

5.5: HOMOLYTIC CLEAVAGE AND BOND DISSOCIATION ENERGIES

Learning Objective

- calculate reaction enthalpies from bond dissociation energies

INTRODUCTION

The homolytic bond dissociation energy is the amount of energy needed to break apart one mole of covalently bonded gases into a pair of radicals. The SI units used to describe bond energy are kiloJoules per mole of bonds (kJ/Mol). It indicates how strongly the atoms are bonded to each other. *Solvation* is the interaction between solvent molecules and the ions or molecules dissolved in that solvent.

Breaking a covalent bond between two partners, A-B, can occur either heterolytically, where the shared pair of electron goes with one partner or another



or



or homolytically, where one electron stays with each partner.



The products of homolytic cleavage are radicals and the energy that is required to break the bond homolytically is called the *Bond Dissociation Energy* (BDE) and is a measure of the strength of the bond.

CALCULATION OF THE BDE

The BDE for a molecule A-B is calculated as the difference in the enthalpies of formation of the products and reactants for homolysis

$$BDE = \Delta_f H(A^\bullet) + \Delta_f H(B^\bullet) - \Delta_f H(A - B) \quad (5.5.4)$$

Officially, the IUPAC definition of bond dissociation energy refers to the energy change that occurs at 0 K, and the symbol is D_0 . However, it is commonly referred to as BDE, the bond dissociation energy, and it is generally used, albeit imprecisely, interchangeably with the bond dissociation *enthalpy*, which generally refers to the enthalpy change at room temperature (298K). Although there are technical differences between BDEs at 0 K and 298 K, those difference are not large and generally do not affect interpretations of chemical processes.

BOND BREAKAGE/FORMATION

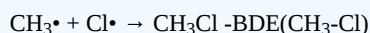
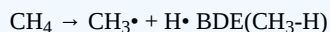
Bond dissociation energy (or enthalpy) is a state function and consequently does not depend on the path by which it occurs. Therefore, the specific mechanism in how a bond breaks or is formed does not affect the BDE. Bond dissociation energies are useful in assessing the energetics of chemical processes. For chemical reactions, combining bond dissociation energies for bonds formed and bonds broken in a chemical reaction using Hess's Law can be used to estimate reaction enthalpies.

Example: Chlorination of Methane

Consider the chlorination of methane



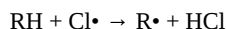
the overall reaction thermochemistry can be calculated exactly by combining the BDEs for the bonds broken and bonds formed



$$\Delta H = BDE(R-H) + BDE(Cl_2) - BDE(HCl) - BDE(CH_3-Cl) \quad (5.5.7)$$

Because reaction enthalpy is a state function, it does not matter what reactions are combined to make up the overall process using Hess's Law. However, BDEs are convenient to use because they are readily available.

Alternatively, BDEs can be used to assess individual steps of a mechanism. For example, an important step in free radical chlorination of alkanes is the abstraction of hydrogen from the alkane to form a free radical.



The energy change for this step is equal to the difference in the BDEs in RH and HCl

$$\Delta H = BDE(R-H) - BDE(HCl) \quad (5.5.8)$$

This relationship shows that the hydrogen abstraction step is more favorable when BDE(R-H) is smaller. The difference in energies accounts for the selectivity in the halogenation of hydrocarbons with different types of C-H bonds.

Table 6.8.1: Representative C-H BDEs in Organic Molecules

R-H	D _O , kJ/mol	D ₂₉₈ , kJ/mol	R-H	D _O , kJ/mol	D ₂₉₈ , kJ/mol
CH ₃ -H	432.7±0.1	439.3±0.4	H ₂ C=CH-H	456.7±2.7	463.2±2.9
CH ₃ CH ₂ -H		423.0±1.7	C ₆ H ₅ -H	465.8±1.9	472.4±2.5
(CH ₃) ₂ CH-H		412.5±1.7	HCCH	551.2±0.1	557.8±0.3
(CH ₃) ₃ C-H		403.8±1.7			
			H ₂ C=CHCH ₂ -H		371.5±1.7
HC(O)-H		368.6±0.8	C ₆ H ₅ CH ₂ -H		375.3±2.5
CH ₃ C(O)-H		374.0±1.2			

TRENDS IN C-H BDES

It is important to remember that C-H BDEs refer to the energy it takes to break the bond, and is the difference in energy between the reactants and the products. Therefore, it is not appropriate to interpret BDEs solely in terms of the "stability of the radical products" as is often done.

Analysis of the BDEs shown in the table above shows that there are some systematic trends:

- BDEs vary with hybridization:** Bonds with sp³ hybridized carbons are weakest and bonds with sp hybridized carbons are much stronger. The vinyl and phenyl C-H bonds are similar, reflecting their sp² hybridization. The correlation with hybridization can be viewed as a reflection of the C-H bond lengths. Longer bonds formed with sp³ orbitals are consequently weaker. Shorter bonds formed with orbitals that have more s-character are similarly stronger.
- C-H BDEs vary with substitution:** Among sp³ hybridized systems, methane has the strongest C-H bond. C-H bonds on primary carbons are stronger than those on secondary carbons, which are stronger than those on tertiary carbons.

INTERPRETATION OF C-H BDES FOR SP³ HYBRIDIZED CARBONS

The interpretation of the BDEs in saturated molecules has been subject of recent controversy. As indicated above, the variation in BDEs with substitution has traditionally been interpreted as reflecting the stabilities of the alkyl radicals, with the assessment that more highly substituted radicals are more stable, as with carbocations. Although this is a popular explanation, it fails to account for the fact the bonds to groups other than H do not show the same types of variation.

