Chapter 2

Thermodynamic stability of organic molecules

The goal on this chapter:

- Using common evaluation tools to determine which molecule, reactant, intermediate is the most stable.
- Predicting thermochemical properties for determining reaction mechanisms and quantitative values of strain/stabilization.

1

The Notion of Stability

Stable *versus* Persistent

- *Thermodynamic stability*: governed by free energy changes, $\Delta G°$. More stable (lower $\Delta G°$) than a reference structure.
- *Kinetic persistence* (long lived): measured by a rate constant (the lifetime inversely related to it). Very context dependent.

e.g.,

Diamond is "unstable" with respect to graphite but is persistent.

The benzyl cation is thermodynamically more stable than the methyl cation but not persistent under typical conditions.

Hoffmann, Schleyer, Schaefer *Angew. Chem. Int Ed.* **2008**, *47*, 7164.

2

Types of Energy

The change in **Gibbs free energy** (ΔG°) between two different chemical states

➔ position of the equilibrium between these states.

The change in **enthalpy** ΔH° between two different compositions (at constant pressure)

➔ change in heat accompanied by a **change in bonding**.

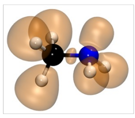
The **entropy**

➔ measure the disorder of a system.

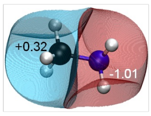
Bond dissociation energy (BDE):

➔ definition of a bond strength.

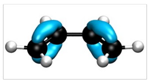
What is a chemical bond: how to quantify?



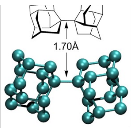
chemical bonds



atomic charges



(hyper-) conjugation



molecular strain

How to quantify?

Gonthier, J.F.; Steinmann, S.N; Wodrich, M.D.; Corminboeuf, C. *Chem. Soc. Rev.* **2012**, 41, 4671.

Homolytic Bond Dissociation Energy

The standard specific bond dissociation energies (BDE or bond dissociation enthalpies), $\Delta H°(R^{\bullet}/X^{\bullet})$:
the enthalpy change involved in breaking one mole of a particular bond R-X at 1 atmosphere and 25°C into two fragments $R^{\bullet}$ and $X^{\bullet}$

$$R\text{-}X \rightleftharpoons R^{\bullet} + X^{\bullet}$$

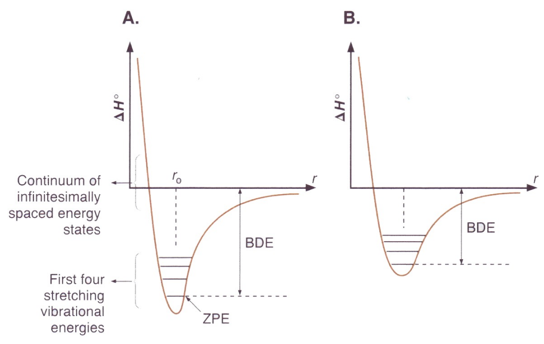
The BDE is: $\Delta H°(R^{\bullet}/X^{\bullet}) = \Delta H_f°(R^{\bullet}) + \Delta H_f°(X^{\bullet}) - \Delta H_f°(RX)$

BDE is not always a meaningful representation of the strength of a particular bond!

Chapter 2

5

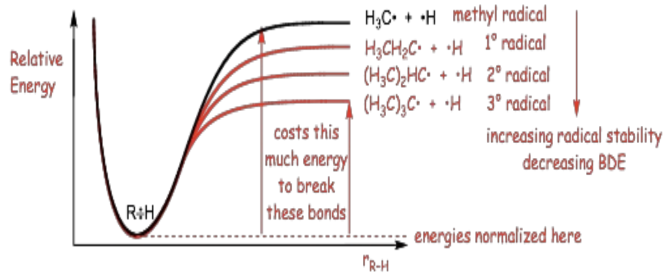
Homolytic Bond Dissociation Energy



Chapter 2

6

BDEs as a Measure of Radical Stability



The radical recombination (the inverse reaction) has a negligible activation barrier
➔Dissociation Energy = bond strength but….

Chapter 2

7

Homolytic Bond Dissociation Energy

Bond Energies (BEs) and Bond Dissociation Energies (BDEs) are different!

BE are based on the total atomization energies (*i.e.*, the dissociation of all the Lewis electron pair bonds) of molecules.
Straightforward for methane (one-fourth of the atomization energy) but more complicated for other systems.
Schleyer and Exner's evaluations give 103.9 kcal mol^{-1} methane, 104.1 ethane, 104.3 propane (CH_2), 104.4 iso-butane (CH).

