theoretical procedures, which today approach the accuracy of the experiments. The “gold standard” of such theoretical procedures has been termed the “G2 method” by Curtiss, Pople, and coworkers (4). This ab initio method, which adds some empirical parameters to improve the agreement with experimental data, is applicable to molecules containing up to about 10 heavy (i.e., non-hydrogen) atoms and generally yields heats of formation and gas-phase BDE's that are within about 6 kJ/mol of the best experimental values. New developments in density functional theory (DFT) are allowing extension with similar accuracy to larger molecules (5). It is now possible and useful to compare theory and experiment in order to provide a check on both.

Comparison of Experiment and Theory

Table 1 is a compilation of experimental and calculated (G2 and DFT) O–H, N–H and C–H BDE's for the unsubstituted compounds HO–H, H₂N–H, and H₃C–H (water, ammonia, methane), and for compounds containing methyl, trifluoromethyl, and phenyl substituents. In the case of our own DFT calculations (5b), we optimized the geometry at a lower level and then did a single-point energy calculation using the B3LYP/6-311+G(2d,2p) method/basis set. For the radical, we used a restricted open-shell calculation (ROB3LYP) and set the electronic energy of the H atom at its exact value—0.50000 hartree, as described fully in the literature (5b). It can be seen that the agreement between the experimental and theoretical values is generally good, except in the problematic case of trifluoromethanol, where the experimental value of 522 ± 15 kJ/mol (3g) is almost certainly high, while an earlier value of 456 kJ/mol (estimated using Benson's bond additivity methods) is almost certainly too low (6). In this case, the theoretical values near 499 kJ/mol are to be preferred.

Trends in HX–H and H₃CX–H BDE's and the Importance of Hyperconjugation

A discussion of trends in bond energies is generally encountered in a first course in general chemistry, usually in connection with MO theory and the definition of bond order. As students become more sophisticated in their understanding of thermodynamics, upper-division courses in organic, physical, and computational chemistry may introduce the concept of the BDE. Now that reasonably reliable BDE data are available through experiment and theory, it is interesting to look at trends in O–H, N–H, and C–H BDE's as a function of the substituent(s) attached to the heavy atom. A study of the

trends shown in Table 1 provides a starting point for a discussing a number of concepts helpful in advanced organic chemistry courses, including electronegativity, conjugation, hyperconjugation, and radical stabilization energy. It also shows how data from electron paramagnetic resonance (EPR) experiments can be used to support conceptual arguments.

From Table 1 we can see that BDE of water is much larger than that of methane, so that the difference, ΔBDE ($[\text{HO-H}] - [\text{HCH}_2\text{-H}]$), is large and positive ($\sim +60$ kJ/mol). On the other hand, the change in BDE between phenol and toluene, ΔBDE ($[\text{PhO-H}] - [\text{PhCH}_2\text{-H}]$), is small and negative (ca. -8 kJ/mol). We are not aware of any previous discussion of these peculiar trends in BDE's, and in this paper we look into the reasons for them.

When the substituent on (O,N,C) is hydrogen, there is a monotonic decrease in the BDE's along the series HO-H, H₂N-H, and H₃C-H (499, 453, 439 kJ/mol; Table 1). This is readily attributed to the monotonic decrease in the Pauling electronegativity of the heavy atoms (O, 3.5; N, 3.0; C, 2.5) and the consequent monotonic lengthening of the heavy atom-hydrogen bond (HO-H, 0.958 Å; H₂N-H, 1.012 Å; H₃C-H, 1.087 Å) (*l*).

Substitution of a methyl group for a hydrogen atom produces a substantial reduction in the heavy atom-hydrogen atom BDE's and also reduces the change in BDE along the series H₃CO-H, H₃CNH-H, H₃CCH₂-H to about 12 kJ/mol (435, 427, 423). This reduction in BDE can be attributed to the ability of the methyl group to stabilize the radical by *hyperconjugation*. In this case, hyperconjugation results from π -overlap between the unpaired (radical) electron in a 2p orbital and a localized MO on methyl formed from the σ_{CH} bond orbitals (see, e.g., Karplus and Porter [7] for a discussion of the EPR evidence for hyperconjugation). This localized CH₃ MO is of the type ($2\sigma_{\text{CH}_1} - \sigma_{\text{CH}_2} - \sigma_{\text{CH}_3}$), so that the positive lobe overlaps the positive lobe of the 2p orbital and similarly for the negative lobe(s). The resulting π -overlap stabilizes (i.e. lowers the energy of) the singly occupied molecular orbital (SOMO) of the radical and thus lowers the BDE. The large magnitude of ΔBDE ($[\text{HO-H}] - [\text{H}_3\text{CO-H}]$), ~ 64 kJ/mol, the small magnitude of ΔBDE ($[\text{HCH}_2\text{-H}] - [\text{H}_3\text{CCH}_2\text{-H}]$), ~ 16 kJ/mol, and the intermediate value for ΔBDE ($[\text{H}_2\text{N-H}] - [\text{H}_3\text{CNH-H}]$), ~ 26 kJ/mol, are again a consequence of the different electronegativities of the heavy atoms and the increase in the H₃C-XH bond lengths along the series: H₃C-OH, 1.425 Å; H₃C-NH₂, 1.471 Å; H₃C-CH₃, 1.535 Å (*l*). The corresponding radicals have calculated H₃C-X· bond lengths that also increase along the series: H₃C-O·, 1.368 Å; H₃C-NH·, 1.445 Å; H₃C-CH₂·, 1.490 Å (J. S. Wright, unpublished results). In this case, the shorter the H₃C-X· bond, the better will be the overlap of the p-orbital on X with the C-H bonds of the methyl group and hence the greater will be the extent of unpaired electron delocalization into the methyl group and the greater will be the stabilization of the radical.

