Physical Organic Chemistry

Second Edition

物理有机化学 第2版

Neil Isaacs

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Through doubting we come to questioning and through questioning we come to the truth.
Peter Abelard, Paris, 1122

Seek for simplicity—and then distrust it.
Alfred North Whitehead (1861–1947)

Foreword to first edition

Physical organic chemistry, the study of the underlying principles and rationale of organic reactions, is over eighty years of age. During this period of development, much has been learned which is now enshrined within the permanent fund of chemical knowledge. At the same time the process of refinement of chemical theory continues, new techniques are developed and viewpoints shift their emphasis. A crucial issue of one decade becomes resolved in another. This then underlies the reason for offering another text on the subject of physical organic chemistry, continuing the series of accounts which began with the notable and still useful book of the same title of 1940 written by Professor Hammett. It is hoped that the present work will help to fill the increasingly large gap between present knowledge and practice and the status of the subject as treated in earlier texts. In particular, the last decade has witnessed the increasing use of sophisticated instrumentation, particularly nuclear magnetic resonance which can probe the structures and even the shapes of molecules in solution. Other trends have been the adoption throughout every branch of the subject of computational techniques including molecular orbital theory both of the simple Hückel type and also at high levels and of molecular mechanics. These aids to understanding are increasing in importance as the reliability of the results is improved and as fast computers become more available to chemists. The trend is likely to continue and computer graphics (cover design) as an aid to making educated guesses as to molecular properties seems likely to make a major contribution to (as Woodward put it) 'the armamentarium of the chemist'. As a result of this, our understanding of chemical processes is shifting more towards the framework of quantum mechanics. The present text has been written with the object of presenting to the senior undergraduate, graduate student and research worker an account of the more important organic reactions including both the traditional evidence—for it is a subject dependent on observation and inference—and modern approaches.

Considerable amounts of data have been included since a firm grasp of a subject is better aided by perusal of collected information than by single representative values. Information up to 1986 is included. Chapters 1 to 9 deal with underlying principles of reaction pathways, of the physical forces which shape bonding between atoms and of the changes of bonding which are chemical reactions. Chapters 10 to 16 describe present knowledge and understanding of the various reaction types which make up organic chemistry and discuss the ingenious techniques which have been devised for mechanistic investigations. Space rather than choice has prevented the inclusion of certain topics including the organic chemistry of sulphur, phosphorus, silicon and metals, now of great importance but requiring a further book to do them justice.

Gratitude is extended to those colleagues who have advised me on the contents and who have read and criticized this text, notably Professors J. B. Lambert, L. K. Montgomery and N. Turro, and to Dr A. Gilbert for his help on the photochemical chapter.

University of Reading, November, 1986.

Foreword to second edition

The end of the twentieth century marks approximately one century of effort in attempting to understand the basis of chemical reactivity and the detailed pathways of reactions of organic compounds. The result can be viewed with some satisfaction in that broad principles have been established and the mechanisms of almost all reactions can now be said to be understood in modest detail. The subject has advanced in the eight years since the first edition was published. In particular, the availability of yet more powerful computers has permitted reaction pathways of processes such as Diels–Alder reactions to be mapped by computation with increasing accuracy and the properties of transition states and inaccessible molecules to be studied. Even a limited number of solvent molecules may be included in the computations which, whatever the precision, has greatly enhanced understanding and increased confidence in results inferred from experimental measurements. Single electron transfer routes have revealed unexpected aspects of what were considered well-understood reactions such as nitration. Linear Free Energy Relationships, increasing in sophistication, continue to contribute powerfully to reactivity theory and the experimental measurement of electronic transmission. The theory and practise of chiral induction has come under increasing scrutiny following the economic importance of asymmetric synthesis while the involvement of metals in organic chemistry has reached the point which makes organometallic chemistry a subject of a size and complexity to warrant separate treatment and too great to be included within a book of this size.

Acknowledgements of any improvements in this volume are due to the interest and helpful criticism of readers of whom, in particular, I would like to thank Professors Senning and Lund, University of Aarhus, and Professor Williams, University of Durham, for careful reading of the manuscript.

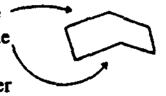
Reading, November, 1994

Symbols and abbreviations

α Coulomb integral (energy unit)
α Brønsted coefficient
α Taft solvation parameter
β resonance integral (energy unit)
β Brønsted coefficient
β Taft solvation parameter
β Bohr magneton
Γ parameter in Kaptein's equation
γ activity coefficient (molal units)
Δ, δ a difference between or change in (a quantity)
Δ spectroscopic term index
Δ pyrolysis (reaction condition)
δ NMR chemical shift
ε relative permittivity (dielectric constant)
ε molar extinction coefficient (absorptivity)
ε energy (occasional use)
ζ mixed solvent composition (occasional use)
θ angle
κ transmission coefficient
λ wavelength
λ term in Marcus equation
λ dual parameter reaction constant
μ reduced mass
ν frequency
$\bar{\nu}$ wave number
π molecular orbital with plane of symmetry
π^* an electronically excited π-orbital
π^* an empirical solvation parameter
ρ reaction constants of the Hammett and related equations
ρ spin density
Φ empirical solvation parameter
ϕ Bunnett–Olson parameter
ϕ fractionation factor
φ angle