BDE involves the dissociation of one bond in the molecule **AND** the relaxation of the radical fragments formed.

The A and B moieties in A-B are potentially quite different from the separated A• and B• radical fragments.

Chapter 2

8

Radical Stabilization Energy (RSE)
a closely related quantity

Relative values of BDEs are also extremely important….

$$CH_3\text{-}H + R^{\bullet} \rightleftharpoons R\text{-}H + CH_3^{\bullet}$$

The enthalpy change for this reaction is defined as the radical stabilization energy of carbon-based hydrocarbon radicals with respect to the smallest possible alkyl radical reference standard (*e.g.*, CH_3•)

Chapter 2

9

Radical Stabilization Energy (RSE)
a closely related quantity

….but controversial as illustrated by titles of papers:

"Choice of bond dissociation enthalpies on which to base the stabilization energies of simple radicals: ΔH(R-H) is preferred because ΔH(R-Me) and ΔH(R-R) are perturbed by changes in chain Branching"
J. Org. Chem. **2008**, *73*, 8921.

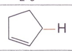
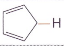
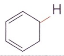
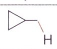
"Shortcomings of basing radical stabilization energies on bond dissociation energies of alkyl groups to hydrogen".
J. Org. Chem. **2010**, *75*, 5697.

Chapter 2

10

Homolytic Bond Dissociation Energy

Some Specific Bond Dissociation Energies (in kcal/mol)*

Bond	BDE	Bond	BDE	Bond	BDE
H–H	104.2 (104.2)	CH_2=CH–H	110 (110.7)	CH_3–CH_3	90.4 (90.1)
CH_3–H	105.1 (105.0)	C_6H_5–H	110.9 (112.9)	CH_3–F	109.9 (115)
CH_3CH_2–H	98.2 (101.1)	HC≡C–H	132 (131.9)	CH_3–Cl	84.6 (83.7)
$(CH_3)_2CH$–H	95.1 (98.6)	$C_6H_5CH_2$–H	88 (89.7)	CH_3–Br	70.9 (72.1)
$(CH_3)_3C$–H	93.2 (96.5)	CH_2=$CHCH_2$–H	86.3 (88.8)	CH_3–I	57.2 (57.6)
$c(CH_2)_3$–H	106.3	$CH_3C(O)$–H	86 (88.1)	CH_3–OH	92.3 (92.1)
$c(CH_2)_4$–H	96.5	HO–H	119 (118.8)	CH_3–NH_2	84.9 (85.2)
$c(CH_2)_5$–H	94.5	CH_3O–H	104.4 (104.6)	CH_3–SH	74
$c(CH_2)_6$–H	95.5	NH_2–H	107.4 (107.6)	CH_3–SiH_3	88.2
	82.3	CH_3S–H	90.7 (87.4)	CH_3–$SiMe_3$	89.4
		HO–OH	51	CH_3–$GeMe_3$	83
	71.1	CH_3O–OCH_3	37.6 (38)	CH_3–$SnMe_3$	71
		$HOCH_2$–H	94 (96.1)	CH_3–$PbMe_3$	57
	73	H_2C=CH_2	(174.1)	CH_3–OCH_3	(83.2)
	97.4	HC≡CH	(230.7)	CH_3–C_2H_5	(89.0)
	90.6	H_2C=O	(178.8)	CH_3–$CH(CH_3)_2$	(88.6)
CH_3–CH=CH_2	(101.4)	CH_3–C_6H_5	(103.5)	CH_3–$C(CH_3)_3$	(87.5)
C_6H_5–C_6H_5	(118)	CH_3–$CH_2C_6H_5$	(77.6)	CH_3–CH_2CH=CH_2	(76.5)

CH_3-H + H-OH ⟶ CH_3-OH + H-H

105.1   119   92.3   104.2

$\Delta H° = 27.6$ kcal/mol

BDEs can be used to predict the exothermicity or endothermicity of a reaction.

BDEs as a Measure of Radical Stability

Trends in BDEs :

methane > ethane > *i*-prop > tert-butane

3° > 2° > 1° > methyl

10 kcal/mol of stabilization along the series

Vinyl and phenyl radicals are less stable than alkyl radicals.

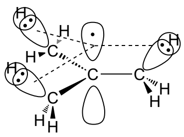
Allyl and benzyl radicals are substantially stabilized

How to rationalize these trends?