This picture of radical stabilization increasing along the series H₃C-CH₂· < H₃C-NH· < H₃C-O· because of increasing delocalization of the unpaired electron into the methyl group (hyperconjugation) is independently supported by electron paramagnetic resonance (EPR) spectroscopy. Because there is a negligible barrier to rotation about H₃C-X· bonds, the three methyl hydrogen atoms in each radical are

magnetically equivalent. The magnitudes of the EPR hyperfine splittings (hfs) by these hydrogens, $a^{\text{H}}(\text{CH}_3)$, are H₃CCH₂·, 27 G (*8a*); H₃CNH·, 34 G (*8b*); H₃CO·, 52 G (*8c*). Thus there is roughly twice as much unpaired spin density on the methyl group in H₃CO· as in H₃CCH₂·. Electron delocalization and the resultant radical stabilization in H₃CO· is very substantial, since a hydrogen atom (which necessarily has 100% of the unpaired spin) has an hfs of 507 G (*9*). The H₃CO· radical therefore has just over 30% of its unpaired spin density located on its three hydrogen atoms.

The Remarkable CF₃ Group

The importance of hyperconjugation in relation to H₃CX-H BDE's is further emphasized by a consideration of the available F₃CX-H BDE's (Table 1) and $a^{\text{F}}(\text{CF}_3)$ values. The F₃CCH₂· radical has $a^{\text{F}}(\text{CF}_3) = 30$ G (*8d*), which at first sight might appear comparable to the $a^{\text{H}}(\text{CH}_3) = 27$ G of H₃CCH₂·. However, a fluorine atom with its unpaired electron in the 2s orbital has $a^{\text{F}} = 17,100$ G (*9*), and so the F₃CCH₂· radical has very little of its unpaired spin density delocalized onto its three fluorine atoms. Electron delocalization into the C-F bonds in F₃CCH₂· (fluorine hyperconjugation) is therefore negligible compared with delocalization into the C-H bonds of H₃CCH₂·. We would therefore expect the F₃CCH₂-H BDE to be very similar to the H₃C-H BDE, and such would appear to be the case (see Table 1).

Similarly, the F₃CO-H BDE value should be close to that in HO-H. Table 1 shows a remarkably high experimental value of 522 ± 15 kJ/mol for F₃CO-H. If true this would be the strongest of any O-H bond. This very high value has generated much discussion in the literature (*3g, 6a-c*), in part because of an earlier value (based on bond additivity) of only 456 kJ/mol (*6b*). The theoretical values are much more consistent, giving around 499 kJ/mol, essentially indistinguishable from values for HO-H. We believe that these theoretical values are more reliable than the experimental values. Finally, we calculated a DFT value for CF₃NH-H (Table 1) and obtained a value very close (within 2 kJ/mol) to the calculated value for H₂N-H. These combined data strongly support our view that the CF₃ substituent does not stabilize an adjacent radical site.

Still another way to understand the lack of interaction with a CF₃ substituent and a radical center is to consider the hyperconjugation arising from the σ_{CF} bond orbitals in trifluoromethyl, which differ significantly from the σ_{CH} bond orbitals in the methyl group. Since fluorine is so much more electronegative than carbon, the σ_{CF} bond orbital contains little contribution from the sp³ hybrid orbital on carbon, and consists mostly of contributions from fluorine, thus reducing overlap with the 2p orbital on X. Given that the C-F bond in trifluoromethyl is much longer than the C-H bond in methyl, both orbital composition and bond distance argue for a much weaker hyperconjugative stabilization by CF₃ than by CH₃, as we observe. Thus both hyperconjugation and electronegativity concepts, supported by EPR measurements, help to interpret these trends in BDE's for CH₃ and CF₃ substituents.

