

HANDBOOK OF
BOND
DISSOCIATION
ENERGIES
IN
ORGANIC
COMPOUNDS

HANDBOOK OF
BOND
DISSOCIATION
ENERGIES
IN
ORGANIC
COMPOUNDS

Yu-Ran Luo



CRC PRESS

Boca Raton London New York Washington, D.C.

Library of Congress Cataloging-in-Publication Data

Luo, Yu-Ran.

Handbook of bond dissociation energies in organic compounds / Yu-Ran Luo.

p. cm.

Includes bibliographical references and indexes.

ISBN 0-8493-1589-1 (alk. paper)

1. Organic compounds--Handbooks, manuals, etc. 2. Chemical bonds--Handbooks, manuals, etc. 3. Dissociation--Handbooks, manuals, etc. I. Title.

QD257.7 .L86 2002

547'.1224--dc21

2002031322

This book contains information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Reasonable efforts have been made to publish reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage or retrieval system, without prior permission in writing from the publisher.

The consent of CRC Press LLC does not extend to copying for general distribution, for promotion, for creating new works, or for resale. Specific permission must be obtained in writing from CRC Press LLC for such copying.

Direct all inquiries to CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton, Florida 33431.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation, without intent to infringe.

Visit the CRC Press Web site at www.crcpress.com

© 2003 by CRC Press LLC

No claim to original U.S. Government works

International Standard Book Number 0-8493-1589-1

Library of Congress Card Number 2002031322

Printed in the United States of America 1 2 3 4 5 6 7 8 9 0

Printed on acid-free paper

To

Dr. Sidney W. Benson

*who introduced me to the field of thermochemical kinetics
during my postdoctoral work at the University of Southern California*

Preface

Three of the most fundamental concepts in organic chemistry are structure, energetics and reactivity, and their interrelationships. Sometimes, attempting to discover reliable data on bond dissociation energies (BDEs) or the strengths of chemical bonds may be a frustrating exercise, analogous to seeking a needle in a haystack.

I began to collect experimental and theoretical values for BDEs in 1990. Four years later, Dr. S.E. Stein of the National Institute of Standards and Technology (NIST) encouraged me to continue in this task, essential for chemical kinetics, free radical chemistry, organic thermochemistry, and physical organic chemistry.

A variety of methods exist for determining BDE values, but almost none are accurate to better than “chemical accuracy” (± 1 kcal/mol, 1 calorie = 4.184 joules). The BDE values of many important compounds have been measured many times; for example, the C–H BDE in methane has been determined about 50 times since the 1930s. BDE values continue to be a source of lively controversy among scientists.

The data presented in this book are from experiments only, although theoretical calculations are very interesting. Collecting experimental BDE data has been like taking a class in the history of chemistry, with many prominent scientists having made significant contributions to the problems surrounding the BDEs. These include E.W.R. Steacie, L. Pauling, M. Szwarc, N.N. Semenov, and S.W. Benson.

The author is very happy to acknowledge the great help, encouragement, and discussions of many scientists in preparing this manuscript. These scientists are Professors S.W. Benson, F.W. Bordwell, Y.T. Lee, R.H. Byrne, A.M. Dean, J.F. Liebman, V.D. Parker, and I.R. Slagle (all of U.S.); P.D. Pacey, J.L. Holmes, D.A. Armstrong, and E. Tschuikow-Roux (all of Canada); J.A. Kerr, R. Walsh, and M.J. Pilling (all of U.K.); C. Rüchardt (Germany); K.D. King (Australia); X.Z. Zhao and J.P. Cheng (China); A.J. Colussi (Argentina); J.A.M. Simões (Portugal); J.A. Seetula (Finland); Drs. S.E. Stein and W. Tsang (NIST); T.J. Wallington (Ford Motor Company); M. Tirtowidjojo (Dow Chemical Company); K.U. Ingold, D.D.M. Wayner (NRC, Canada); and E.T. Denisov (Russia). I also would like to thank the reviewers for their suggestions and comments.