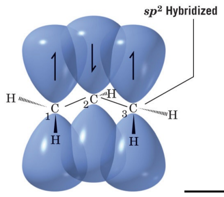
BDEs as a Measure of Radical Stability

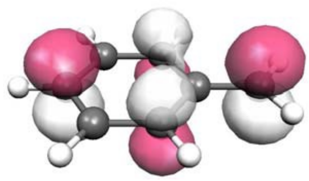
Interpretation of BDE Trends :

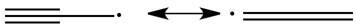
Tert-butyl is more stable than methyl: hyperconjugative interactions



Stabilization of allyl, benzyl and propargyl radicals: delocalization of the unshared electron into the benzene ring or pi-orbital framework.



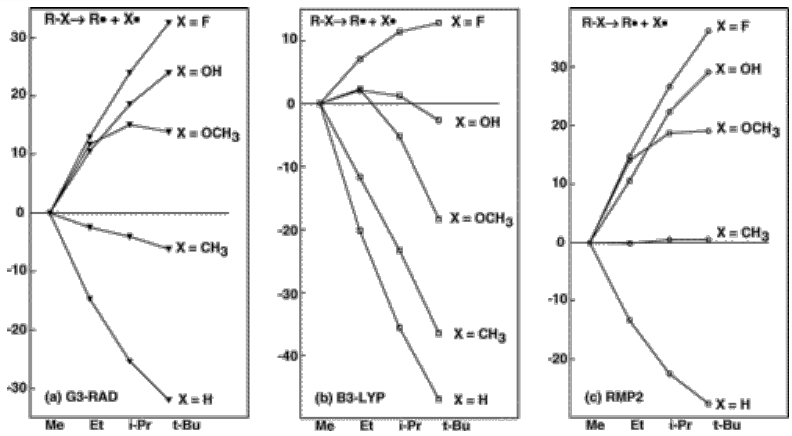




Chapter 2

13

BDEs as a Measure of Radical Stability



- The R-X BDE is strongly dependent on the nature of X.
- B3LYP underestimates BDEs.
- B3LYP fails to reproduce qualitative trends in relative BDEs

Chapter 2

14

BDEs as a Measure of Radical Stability

Computed (NBO) Charges on X of R-X

R	X = CH_3	X = OCH_3	X= OH	X =F
Me	0.000	-0.298	-0.282	-0.387
Et	0.008	-0.303	-0.285	-0.393
i-Pr	0.018	-0.309	-0.289	-0.400
t-Bu	0.028	-0.317	-0.294	-0.407

As R becomes more substituted, its electron-donating ability increases, and thus the stabilization of the bond via resonance increases. The bond dissociation reaction is expected to be less favorable with electronegative X.

Radom et al. *J. Phys. Chem. A* **2005**, *109*, 7558.

Chapter 2

15

BDEs as a Measure of Radical Stability

$$R_1R_2C{=}NOH \longrightarrow R_1R_2CH{=}NO^{\bullet} + H^{\bullet}$$

Experimental and Computed O-H BDE (kcal/mol) of some oximes

		Experimental BDE		Computed BDE	
R_1	R_2	Calor.[1]	Electro.[2]	DFT	CBS-QB3
H	Me	86.0	98.2	83.0	85.0
Me	Me	84.3	95.8	82.6	85.1
i-Pr	*i*-Pr	79.7	87.7	80.7	82.5
t-Bu	*i*-Pr	82.6	86.0	79.5	
t-Bu	*t*-Bu	79.2	84.2	75.6	

Computational work can be critical to resolve experimental disagreements!

[1]Ingold *et al. J. Am. Chem. Soc.* **1973**, *95*, 8610. [2]Bordwell *et al. J. Org. Chem.* **1992**, *57*, 3019.

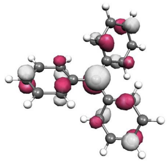
Chapter 2

16

Radical Persistence

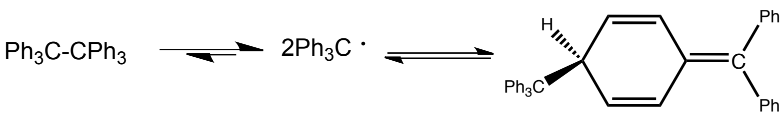
In general, radical species have a very short lifetime ($t_{1/2}$ ~10^{-10} s).

Trityl was the first radical that was characterized.



$$Ph_3C\text{-}Cl + Ag \longrightarrow Ph_3C^{\bullet} + AgCl$$

The overall stabilization of the trityl radical is not 3 times that of the benzyl stabilization but it persists in solution. Why?

