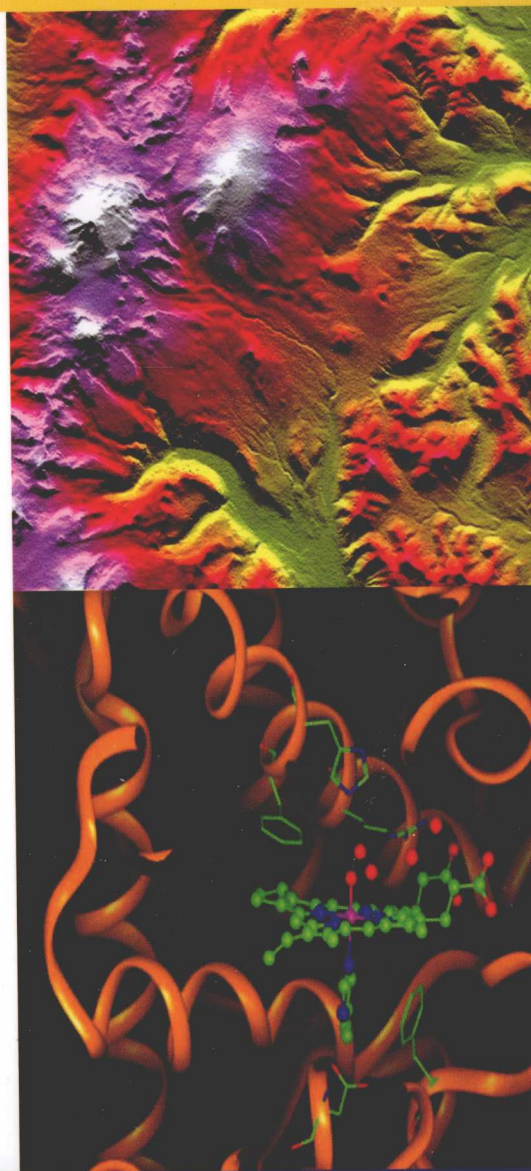


4th Edition

ORGANIC REACTION MECHANISMS

RAJ K BANSAL



New Academic Science

ORGANIC REACTION MECHANISMS

(FOURTH EDITION)

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ORGANIC REACTION MECHANISMS

*To my wife
Kusum
whose forbearance, steadfast
encouragement and inspiration
made this work possible*

PREFACE

My fourth edition of "Organic Reaction Mechanisms," has been greatly anticipated by the academic community. This updated version presents new outstanding methodologies for the elucidation of reaction mechanisms, the understanding of which is critical for the mastery of organic chemistry at the graduate and postgraduate level students. The text is written in simple and comprehensive language and focuses on the role of reaction mechanisms in the organic environment. As the text is directed to enhance the student's ability to predict the future behavior of chemical reactants, this book constitutes an important component of chemistry syllabi for all the academic institutions.

As in previous editions, the text is meticulously organized to enhance understanding. First, students are familiarized with the prototypical concepts of mechanisms. Then they are guided through both simple and involved mechanisms that include experimental probes for testing. All material discussed is presented with appropriate examples. This format enables students to gain meaningful expertise in deducting mechanisms while simultaneously sharpening their reasoning ability to predict and establish mechanisms of a new reaction.

As an enhancement, every chapter has a new 'look' while the text structure retains the logical organization of previous editions. All chapters are systematized and vastly improved with extraneous portions dropped and new problems added in each chapter appendage. Chapters 1-6 include new examples and experimental data from recent chemical literature. Chapters 7-9 and the pericyclic reaction section in Chapter 11 are reorganized with updated information. Further, topics such as Swern oxidation, semi pinacol-pinacolone rearrangement, Schmidt rearrangement, di-pi-methane rearrangement, and ipso substitution are added. Outdated deleted portions include decomposition of certain peroxides, the Grovenstein-Zimmermann rearrangement, Prins reaction, Hofmann-Loeffler reaction, Gomberg reaction and benzdine rearrangement, etc. All the references prior to 1960 have also been removed from the reference section. The bibliography is updated and diagrams refurbished.