All comments and suggestions are welcomed. Anyone may contact me by e-mail at luo@molenergetics.com.

Yu-Ran Luo

List of notations and abbreviations

AE	appearance energy measurements
AP	appearance potentials
AOP	acidity–oxidation potential measurements
BDE	bond dissociation energy (or enthalpy)
CID	collision-induced dissociation
detect.	detection
DH ^o	i.e., BDE, where H emphasizes the BDE is an enthalpy change of thermochemistry
electrochem.	electrochemical technique
EA	electron affinity measurements
EPR	electron paramagnetic resonance spectrometry
ESR	electron spin resonance spectrometry
FT-ICR	Fourier transform ICR
FT-MS	Fourier transform mass spectrometry
FT-IR	Fourier transform infrared spectrometry
GPA	gas-phase acidity measurements
GC	gas chromatographic analysis
HPLC	high performance liquid chromatography
ICR	ion cyclotron resonance spectrometry
IE	electron impact method
IR	infrared spectrometry
MS	mass spectrometry
NMR	nuclear magnetic resonance spectrometry
PAC	photoacoustic calorimetry
PIMS	photoionization mass spectrometry
photobromin.	photobromination
photochlorin.	photochlorination
photodetach.	photodetachment
photodissocn.	photodissociation
photoelectr.	photoelectron
re-anal.	re-analysis of experimental data, i.e., revised
re-cal.	re-calculated BDEs from experimental data, i.e., revised
recommend.	recommended value
spectrom.	spectrometry
SPST	single-pulse shock tube technique

TR-PAC	time-resolved photoacoustic calorimetry
UV/VIS	ultraviolet and visible spectrometry detection
VLPP	very low pressure pyrolysis technique
VLPR	very low pressure reactor method

Contents

Chapter One Introduction

- 1.1 A database of the BDEs
- 1.2 What is the BDE?
- 1.3 Why we need reliable BDEs
- 1.4 Scope of this book
- 1.5 On energy units
- 1.6 How to search for BDEs in this book
- 1.7 How to use the tables of the BDE data

Chapter Two Experimental methods for measuring BDEs

Chapter Three Tabulated BDEs of C–H bonds

- 3.1 Chain saturated hydrocarbons
- 3.2 Chain unsaturated hydrocarbons
- 3.3 Cyclic hydrocarbons
- 3.4 Aromatic hydrocarbons
- 3.5 Halogenated hydrocarbons
- 3.6 Organic compounds containing heteroatoms
 - 3.6.1 C–H BDEs with α -OH, -OR, -C(O), and -C(O)O
 - 3.6.2 C–H BDEs with α -N, -CN, -NO, -NO₂, and -NN
 - 3.6.3 C–H BDEs with α -O, -N, and their groups
 - 3.6.4 C–H BDEs with α -C(S), -S, -SO, and -SO₂
 - 3.6.5 C–H BDEs with other heteroatoms at α -position

Chapter Four Tabulated BDEs of C–C bonds

- 4.1 Saturated hydrocarbons
- 4.2 Chain unsaturated hydrocarbons
- 4.3 Aromatic hydrocarbons
- 4.4 Halogenated hydrocarbons
- 4.5 Organic compounds containing heteroatoms
 - 4.5.1 Organic compounds containing oxygen atoms
 - 4.5.2 Organic compounds containing nitrogen atoms
 - 4.5.3 Organic compounds containing sulfur atoms

Chapter Five Tabulated BDEs of C–halogen bonds

- 5.1 C–F bonds
- 5.2 C–Cl bonds
- 5.3 C–Br bonds
- 5.4 C–I bonds

Chapter Six Tabulated BDEs of O–X bonds

- 6.1 O–H bonds
 - 6.1.1 O–H bonds in nonphenols
 - 6.1.2 O–H bonds in oximes and hydroxylamines
 - 6.1.3 O–H bonds in phenols
 - 6.1.4 O–H bonds in sterically hindered phenols
- 6.2 O–O bonds
- 6.3 O–C bonds
 - 6.3.1 O–C bonds in alcohols
 - 6.3.2 O–C bonds in ethers
 - 6.3.3 O–C bonds in esters, acids, and anhydrides
 - 6.3.4 O–C bonds in peroxides and peroxy
 - 6.3.5 O–C bonds in other species
- 6.4 O–N bonds
- 6.5 O–S, O–halogen, and O–P bonds