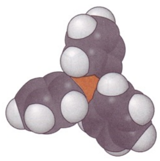


The major factor influencing the persistence of radicals is sterics and not a stabilization provided by their substituents.

Chapter 2

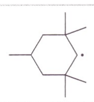
17

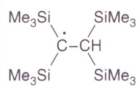
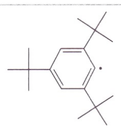
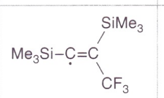
Radical Persistence



The overall stabilization of the trityl radical is not 3 times that of the benzyl stabilization but it persists in solution. Why?

The Persistence of Various Radicals*

R•	$t_{1/2}$, 25 °C, 10^{-5} M
$CH_3\cdot$	20 µs
	1 min
	4.2 min
$(t\text{-Bu})_3C\cdot$	8.4 min
$(Me_3Si)_3C\cdot$	2.3 days

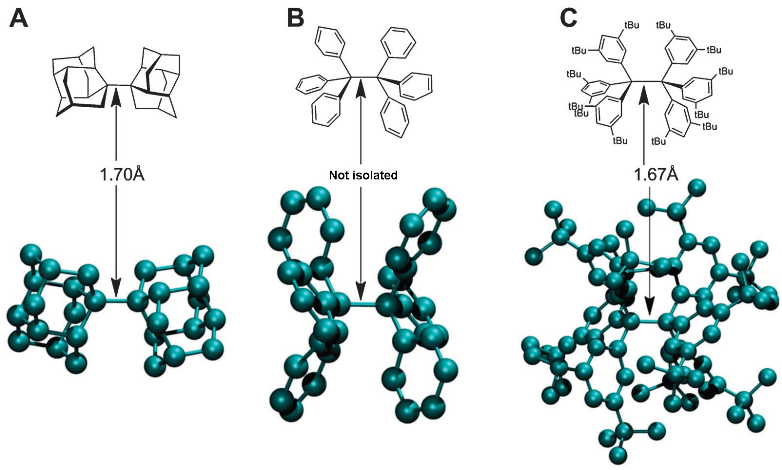
R•	$t_{1/2}$, 25 °C, 10^{-5} M
	> 110 days
	6 ms
	1 min

The major factor influencing the persistence of radicals is sterics and not stabilization provided by their substituents.

18

Radical Persistence

Can you explain the following? (see later)



19

Additivity Schemes

Additivity schemes aims at identifying useful energy patterns in a small set of representative molecules. These patterns can then be used as a fast prediction of thermochemical properties of novel systems.

20

Benson's Group Enthalpy Increments

Values of Heats of Formation of Simple Linear Alkanes (in kcal/mol)

		ΔH_f° (gas)	Difference	Group
methane	CH_4	-17.89		
			-2.35	[C-(C)(H)(H$_2$)]
ethane	CH_3-CH_2-H	-20.24		
			-4.58	[C-(C)$_2$(H)$_2$]
n-propane	CH_3-CH_2-CH_3	-24.82		
			-5.54	[C-(C)$_2$(H)$_2$]
n-butane	CH_3-CH_2-CH_2-CH_3	-30.36		
			-4.74	[C-(C)$_2$(H)$_2$]
n-pentane	CH_3-CH_2-CH_2-CH_2-CH_3	-35.10		
			-4.82	[C-(C)$_2$(H)$_2$]
n-hexane	CH_3-CH_2-CH_2-CH_2-CH_2-CH_3	-39.92		

statistically: -4.92 kcal/mol for [C-(C)$_2$(H)$_2$]

ΔH_f° (CH_3-CH_3) = 2 group equivalents of [C-(C)(H)$_3$]

statistically: -10.12 kcal/mol for [C-(C)(H)$_3$]

Benson *Chem. Rev.* Thermochemical Kinetics, 2nd ed. Wiley, 1976; updated, *Chem. Rev.* **1993**, *93*, 2419.