I extend great appreciation to my former colleagues at the Indian Institute of Technology, Delhi for the assistance I received in preparing this book for publication. Their comments and suggestions, which were continuous and highly constructive throughout the endeavor, were of great value.

I extend my heartfelt gratitude to my family—to my wife who stood as my pillar of strength and support during every stage of this effort, and to my sons, for their extended support and encouragement. This book is complete because of their combined and steadfast cooperation.

Lastly, I thank all the professionals at New Academic Science for their adept and diligent handling of this project.

Raj K Bansal

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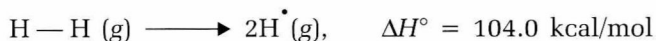
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BASIC CONCEPTS

The outlook towards organic chemistry has undergone great changes in recent years. Besides synthesis and the determination of the structure of molecules, the study, both chemical and kinetic, of organic reactions has been given considerable attention with a view to understanding the mechanism of reactions. Organic chemists continue to be engaged in the search for new reagents and new reactions. Yet, simultaneously, old reactions are being reinvestigated in order to establish their mechanisms. This has been possible by new experimental, analytical and spectroscopic techniques. Lewis first presented the concept of covalent bond in chemistry. The covalent bond was subsequently classified into polar and non-polar, depending on the electronegativities of the bonded atoms. A knowledge of the nature and strength of bonds is essential for the chemical investigation of organic molecules. Moreover, the properties of a molecule are always influenced by its structure. A brief description of certain basic concepts has been attempted in this chapter.

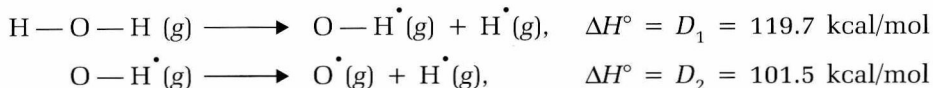
1.1 BOND DISSOCIATION ENERGY

It is a well known fact that when a covalent bond is formed between two atoms, a certain amount of energy is released. For instance, when hydrogen atoms combine to form hydrogen molecules, 104 kcal of heat is evolved for each mol of hydrogen formed. The **bond dissociation energy** instead, is the energy required (ΔH° at 25°C and 1 atm pressure) in cleaving a bond into two radicals. In the case of hydrogen molecule, a certain amount of energy is expended in splitting the molecule, *i.e.*,

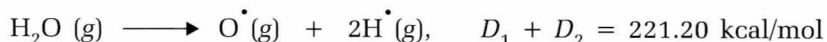


The dissociation energy of the H—H bond is thus 104 kcal/mol. Such a process is an endothermic process, therefore, ΔH° will be a positive value. This information is obtained by molecular spectroscopy, thermal methods and electron impact studies.¹ Walsh argued theoretically that the strength of a covalent bond increased with increase in the difference of electronegativity of the bonded atoms. This is apparent from the values listed in Table 1.1 (cf. carbon—halogen bonds).

The bond dissociation energy is not equal to the bond energy. The definition of **bond energy** is though less precise, since it is the average value of the energy required to break a bond between two atoms in a molecule. Let us, for instance, consider a water molecule which contains two H—O bonds. It is possible to measure the bond dissociation energy for the removal of one and then the second H atom from H₂O. The result is computed as follows:



It is apparent that the bond dissociation energy for the two steps is different but from Hess's Law one can state that their sum is equal to the energy of atomization (conversion of a molecule to its atoms) of the water molecule, i.e., 221.20 kcal/mol.



In water molecule there are two O—H bonds present that are equivalent and energy value can be assigned to each bond which is equal to the average value of D_1 and D_2 .

$$\frac{1}{2} (D_1 + D_2) \longrightarrow 110.6 \text{ kcal/mol.}$$

This is the bond energy and is often referred to as the mean theoretical bond energy and should be distinguished from the bond dissociation energy.

For diatomic molecules such as H_2 , Cl_2 , HCl , etc. bond energies and bond dissociation energies are equal. The bond dissociation energy for the same molecule may differ from molecule to molecule (see Table 1.1). The higher the bond energy, the stronger is the bond. Also increasing s -character shortens a bond so bond strength increases with s -character.