Chapter Seven Tabulated BDEs of N–X bonds

- 7.1 N–H bonds
 - 7.1.1 N–H bonds in nonanilines
 - 7.1.2 N–H bonds in anilines
 - 7.1.3 N–H bonds in cyclic compounds
- 7.2 N–N bonds
- 7.3 N–C bonds
- 7.4 N–S bonds
- 7.5 N–halogen bonds

Chapter Eight Tabulated BDEs of S–X bonds

- 8.1 S–H bonds
- 8.2 S–S bonds
- 8.3 S–C bonds
- 8.4 S–halogen and S–P bonds

Chapter Nine Tabulated BDEs of Si–, Ge–, Sn–, P–, and Se–X bonds

- 9.1 Si–X bonds
- 9.2 Ge–X bonds
- 9.3 Sn–X bonds
- 9.4 P–X bonds
- 9.5 Se–X bonds

Chapter Ten Tabulated BDEs in some inorganic compounds

Chapter Eleven Heats of formation of atoms, inorganic and organic radicals

- 11.1 Gaseous atoms
- 11.2 Small inorganic radicals in the gas phase
- 11.3 Organic radicals in the gas phase
 - 11.3.1 C-centered radicals
 - 11.3.2 O-centered radicals
 - 11.3.3 N-centered radicals
 - 11.3.4 S-centered radicals
 - 11.3.5 Si-, Ge-, and Sn-centered radicals
- 11.4 Group additivity values for organic radicals
 - 11.4.1 GAVs of C/H radicals
 - 11.4.2 GAVs of O/C/H radicals
 - 11.4.3 GAVs of N/C/H/O radicals
 - 11.4.4 GAVs of S/C/H/O radicals

References

chapter one

Introduction

1.1 A database of the BDEs

Chemistry and biochemistry are based on the concept of chemical bonds. The breaking and making of chemical bonds are involved in most chemical reactions. Chemists, biochemists, and chemical engineers thus need a complete database of the experimental data of bond dissociation energies (BDEs).

This book contains the experimental BDE data of **2700** bonds in **2400** organic compounds. It is the first comprehensive book on experimental BDE data. It is very helpful to end users searching for BDE data.

1.2 What is the BDE?

The homolytic BDE is defined as the enthalpy change in the following fission:



The BDE, $\text{DH}^\circ(\text{R-X})$, of an R-X bond is derived in the usual way from heats of formation of the species involved in the previous reaction:

$$\text{DH}^\circ(\text{R-X}) = \Delta_f\text{H}^\circ(\text{R}) + \Delta_f\text{H}^\circ(\text{X}) - \Delta_f\text{H}^\circ(\text{RX}) \quad (1.2)$$

Here $\Delta_f\text{H}^\circ$ represents the heats of formation of the respective species in the ideal gas state at standard pressure and a reference temperature of 298.15 K. The BDE is also called the bond dissociation enthalpy.

Today, heats of formation, $\Delta_f\text{H}^\circ(\text{RX})$, of about **four thousand** organic compounds are known. Most of them are available in the following publications: 1994FRE/KAB, 1994PED, 1994GUR/VEY, 1989COX/WAG, 1988LIA/BAR, 1986PED/NAY, and <http://webbook.nist.gov>. The experimental uncertainty of heats of formation of organic compounds is generally within the "chemical accuracy" (± 1 kcal/mol, 1 calorie = 4.184 joules). From Equation 1.2, measurements of BDEs are equivalent to measurements of heats of formation of free radicals, and vice versa. Experimental BDEs can be determined directly, and can be derived from Equation 1.2. For example, we may derive the BDE values of $\text{CH}_3\text{-X}$ and $\text{C}_2\text{H}_5\text{-X}$, where $\text{X} = \text{H, F, Cl, Br, I, OH, SH, NH}_2, \text{CN, NO, NO}_2, \text{CH}_3, \text{ and C}_2\text{H}_5$, if $\Delta_f\text{H}^\circ(\text{CH}_3)$ and $\Delta_f\text{H}^\circ(\text{C}_2\text{H}_5)$ are known.