Chapter 2

21

Benson's Group Enthalpy Increments

Group Increments (in kcal/mol) for Fundamental Groupings*

Group	ΔH_f°	Group	ΔH_f°	Group	ΔH_f°
C–(H)$_3$(C)	–10.20	C–(O)(C$_d$)(H)$_2$	–6.5	C–(O)$_2$(C)$_2$	–18.6
C–(H)$_2$(C)$_2$	–4.93	C$_B$–(O)	–0.9	C–(O)$_2$(C)(H)	–16.3
C–(H)(C)$_3$	–1.90	O–(C)$_2$	–23.2	C–(O)$_2$(H)$_2$	–16.1
C–(C)$_4$	0.50	O–(C)(H)	–37.9	C–(N)(H)$_3$	–10.08
C$_d$–(H)$_2$	6.26	O–(C$_d$)$_2$	–33.0	C–(N)(C)(H)$_2$	–6.6
C$_d$–(H)(C)	8.59	O–(C$_d$)(C)	–30.5	C–(N)(C)$_2$(H)	–5.2
C$_d$–(C)$_2$	10.34	O–(C$_B$)$_2$	–21.1	C–(N)(C)$_3$	–3.2
C$_d$–(C$_d$)(H)	6.78	O–(C$_B$)(C)	–23.0	C$_B$–(N)	–0.5
C$_d$–(C$_d$)(C)	8.88	O–(C$_B$)(H)	–37.9	N–(C)(H)$_2$	4.8
C$_d$–(C$_B$)(H)	6.78	C–(CO)(C)$_3$	1.58	N–(C)$_2$(H)	15.4
C$_d$–(C$_B$)(C)	8.64	C–(CO)(C)$_2$(H)	–1.83	N–(C)$_3$	24.4
C$_d$–(C$_d$)$_2$	4.6	C–(CO)(C)(H)$_2$	–5.0	N–(C$_B$)(H)$_2$	4.8
C$_B$–(H)	3.30	C–(CO)(H)$_3$	–10.08	N–(C$_B$)(C)(H)	14.9
C$_B$–(C)	5.51	C$_B$–(CO)	9.7	N–(C$_B$)(C)$_2$	26.2
C$_B$–(C$_d$)	5.68	CO–(C)$_2$	–31.4	N–(C$_B$)$_2$(H)	16.3
C$_B$–(C$_B$)	4.96	CO–(C)(H)	–29.1	N$_I$–(H)	16.3
C–(C$_d$)(C)(H)$_2$	–4.76	CO–(H)$_2$	–26.0	N$_I$–(C)	21.3
C–(C$_d$)$_2$(H)$_2$	–4.29	CO–(C$_B$)$_2$	–25.8	N$_I$–(C$_B$)	16.7
C–(C$_d$)(C$_B$)(H)$_2$	–4.29	CO–(C$_B$)(C)	–30.9	CO–(N)(H)	–29.6
C–(C$_B$)(C)(H)$_2$	–4.86	CO–(C$_B$)(H)	–29.1	CO–(N)(C)	–32.8
C–(C$_d$)(C)$_2$(H)	–1.48	CO–(O)(C)	–35.1	N–(CO)(H)$_2$	–14.9
C–(C$_B$)(C)$_2$(H)	–0.98	CO–(O)(H)	–32.1	N–(CO)(C)(H)	–4.4
C–(C$_d$)(C)$_3$	1.68	CO–(O)(C$_d$)	–32.0	N–(CO)(C)$_2$	—
C–(C$_B$)(C)$_3$	2.81	CO–(O)(C$_B$)	–36.6	N–(CO)(C$_B$)(H)	0.4
C–(O)(C)$_3$	–6.6	CO–(C$_d$)(H)	–29.1	N–(CO)$_2$(H)	–18.5
C–(O)(C)$_2$(H)	–7.2	O–(CO)(C)	–43.1	N–(CO)$_2$(C)	–5.9
C–(O)(C)(H)$_2$	–8.1	O–(CO)(H)	–58.1	N–(CO)$_2$(C$_B$)	–0.5
C–(O)(H)$_3$	–10.08	C$_d$(CO)(C)	7.5		
C–(O)(C$_B$)(H)$_2$	–8.1	C$_d$–(CO)(H)	5.0		