Trends in C₆H₅X-H BDE's and the Role of Direct Conjugation

Electron delocalization by *direct conjugation* into a neighboring phenyl group, C₆H₅X·, provides considerably more stabilization to a radical than does hyperconjugation with a

methyl group, $\text{CH}_3\text{X}\cdot$. The BDE's for $\text{C}_6\text{H}_5\text{O}\cdot\text{H}$, $\text{C}_6\text{H}_5\text{NH}\cdot\text{H}$, and $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{H}$ are undoubtedly very similar; but, most interestingly, experimental data suggest that the O–H bond is now the weakest, not the strongest, in this series (361, 374, 372 kJ/mol are the average experimental values for O–H, N–H, and C–H, respectively). This unexpected ordering, $\text{N}\cdot\text{H} \approx \text{C}\cdot\text{H} > \text{O}\cdot\text{H}$, is consistent with the order obtained from DFT calculations, 363 (OH), 382 (NH), 375 (CH) kJ/mol. It is also consistent with the EPR data, which indicate an increase in electron delocalization into the phenyl ring along the series $\text{C}_6\text{H}_5\text{CH}_2\cdot < \text{C}_6\text{H}_5\text{NH}\cdot < \text{C}_6\text{H}_5\text{O}\cdot$, as measured by both the ortho-hydrogens hfs (5.1 [8e], 6.2 [8f], and 6.6 G [8g], respectively) and the para-hydrogen hfs (6.0 [8e], 8.2 [8f], and 10.2 G [8g], respectively). Since the benzene radical anion and cation both have $a^{\text{H}} \approx 4\text{G}$ ($8i$) ($\Sigma a^{\text{H}} \approx 24\text{G}$), it is obvious that the phenoxyl radical's unpaired electron is very largely conjugatively delocalized into the aromatic ring; that is, it may be better to regard the phenoxyl radical as a delocalized carbon-centered radical than as an oxygen-centered radical! The $\text{C}_6\text{H}_5\text{X}\cdot$ EPR data are also fully consistent with the calculated C–X \cdot bond lengths (J. S. Wright, unpublished results), which increase from C–O \cdot (1.25 Å) to C–NH \cdot (1.34 Å) to C–CH $_2\cdot$ (1.40 Å).

"Best" BDE's and Radical Stabilization Energies

When considered in the manner described above, the trends in O–H, N–H and C–H BDE's are not monotonic and one is tempted to look at additional stabilization (or destabilization) that may be present, to varying degrees, in the *parent molecule*. While such an extended treatment can be justified and may be appropriate in many circumstances, for the compounds and BDE's considered in this note there is a simple (first approximation) way to explain the data. To show this clearly, "best" BDE's are given in Table 2; we chose the experimental number when the uncertainty is small and used the theoretical values, when appropriate, to help select among the experimental data. For $\text{CF}_3\text{O}\cdot\text{H}$, we chose a theoretical value weighted towards G2.

It is common to define the radical stabilization energy (RSE) as the difference in X–H BDE's between the unsubstituted compound, for example HO–H, and the compound containing a substituent, for example $\text{CH}_3\text{O}\cdot\text{H}$. As shown in Table 2, the parent (unsubstituted) compound is defined so as to have an RSE = 0; that is, the radical HO \cdot is unstabilized. In the reaction $\text{CH}_3\text{O}\cdot\text{H} \rightarrow \text{CH}_3\text{O}\cdot + \text{H}\cdot$, the product radical $\text{CH}_3\text{O}\cdot$ has an RSE equal to 499 – 435 or 64 kJ/mol. Proceeding in this way, RSE's are obtained (Table 2). Now consider the series ($\text{H}_3\text{CO}\cdot\text{H}$, $\text{H}_3\text{CNH}\cdot\text{H}$, $\text{H}_3\text{CCH}_2\cdot\text{H}$) with RSE's (64, 26, 16) and the series (PhO–H, PhNH–H, PhCH $_2$ –H) with RSE's (135, 76, 67). In each series the decrease in RSE is strictly monotonic: phenyl substituents decrease the BDE more than methyl substituents, and in a (qualitatively) predictable manner. The CF_3 substituent, as argued above, shows

Table 2. "Best" BDE's for RX–H Bond and RSE's for RX \cdot Radical

Bond	BDE kJ/mol	RSE
HO–H	499	0
$\text{H}_2\text{N}\cdot\text{H}$	453	0
$\text{H}_3\text{C}\cdot\text{H}$	439	0
$\text{H}_3\text{CO}\cdot\text{H}$	435	64
$\text{H}_3\text{CNH}\cdot\text{H}$	427	26
$\text{H}_3\text{CCH}_2\cdot\text{H}$	423	16
$\text{F}_3\text{CO}\cdot\text{H}$	499	0
$\text{F}_3\text{CNH}\cdot\text{H}$	452	1
$\text{F}_3\text{CCH}_2\cdot\text{H}$	439	0
PhO–H	364	135
PhNH–H	377	76
PhCH $_2$ –H	372	67

no RSE at all, as might be expected from the fact that essentially no unpaired spin density is delocalized onto the substituent.

In conclusion, the concepts of radical stabilization energy, conjugation, hyperconjugation, and the measurements of unpaired spin density are all helpful in understanding the otherwise peculiar trends in BDE's for the C–H, N–H and O–H bonds.

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