The number of organic compounds confirmed is about **twenty million**. We must estimate the heats of formation of organic compounds and BDEs using *ab initio* MO theory,

density functional theory (DFT), semiempirical methods (such as PM3, AM1), molecular mechanics, group additivity, and others. The theoretical calculations are very interesting, but calculated BDEs are not included in this book.

1.3 Why we need reliable BDEs

The BDE measurements of organic compounds started in the 1930s. Szwarc first summarized many experimental BDEs in organic compounds (1950SZW). The earlier experimental data were collected by several publications: 1946STE, 1958COT, 1958SEM, 1962MOR, and 1966VED/GUR. Since then, almost all of these data have been updated. For example, the H-C BDE value in benzene increases to 111.2 ± 0.8 kcal/mol (1994BER/ELL) from 102 kcal/mol (1966VED/GUR).

The equilibrium constant K_{eq} is very sensitive to any error in the BDEs. An error of 1, 2, or 3 kcal leads to an error of a factor of 5.4, 29.2, or 158, respectively, in the equilibrium constant K_{eq} at 298 K! The currently experimental uncertainty of the absolute majority of BDE data is within 1 to 2 kcal/mol, which means the uncertainty is more than “chemical accuracy” (± 1 kcal/mol). Experimental BDE values thus will continue to be a source of lively controversy among scientists now and in the foreseeable future.

Several senior reviewers made efforts to update known BDEs as soon as possible, such as 1966KER, 1969GOL/BEN, 1970ONE/BEN, 1978BEN, 1982MCM/GOL, 1988COL, 1994BER/ELL, 1996TSA, and 1999COH. However, the number of experimental BDEs is increasing sharply. For example, the *CRC Handbook of Chemistry and Physics* (2002CRC) collected the BDEs of about **400** bonds in organic compounds. Now we have collected experimental data for more than **2700** bonds. Chemists, biochemists, and chemical engineers need a new publication which completely compiles the BDEs available.

By the way, a good BDE database of diatomic molecules can be found in Section 9 of the *CRC Handbook of Chemistry and Physics* (2002CRC), which collects over **800** data. BDEs of diatomic and smaller molecules can also be derived by using the *NIST-JANAF Thermochemical Table* (1998CHA).

1.4 Scope of this book

Experimental BDEs of many important organic compounds have been remeasured many times. A typical example is C-H BDE in methane. It has been reported up to 50 times since the 1930s, and the value spreads from an early 98 kcal/mol to the current 105 kcal/mol. We have collected all experimental data; however, it is not necessary to copy all of the data into this book, because most users are concerned with reliable experimental values only.

This book will present recent experimental data for the given bonds, a maximum of five values for each bond. Which is the most reliable or best data for the BDEs? It is hard to answer this question. Recent measurements are likely to be more reliable generally. Readers may search more experimental data by using the references listed.

The BDEs have been tabulated based on the center atom in the radicals. They are distinguished by C-X, O-X, N-X, S-X, Si-X, Ge-X, Sn-X, P-X, and Se-X BDEs, and are organized in [Chapters Three](#) through [Nine](#).

The BDE data in some but not all inorganic compounds are listed in [Chapter Ten](#). At present, this book does not collect the BDE data in metallorganic compounds. A great number of experimental data for ionic species are beyond the scope of this book, because

these data have been available in other databases: 1988LIA/BAR and <http://webbook.nist.gov>.