Chapter 2

22

Benson's Group Enthalpy Increments

Table 2.7
Group Increment Values for Free Radicals (kcal/mol)*

Radical	$\Delta H_f°$	Radical	$\Delta H_f°$
[•C–(C)(H)$_2$]	35.82	[C–(O•)(C)(H)$_2$]	6.1
[•C–(C)$_2$(H)]	37.45	[C–(O•)(C)$_2$(H)]	7.8
[•C–(C)$_3$]	38.00	[C–(O•)(C)$_3$]	8.6
[•C–(H$_2$)(C$_d$)]	23.2	[C–(CO$_2$•)(H)$_3$]	–47.5
[•C–(H)(C)(C$_d$)]	25.5	[C–(CO$_2$•)(H)$_2$(C)]	–41.9
[•C–(C)$_2$(C$_d$)]	24.8	[C–(CO$_2$•)(H)(C)$_2$]	–39.0
[•C–(C$_B$)(H)$_2$]	23.0	[•N–(H)(C)]	(55.3)
[•C–(C$_B$)(C)(H)]	24.7	[•N–(C)$_2$]	(58.4)
[•C–(C$_B$)(C)$_2$]	25.5	[C–(•N)(C)(H)$_2$]	–6.6
[C–(C•)(H)$_3$]	–10.08	[C–(•N)(C)$_2$(H)]	–5.2
[C–(C•)(C)(H)$_2$]	–4.95	[C–(•N)(C)$_3$]	(–3.2)
[C–(C•)(C)$_2$(H)]	–1.90	[•C–(H)$_2$(CN)]	(58.2)
[C–(C•)(C)$_3$]	1.50	[•C–(H)(C)(CN)]	(56.8)
[C$_d$–(C•)(H)]	8.59	[•C–(C)$_2$(CN)]	(56.1)
[C$_d$–(C•)(C)]	10.34	[•N–(H)(C$_B$)]	38.0
[C$_B$–C•]	5.51	[•N–(C)(C$_B$)]	42.7
[C–(•CO)(H)$_3$]	–5.4	[C$_B$–N•]	–0.5
[C–(•CO)(C)$_2$(H)]	2.6		
[C–(•CO)(C)(H)$_2$]	–0.3		

C$_d$ = double bond; C$_B$ = benzene carbon; N$_I$ = imine nitrogen. Values in parentheses are highly approximate.

*Data are from Benson, S. W. (1976). *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2d ed., John Wiley & Sons, New York.

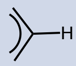
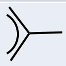
Chapter 2

23

Benson's Group Enthalpy Increments

Benson *Chem. Rev.* Thermochemical Kinetics, 2[nd] ed. Wiley, 1976; updated, *Chem. Rev.* **1993**, *93*, 2419.

	$\Delta H_f°$ (kcal mol^{-1})	
	1976	1993
[CH$_3$(C)]	-10.20	-10.00
[CH$_2$(C)$_2$]	-4.93	-5.00
[CH(C)$_3$]	-1.9	-2.4
[C-(C)$_4$]	-0.5	-0.1

	$\Delta H_f°$ (kcal mol^{-1})
	1993
=CH$_2$	6.27
=CH-	8.55
=C(C)$_2$	10.19
	3.29
	5.49
≡C—H	27.1
≡C—	27.3

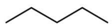
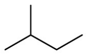
Basic groups for hydrocarbons

Chapter 2

24

Benson's Group Enthalpy Increments

Benson *Chem. Rev.* Thermochemical Kinetics, 2nd ed. Wiley, 1976;
updated, *Chem. Rev.* **1993**, *93*, 2419.

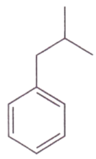
n-pentane		2-methylbutane		2,2-dimethylpropane	
					
ΔH_f° (gas): -35.10		-36.85		-40.27 kcal/mol	
2 $[C\text{-}(C)(H)_3]$:	-20.24	3 $[C\text{-}(C)(H)_3]$:	-30.36	4 $[C\text{-}(C)(H)_3]$:	-40.48
3 $[C\text{-}(C)_2(H)_2]$:	-14.76	1 $[C\text{-}(C)_2(H)_2]$:	-4.92		
first estimation:		1 $[C\text{-}(C)_3(H)]$:	-1.57	4 $[C\text{-}(C)_4]$:	+0.21
TOTAL:	-36.00	exp. ΔH_f°:	-36.85	exp. ΔH_f°:	-40.27 kcal/mol

Chapter 2

25

Benson's Group Enthalpy Increments

Calculate ΔH_f° using group increments:



5 $C_B-(H)$ =

1 $C_B-(C)$ =

1 $C-(C_B)(C)(H)_2$ =

1 $C-(H)(C)_3$ =

2 $C-(H)_3(C)$ =

Experimental: -5.15 ± 0.34 kcal/mol

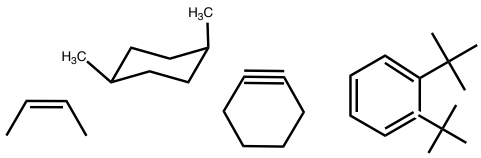
Chapter 2

26

Benson's Group Enthalpy Increments

The limit of group enthalpy increments:

- The Benson group method ignores interactions between groups (e.g. ring strain, bond eclipsing, (hyper)conjugation).



- The Benson group values might fail in case of insufficient thermochemical data (e.g. diazenes, oximes).

Illustrative Applications

The knowledge of reliable specific bond dissociation energies, *i.e.*, in particular the variation in bond strength with changes in structure, provides the quantitative information about the reactivity/structure relationship.