In a chemical reaction a new bond is usually formed while the old one is broken. It is, therefore, important to know the bond dissociation energy, which is a measure of the strength of a bond, to understand a chemical reaction. This may also reflect on the nature of the reaction.

TABLE 1.1: Bond Dissociation Energies (kcal/mol)

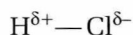
<i>Bond</i>	<i>Bond Dissociation Energy (ΔH°)</i>	<i>Bond</i>	<i>Bond Dissociation Energy (ΔH°)</i>
D — D	106.0	Na — Cl	98.1
H — H	104.2	H — F	136
C — C	83.1	H — Cl	103
N — N	38.4	H — Br	88
O — O	33.2	H — I	71
F — F	36.6	I — Cl	50.3
Cl — Cl	58.0	Si — F	129.3
Br — Br	46.1	C — N	69.7
I — I	36.1	C — F	108
Si — Si	42.2	C — Cl	84
P — P	51.3	C — Br	70
S — S	50.9	C — I	56
Si — H	76.0	CH_3 — Cl	81
H — O	102.4	CH_3CH_2 — Cl	81
CH_3 — H	104	$(\text{CH}_3)_2\text{C}$ — Cl	81
CH_3CH_2 — H	98		
$(\text{CH}_3)_2\text{C}$ — H	94	H	
		$(\text{CH}_3)_3\text{C}$ — Cl	78
H		$\text{C}_6\text{H}_5\text{CH}_2$ — H	85
$(\text{CH}_3)_3\text{C}$ — H	90	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$ — H	70
Si — C	85.7	$\text{CH}_2 = \text{CHCH}_2$ — H	85
Si — Br	69.1		
C — Si	69.3		

Except for the values of H—O, D—D and Na—Cl, other values are taken from S W Benson, *J. Chem. Educ.*, **42**, 502 (1965). The values of H—O, D—D and Na—Cl are from K S Pitzer, *J. Am. Chem. Soc.*, **70** 2140 (1948).

It is noticed from the above Table that C—H bond dissociation energies for ethane (98 kcal/mol) and for toluene (85 kcal/mol) are considerably different and smaller for toluene. The obvious reason for this difference is that the benzyl radical produced by bond dissociation in toluene is substantially stabilized by resonance.

1.2 ELECTRONEGATIVITY

A fundamental property of a chemical bond is polarity. The polarity of a bond depends on the nature of the atoms linking that bond. The preferred tendency shown by an atom of a covalent bond to attract the shared pair of electrons towards itself is termed as a measure of **electronegativity** of that atom. This unequal attraction of electrons causes a charge separation between the atoms and produces a dipole, indicated by a charge notation (δ^+ or δ^-) and shown for a bond between two atoms, i.e., HCl molecule:



The partial negative charge on the chlorine atom indicates that the chlorine atom has a greater tendency to attract the shared electron pair towards it. As a result the electron density of the bonding electrons lies more towards Cl atom. Chlorine is more electronegative than hydrogen. A complete transfer of electrons takes place in the case of ionic bonds. We often use electronegativities as a guide to predict whether a given bond will be polar or not and also the direction of its dipole moment.

Electronegativity values have been measured from a consideration of bond distances, bond energies and dipole moments. The data for some elements are listed in Table 1.2.

TABLE 1.2: Electronegativity Values of Different Elements

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca		Ge	As	Se	Br
0.8	1.0		1.7	2.0	2.4	2.8
Cs	Ba					
0.7	0.9					

Source: L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, (1960).

From these values the following conclusions may be drawn:

1. On going from top to bottom in a group, as the atomic size of the element increases the electronegativity decreases.
2. In a given period, electronegativity increases with increasing atomic number.
3. The more non-metallic an element, the greater is the electronegativity. The value of electronegativity for fluorine is the largest.

The electronegativity of carbon is almost similar to that of hydrogen, as a result C—H bond is usually considered as non-polar. As we will study in Chapter 4, nucleophilicity decreases with increasing electronegativity of the attacking atom. The electronegativity order for hybridized carbon orbitals is $sp > sp^2 > sp^3$.