1.5 On energy units

The SI unit of energy is joule (1 calorie = 4.184 joules). There are three options for energy units: (1) joule only, (2) calories only, and (3) both units. Using both units is a better choice.

Why? There are two reasons: (1) most heats of formation of radicals and BDEs used to be measured in kcal/mol and (2) the range of the BDE values for common organic species is from about 40 (as RO-OR) to 110 (as H-C₆H₅, H-C₂H₃) kcal/mol. As you know, a lower number is easy to remember in everyday life; it is the same in science. For example, we may easily remember 105.0 kcal/mol of H-CH₃ BDE rather than 439.3 kJ/mol.

1.6 How to search for BDEs in this book

We encountered a great number of experimental BDEs from over 1000 publications. The data are like “goods” in a large department store: they should be organized on different “shelves” or locations for our “shopping.” In this book, these data are managed in various categories. The chemical bonds with most similar structural environments are assembled in tables: “goods shelves.” There are 49 tables for BDE data in this book. All tabulated values of the BDEs are systematized by the following seven orders:

1. **Bond class**, such as C-H, C-C, C-O, C-N, C-S, C-F, C-Cl, C-Br, C-I, and so on.
2. **Heteroatom(s) and functional group(s) at α -position** (relative to the broken bond), such as O, CO, C(O)O, N, CN, NO, NO₂, NN, S, SO, SO₂, and more. The heteroatom(s) and functional group(s) have significant influence on the BDEs. Organic chemistry is usually organized by the concept of functional groups. Therefore, users must first figure out heteroatom(s) and functional group(s) before searching the data. For example:
 - The primary C-H BDE in C₆H₅CH₂-H is listed in [Table 3.4](#). In this book, the **boldface** emphasizes the dissociated atom or group.
 - The secondary C-H BDE in PhCH₂COCH₃ is listed in [Table 3.6.1](#). There is a CO group at the α -position of the C-H bond.
 - The secondary C-H BDE in PhCOCH₂NMe₂ is listed in [Table 3.6.3](#). There are a CO group and an N atom at the α -position of the C-H bond.
 - The secondary C-H BDE in PhCOCH₂SO₂Ph is listed in [Table 3.6.4](#). There are a CO group and a SO₂ group at the α -position of the C-H bond.
3. **Bond order** (triple, double, and single) and the **bond degree** (primary, secondary, or tertiary). The compounds with triple bond and primary BDEs are listed first.
4. **Saturated or unsaturated** compounds. Saturated ones are listed first.
5. **Molecular size**. The BDEs of smaller molecules are arranged first.
6. **Molecular shape (chain or cyclic)**. The BDEs of chain molecules are arranged first.
7. While **substituent(s)-containing**, please first search the bonds in the parent molecules. For example, the C-H BDEs in substituted toluene are listed under C₆H₅CH₂-H.

Two indexes may also help your search, one of compound classes and the other of compound names.

1.7 How to use the tables of the BDE data

All BDE data are filed into 49 different tables. How can you find the BDEs? Let us see a first example, the C–H BDE in methane:

The broken bonds (boldface = dissociated atom) $\Delta_f H^\circ(R)$, kcal/mol (kJ/mol)	BDEs (boldface = recommended data; references in parentheses)		Methods (references in parentheses)	References
	kcal/mol	kJ/mol		
	methane	(1) 105.0±0.1	439.3±0.4	(1) VLPP
CH ₃ –H	(2) 105.3±0.7	440.6±2.9	(2) PIMS detection	(2) 1988RUS/SEE(b)
	(3) 104.8±0.2	438.5±0.8	(3) Spectrometric detection	(3) 1988RUS/SEE
$\Delta_f H^\circ(R) = 35.06 \pm 0.1$ (146.69±0.4)	(4) 105.3±0.6	440.6±2.5	(4) Resonance detection	(4) 1991NIC/DIJ
	(5) 104.99±0.03	439.28±0.13	(5) AE, revised	(5) 1999RUS/LIT

The first column in this table shows the broken bonds. The **boldface** emphasizes the dissociated atom or group; here the H is **boldfaced**. For example, CH₃CH₂CH₂CH₃ shows a secondary C–H bond in n-butane is broken; (CH₃CH₂)₃N shows a secondary C–H bond in triethylamine is broken. All expressions are similar. The heat of formation of free radicals is shown in this cell. [Chapter Eleven](#) includes tables of all $\Delta_f H^\circ(R)$.