For examples, BDE and Benson Increments can be used to estimate thermochemical properties and discriminate amongst reaction mechanisms:

Example (case study): determination of the mechanism of a pericyclic reaction.

Terminology in Pericyclic Chemistry

A pericyclic reaction involves a transition state with a cyclic array of atoms and a cyclic array of interacting orbitals.

A concerted reaction occurs in a single step without intermediate

A stepwise process has one or more intermediates (carbocations, radicals, carbenes or carbanions)

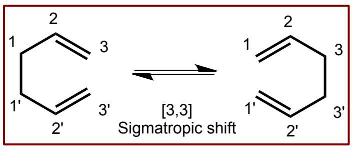
Not all concerted reactions are pericyclic (e.g. S_N2 reactions)

The term synchronous means that all bond making and bond breaking Have occurred at the same extent at the transition state.

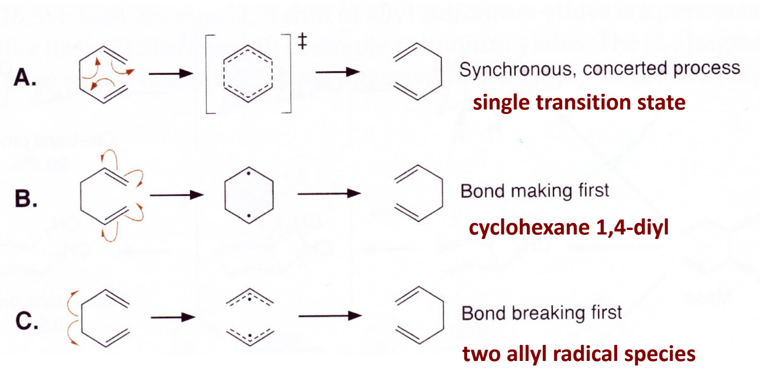
Chapter 2

29

What is the precise mechanism of the parent degenerate Cope Rearrangement: [3,3] Sigmatropic shift ?



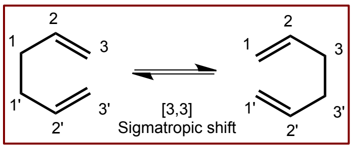
ΔH_a = 33.5 kcal mol^{-1} from experiment



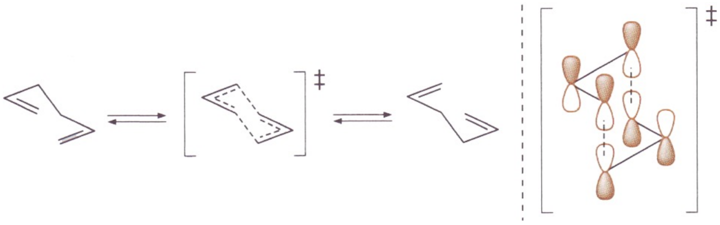
Chapter 2

30

What is the precise mechanism of the parent degenerate Cope Rearrangement ?



ΔH_a = 33.5 kcal mol^{-1} from experiment

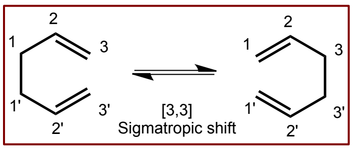


Concerted and pericyclic or not ?

Chapter 2

31

What is the precise mechanism of the parent degenerate Cope Rearrangement ?



ΔH_a = 33.5 kcal mol^{-1} from experiment

This cleavage pathway can be discounted for two reasons:

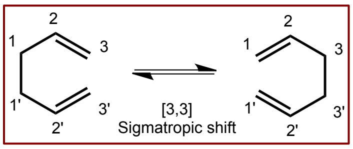
1. **Because of the too high dissociation energy of 1,5-hexadiene into two allyl radicals. Try to obtain this energy based on the Benson Increments.**

2. **Experiments show no crossover products.**

Chapter 2

32

What is the precise mechanism of the parent degenerate Cope Rearrangement ?

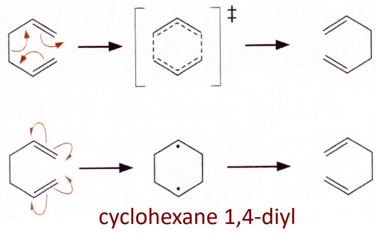


ΔH_a = 33.5 kcal mol^{-1} from experiment

Which cleavage pathway is favored? A or B?

Use the Benson increments and BDE to answer this question.

A.



Synchronous, concerted process

B.