R	BDE(R-CH ₃)	BDE(R-Cl)	BDE(R-Br)	BDE(R-OH)
CH ₃ -	377.0±0.4	350.2±0.4	301.7±1.3	385.3±0.4
CH ₃ CH ₂ -	372.4±1.7	354.8±2.1	302.9±2.5	393.3±1.7
(CH ₃) ₂ CH-	370.7±1.7	356.5±2.1	309.2±2.9	399.6±1.7
(CH ₃) ₃ C-	366.1±1.7	355.2±2.9	303.8±2.5	400.8±1.7

Therefore, although C-CH₃ bonds get weaker with more substitution, the effect is not nearly as large as that observed with C-H bonds. The strengths of C-Cl and C-Br bonds are not affected by substitution, despite the fact that the same radicals are formed as when breaking C-H bonds, and the C-OH bonds in alcohols actually *increase* with more substitution.

Gronert has proposed that the variation in BDEs is alternately explained as resulting from destabilization of the reactants due to steric repulsion of the substituents, which is released in the nearly planar radicals.¹ Considering that BDEs reflect the relative energies of reactants and products, either explanation can account for the trend in BDEs.

Another factor that needs to be considered is the electronegativity. The Pauling definition of electronegativity says that the bond dissociation energy between unequal partners is going to be dependent on the difference in electronegativities, according to the expression

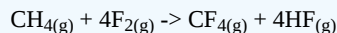
$$D_o(A-B) = \frac{D_o(A-A) + D_o(B-B)}{2} + (X_A - X_B)^2 \quad (5.5.9)$$

where X_A and X_B are the electronegativities and the bond energies are in eV. Therefore, the variation in BDEs can be interpreted as reflecting variation in the electronegativities of the different types of alkyl fragments.

There is likely some merit in all three interpretations. Since Gronert's original publication of his alternate explanation, there have been many desperate attempts to defend the radical stability explanation.

Exercise

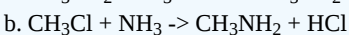
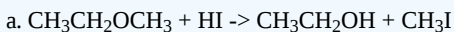
1. Given that ΔH° for the reaction



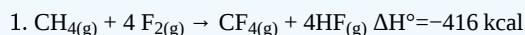
is -1936 kJ , use the following data to calculate the average bond energy of the C-F bonds in CF_4 .

Bond	Average Bond Energy
C-H	$413 \text{ kJ} \cdot \text{mol}^{-1}$
F-F	$155 \text{ kJ} \cdot \text{mol}^{-1}$
H-F	$567 \text{ kJ} \cdot \text{mol}^{-1}$

2. Calculate ΔH° for the reactions given below.



Answer



Bonds broken:

$$4 \text{ mol C-H bonds} \times \frac{(413 \text{ kJ})}{(1 \text{ mol})} = 1652 \text{ kJ}$$

$$4 \text{ mol F-F bonds} \times \frac{(155 \text{ kJ})}{(1 \text{ mol})} = 620 \text{ kJ}$$

Bonds formed:

$$4 \text{ mol C-F bonds} \times \frac{(x \text{ kJ})}{(1 \text{ mol})} = 4x \text{ kJ}$$

(where x = the average energy of one mole of C-F bonds in CF_4 , expressed in kJ)

$$4 \text{ mol H-F bonds} \times \frac{(567 \text{ kJ})}{(1 \text{ mol})} = 2268 \text{ kJ}$$

$$\begin{aligned} \Delta H^\circ &= \Delta H^\circ(\text{bonds broken}) - \Delta H^\circ(\text{bonds formed}) \\ &= (1652 \text{ kJ} + 620 \text{ kJ}) - (4x + 2268 \text{ kJ}) \\ &= 1652 \text{ kJ} + 620 \text{ kJ} - 4x - 2268 \text{ kJ} \\ &= -1936 \text{ kJ} \end{aligned}$$

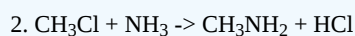
Thus,

$$\begin{aligned} 4x &= 1936 \text{ kJ} - 2268 \text{ kJ} + 620 \text{ kJ} + 1652 \text{ kJ} \\ &= 1940 \text{ kJ} \end{aligned}$$

and

$$\begin{aligned} x &= \frac{1940 \text{ kJ}}{4 \text{ mol}} \\ &= 385 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

The average energy of a C-F bond in CF_4 is $385 \text{ kJ} \cdot \text{mol}^{-1}$



Reactant bonds broken	D	Product bonds formed	D
CH_3-Cl	351 kJ/mol	CH_3-NH_2	335 kJ/mol
NH_2-H	449 kJ/mol	$\text{H}-\text{Cl}$	432 kJ/mol
	800 kJ/mol		767 kJ/mol

$$\begin{aligned}\Delta H^\circ &= D_{\text{bonds broken}} + D_{\text{bonds formed}} \\ &= 800 \text{ kJ/mol} - 767 \text{ kJ/mol} \\ &= +33 \text{ kJ/mol}\end{aligned}$$

REFERENCES

1. Gronert, S. J. *Org. Chem.* **2006**, *13*, 1209

FURTHER READING

MasterOrganicChemistry

Bond Strengths And Radical Stability

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