The second column shows the experimental values of BDEs for the given bond. The numbers (1), (2), (3), (4), and (5) show five different resources or references. The recommended value is emphasized by **boldface**.

The third column shows various experimental methods for the relevant BDE value. For an explanation of terms, see the Notations and Abbreviations list in this book.

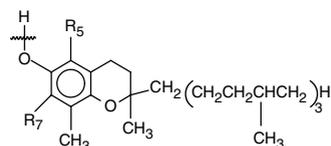
The fourth column shows the references for the given experimental methods and for the relevant BDE value. A maximum of five values are provided. This is sufficient for most users. Readers can search for more references while using the references here.

Following are another three examples:

1. The C–O BDE in methoxybenzene or anisole. The experimental data of BDE(C–O) are from four different methods. The first three values are contributed from independent measurements of different research groups. The last one is derived by Equation 1.2, in which heats of formation of the parent molecules are taken from the given reference, and heats of formation of atoms and radicals are taken from Chapter Eleven.
2. The weakest H–O BDEs in four tocopherols (vitamin E). They emphasize the difference of experimental H–O BDEs in gas phase and in liquid phase.
3. The H–N BDEs in substituted diphenylamine. They show the effect of various remote substituents Y on the H–N BDEs.

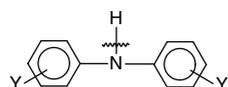
The broken bonds (boldface = dissociated group)	BDEs (boldface = recommended data; references in parentheses)		Methods (references in parentheses)	References
	kcal/mol	kJ/mol		
methoxybenzene or anisole	(1) 64.8	271.1	(1) VLPP	(1) 1989SUR/KAF
CH₃-OC₆H₅	(2) 65.2	272.8	(2) Tubular flow reactor	(2) 1993ARE/LOU
	(3) 65.3	273.2	(3) VLPP	(3) 2001PRA/HEE
	(4) 64.2±1.7	268.6±7.1	(4) Derived from $\Delta_f H^\circ$ in ref.	(4) 1986PED/NAY

α -tocopherol



$R_5 = R_7 = \text{CH}_3$ (vitamin E)	(1) 80.4	336.4	(1) Estimated by rate constants	(1) 1985BUR/DOB
	(2) 78.9	330.1	(2) EPR	(2) 1992JAC/HOS
	(3) 78.9	330.1	(3) EPR	(3) 1994LUC/PED
	(4) 80.9±1.0, in solution	338.5±4.2	(4) AOP	(4) 1996BOR/LIU
	(5) 79.3 , in solution	331.8	(5) APC	(5) 1996WAY/LUS
	(5) 77.3 , in gas	323.4		
δ -tocopherol $R_5 = R_7 = \text{H}$	(5) 82.2, in solution	343.9		
	(5) 80.2, in gas	335.6		
	(6) 81.9	342.8	(6) Correlation	(6) 2000DEN/DEN
β -tocopherol $R_5 = \text{CH}_3, R_7 = \text{H}$	(6) 80.2	335.6		
γ -tocopherol $R_5 = \text{H}, R_7 = \text{CH}_3$	(6) 80.1	335.1		

diphenylamine, substituted



(continued)

Table (continued)