Bond making first

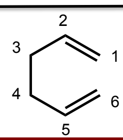
cyclohexane 1,4-diyl

The 1,4-diyl is estimated to be ? Kcal/mol^{-1} above 1,5-hexadiene!

Which computational methods?

TABLE 3.5. Energies (kcal mol^{-1}) and R_{16} for Transition States and Intermediates for the Cope Rearrangement.

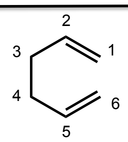
Method	R_{16} (Å)	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}_{298}$
Transition State			
RHF/6-31G*[a]	2.046	56.6	55.0
CASSCF(6,6)/6-31G*[a]	2.189	48.7	46.9
CASPT2 N/6-31G*[b]	1.745	31.2	30.8
CASPT2 N/6-311G(2d,2p)[b]	1.775	33.1	32.2
CCD/6-31G*[c]	1.874	42.1	41.1
CCSD/6-31G**[h]	1.89	41.1	
CCSD(T)/6-311G**[h]	1.82	35.2	
CR-CCSD(T)/6-311G**[h]	1.86	37.7	
B3LYP/6-31G*[a]	1.966	34.4	33.2
B3LYP/6-31+G(d,p)[d]	2.004		34.0
B3LYP/6-311+G*[e]		33.7	32.2
B3PW91/6-31G*[a]	1.877	32.1	31.0
CBS-QB3[f]			33.0
MD-CISD(CAS6,6)/6-31G*[g]		40.5	
MR-AQCC(CAS6,6)/6-31G*[g]	1.725	37.3	
MR-AQCC(CAS6,6)/6-311G(2d,1p)[g]	1.902	36.8	
MR-AQCC-ars(CAS6,6)/6-311G(2d,1p)[g]		33.4	
MCQDPT/6-311G**[h]	1.88	28.3	
Intermediate			
UHF/6-31G*[a]	1.558	20.4	19.2
CASSCF(6,6)/6-31G*[a]	1.641	46.8	47.0
MP2/6-31G*[e]	1.784	28.5	28.1
CCSD(T)/6-31G*[h]	1.72	36.2	
CCSD(T)/6-311G**[h]	1.72	35.3	
UB3LYP/6-31G*[a]	1.652	37.4	36.4
B3PW91/6-31G*[a]	1.611	32.3	31.5



- Hartree-Fock overestimates the barrier to the pericyclic TS.
- CASSCF overestimates the barrier height and does not distinguish the pathways.
- CASPT2: no diyl intermediate.
- Post-HF numbers are disappointing
- DFT works surprisingly well.

➔Dynamic and static electron correlations are important!

A Chameleonic model



B3LYP/6-31G* activation enthalpies (kcal/mol) and R_{16} (Å)

Substituents	ΔH_{298} Calc.	ΔH_{298} Expt.	R_{16}
H	33.2	33.5 ± 0.5[b]	1.965
1-CN	35.5		2.082, 2.131
3-CN	29.3		2.131, 2.082
1,4-diCN	29.9		2.236
1,3,4,6-tetraCN	24.7		2.467
2-CN	28.0		1.825
	27.8		**1.607**
2,5-diCN	24.4	(23.3)[c]	1.752
	20.2		**1.575**
2,4-diCN	26.5		1.915, 1.966
1,2,3-triCN	29.1		2.104
1-phenyl	36.2		2.062, 2.122
3-phenyl	28.4	28.1 ± 0.4[d]	2.122, 2.062
1,4-diphenyl	29.2	29.9 ± 1.6[e]	2.241
1,3,4,6-tetraphenyl	19.1	21.3 ± 0.1[f]	2.649
2-phenyl	30.3	29.3 ± 1.6[d]	1.777, 1.700
	29.4		**1.599**
2,5-diphenyl	24.8	21.3 ± 0.3[d,g]	1.839, 1.667
	21.3		**1.576**
2,4-diphenyl	26.7	24.6 ± 0.8[d]	1.979, 1.900
1,3,5-triphenyl	29.2	27.8 ± 0.2	2.113, 2.106

- Outstanding agreement between theory and experiment.
- Radical stabilizing substituents can decrease the reaction barrier -> *Greater participation of the radical contributors to the wavefunction*.

Chapter 2

35

Mini Quiz 3

Use the group increment tables to refute or substantiate the following statements:

1. Iso-butane is more stable than *n*-butane.
2. For alkenes in a linear chain, an internal double bond is more stable than a terminal double bond.
3. Hydrogenation of olefines is generally more exothermic than hydrogenation of analogous carbonyls.

Chapter 2

36