The broken bonds (boldface – dissociated group)	BDEs (boldface = recommended data; references in parentheses)		Methods (references in parentheses)	References
	kcal/mol	kJ/mol		
Y = p-Br	(1) 88.1 (2) 87.0	368.6 364.2	(1) AOP (2) Correlation	(1) 1993BOR/ZHA (2) 2000DEN/DEN
p-MeO	(1) 84.2 (2) 83.3 (4) 81.8	352.3 348.6 342.2		
p-Me	(2) 85.4 (3) 86.3 in sol. (3) 86.2 in gas (4) 83.3	357.5 361.1 in sol. 360.7 in gas 348.5	(3) PAC (4) EPR	(3) 1997MAC/WAY (4) 2002PRA/DIL
p-tBu	(2) 85.8	358.8		
p-N(CH ₃) ₂	(4) 79.5	332.6		

chapter two

Experimental methods for measuring BDEs

The object of most end users is to find reliable data. However, it is very helpful if the users know the sources of experimental BDE data.

A very concise description of experimental methods is summarized below. It provides main methods, measured quantities, applications, and references. It is hoped that it may help the reader to better interpret the tables of BDE data from [Chapters Three](#) through [Ten](#).

Table 2.1 A Summary of Main Experimental Methods for Measuring BDEs

Experimental Methods	Measured Quantities	Applications	References
Spectrometry	Spacing of vibrational energy levels	Diatomic molecules in gas phase	(1) 1968GAY (2) 1970DAR (3) 1979HUB/HER
Pyrolysis kinetics, including <ul style="list-style-type: none">• Toluene carrier tech• Very low pressure pyrolysis (VLPP)• Shock tubes• Single-pulse shock tubes (SPST)• Laser-powered pyrolysis	Concentration of atoms, free radicals, and molecules vs. time at different temperatures, using various detecting techniques, such as GC, HPLC, MS, FT-IR, UV/VIS, EPR, NMR, resonance fluorescence, chemiluminescence, etc.	Species in gas and solution phase	1950SZW (1) 1973GOL/SPO (2) 1979ROS/KIN (3) 1982MCM/GOL (1) 1992DOU/MAC (2) 1997KIE/ZHA (1) 1981TSA (2) 1999TSA (1) 1982MCM/LEW (2) 1984LEW/GOL

(continued)

Table 2.1 (continued) A Summary of Main Experimental Methods for Measuring BDEs

Experimental Methods	Measured Quantities	Applications	References
Chemical equilibrium and kinetics	Concentration of atoms, free radicals, and molecules at one or several temperatures, using various detecting methods	Species in gas and solution phase	(1) 1966KER (2) 1977KER (3) 1982CAS/GRI (4) 1982MCM/GOL (5) 1984PAC/WIL (6) 1990KOE/SCO (7) 1990HAL (8) 1992WAL (9) 1994BER/ELL
	Correlation between BDEs and rate constants or activation energies		(1) 1966KER (2) 1978KAT/RAJ (3) 2000DEN/DEN
Photolysis, including	Concentration at one or several temperatures, using various analytical methods	Species in gas and solution phase	
• UV			(1) 1971LAU/OKA (2) 1995BOY/NOZ
• Radiolysis			(1) 1990LIN/SHE (2) 2001DAS
• Laser			(1) 1987CHU/FOL (2) 1988PEN/CAO (3) 1997BEC/CAR
• Photosensitized			1967LOU/LAI
Mass spectrometry (MS), including	Measure the given quantities and describe their correlation with BDEs	Species in gas phase	2001ERV
• Electron impact	Ion intensities vs. electron energy		(1) 1979BER (2) 1984HOL/LOS (3) 1992HOL
• Guided ion beam	Ion intensities vs. ion kinetic energy		(1) 1995ARM (2) 1998DET/ERV
• High pressure	Ion intensities vs. temperature		(1) 1994BUS/KEM (2) 1994BOW (3) 1999MCM

• Ion cyclotron resonance (ICR)	Ion intensities vs. time, vs. electron or photon energy	(1) 1980DEF/MCI (2) 2000BOR/ING (3) 1999ABB/NOT
• High temperature	Ion intensities vs. temperature	1984MAR
• Photoionization (PIMS)	Ion intensities vs. photon energy	(1) 1994BER/ELL (2) 1994BAR
• Pulsed high pressure	Ion intensities at one or several temperatures	(1) 1989MEO (2) 1993SHA/KEB
• Kinetic method	Ion intensities	1994COO/PAT
• Kinetic energy release distributions	Ion intensities vs. product kinetic energy	1992BEA

Photospectrometry, including	Measure the given quantities and describe their correlation with BDEs	Species in gas phase
• Photoelectron	Electron count vs. electron kinetic energy	(1) 1984MEA (2) 1994BER/ELL
• Electron photo-detachment	Ion intensities vs. photon energy	(1) 1987WET/BRA (2) 1989CHE/ALB
• Flowing afterglow	Ion intensities vs. time, or vs. ion kinetic energy	(1) 1992SQU (2) 1994BER/ELL
• Collision-induced dissociation	Collision energy vs. cross section	(3) 1994WEN/SQU (4) 2001HAM/WEN

Electrochemical, including acidities and oxidation potentials (AOP)	Acidity, reversible redox potentials	Species in solution	(1) 1993BOR/ZHA (2) 1993WAY/PAR (3) 1993ARN/FLO (4) 1995BOR/SAT
---------------------------------------------------------------------	--------------------------------------	---------------------	--------------------------------------------------------------------------

Photoacoustic calorimetry (PAC)	Amplitude of photoacoustic signal and solution transmittance	Species in solution	(1) 1989KAM/GIL (2) 1994PET (3) 1999LAA/MUL (4) 1999SAN/LAG
	Time-resolved PAC		(5) 2002SAN/MUR

chapter three

Tabulated BDEs of C–H bonds

3.1 Chain saturated hydrocarbons

Table 3.1 C-H BDEs in Chain Saturated Hydrocarbons

The broken bonds (boldface = dissociated atom) $\Delta_f H^\circ(\text{R})$, kcal/mol (kJ/mol)	BDEs (boldface = recommended data; references in parentheses)		Methods (references in parentheses)	References
	kcal/mol	kJ/mol		
methane CH₃-H $\Delta_f H^\circ(\text{R}) = 35.06 \pm 0.1$ (146.69 \pm 0.4)	(1) 105.0 \pm 0.1	439.3 \pm 0.4	(1) VLPP	(1) 1987DOB/BEN
	(2) 105.3 \pm 0.7	440.6 \pm 2.9	(2) PIMS detection	(2) 1988RUS/SEE(b)
	(3) 104.8 \pm 0.2	438.5 \pm 0.8	(3) Spectrometric detection	(3) 1990SEE/RUS
	(4) 105.3 \pm 0.6	440.6 \pm 2.5	(4) Resonance fluorescence detection	(4) 1991NIC/DIJ
	(5) 104.99 \pm 0.03	439.28 \pm 0.13	(5) AE, revised	(5) 1999RUS/LIT
ethane CH₃CH₂-H $\Delta_f H^\circ(\text{R}) = 28.4 \pm 0.3$ (118.8 \pm 1.3)	(1) 100.5 \pm 0.5	420.5 \pm 2.1	(1) Kinetics	(1) 1984PAC/WIN
	(2) 100.5 \pm 0.5	420.5 \pm 2.1	(2) Resonance fluorescence detection	(2) 1986BRO/LIG
	(3) 100.8 \pm 0.7	421.7 \pm 2.9	(3) PIMS detection	(3) 1988RUS/SEE(b)
	(4) 101.0 \pm 0.4	422.6 \pm 1.7	(4) PIMS detection	(4) 1992SEA/PIL
	(5) 100.5 \pm 0.3	420.5 \pm 1.3	(5) VLPP	(5) 1997DOB/BEN
propane CH₃CH₂CH₂-H	(1) 99.9 \pm 1.0	418.0 \pm 4.2	(1) Radical buffer	(1) 1982CAS/GRI
	(2) 99.8 \pm 2	417.6 \pm 8.4	(2) AE	(2) 1992HOL

(continued)