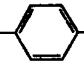
ϕ	atomic orbital wavefunction
σ	Hammett substituent constant
Ψ	molecular orbital wavefunction
χ	empirical solvation parameter
A	Helmholtz free energy
A	antisymmetric (orbital)
A	anchimeric assistance, extent of
A	pre-exponential term in Arrhenius equation
Ad	adamantyl
Ad	addition (reaction type)
AN	acceptor number (solvation parameter)
AO	atomic orbital
a	hyperfine coupling constant, ESR
anti-	on opposite sides (cf. syn-)
b	principal polarizability
B	hydrogen-bonding solvation parameter
$\mathbf{B}$	magnetic flux density
Bu	butyl
Bros	*p*-bromobenzenesulphonate
C	Coulomb (electrical charge)
C_p, C_V	heat capacity (constant pressure, constant volume)
CIDNP	Chemically Induced Dynamic Nuclear Polarization
c	concentration (molar)
D	bond dissociation enthalpy
D	cohesive energy density
D_π^*	empirical solvation parameter
DNB	dinitrobenzoate
d	density
d	diffusion coefficient
E	energy
E	elimination (reaction type)
Et	ethyl
E_q, E_{pol}, E_{exch}, E_{ct}	electrostatic, polarization, exchange and charge transfer energy
E_s, E_s^c	steric constants
E, E^+	a generalized electrophile
F, ES	(in structures) enzyme, enzyme–substrate complex
E_A	Arrhenius activation energy
E_T	empirical solvation parameter
E_N	Edwards nucleophilicity parameter
$\mathbf{E}_R$	reaction field
EC	effective concentration
ERE	empirical rate equation
ESR	electron spin resonance (= electron paramagnetic resonance, EPR, PMR)
exo, *endo*	stereochemistry with reference to a component of structure related to 'boat' cyclohexane:

exo side
endo side



F	force
F	field effect parameter
$\mathscr{F}$	Swain–Lupton field effect parameter
$f\,(f_o, f_m, f_p)$	partial rate factor (relating to *ortho, meta, para* positions of a substituted benzene)
f_t, f_n	Kirkwood electrostatic solvation functions
f	activity coefficient (mole fraction units)
G	Gibbs free energy
ΔG_{tr}	free energy of transfer
G_A, G_B	constants in the Brønsted catalysis law
g	gyromagnetic ratio
H	enthalpy (heat)
$\mathrm{H}_{i,i}$	Coulomb integral
$H_{i,j}$	resonance integral
$\mathscr{H}$	Hamiltonian operator
ΔH_{at}	standard heat of atomization
HMO	Hückel molecular orbital
HOMO	highest occupied molecular orbital
ΔH_f	standard heat of formation
H_0, H_I, H_R, H_A, H_-	acidity functions
H_N	Edwards nucleophilicity parameter
h	Planck's constant
I	indicator ratio
+I, −I	inductive effect (electron-donating, electron-withdrawing)
J_0	acidity function (see H_0)
K	Kelvin (temperature scale)
K	equilibrium constant
K_A	acid dissociation constant
K_M	Michaelis constant
k	specific rate constant: $k_1, k_2, k_3, \ldots$ are used both to denote rates of successive stages of a reaction and also to distinguish unimolecular, bimolecular, termolecular ... processes
k_{rel}	relative rate constant
k_H, k_D	rate constants for reaction of isotopic species containing H, D respectively
k_c, k_s, k_Δ	rate constants for components of solvolysis
k	Boltzmann constant
L	Avogadro's number
L	a generalized hydrogen isotope (i.e. H, D or T)
L_+, L_-	localization energy
LUMO	lowest unoccupied molecular orbital
l	nucleophilicity coefficient in Grunwald–Winstein equation
M	molar mass (molecular weight)
MO	molecular orbital
m	meter

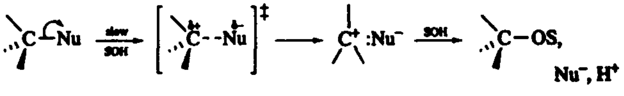
m_s	polarity coefficient in Grunwald–Winstein equation
mes	methanesulphonate ($-SO_2Me$)
N	Newton (unit of force)
N, N_+	nucleophilicity parameters
Nu:, Nu^-:	a generalized nucleophile
NAD (NADH)	nicotinamide adenosine dinucleotide (reduced form)
NGP	neighbouring-group participation
n	refractive undex
n	nucleophilicity parameter
n-	unshared pair (electrons, MO)
n	an integer
$\mathbf{p}$	dipole moment
P_E	total polarizability
P	empirical solvation parameter
PKIE	primary kinetic isotope effect
P	total bond order
Ph	phenyl
Pnp	paranitrophenyl
Pr	propyl
p	pressure (vapour pressure)
p, p_π	partial (π) bond order
Q	partition function
Q	constant in McConnell's equation
q	electric charge
q	integer in Woodward–Hoffmann rule
q	heat
R	gas constant
R—	a generalized unit of structure, usually an alkyl group
+R, −R	resonance effect (electron-donating, electron-withdrawing, respectively)
R	molar refraction
$\mathscr{R}$	Swain–Lupton resonance effect constant
r	correlation coefficient
r	integer in Woodward–Hoffmann rule
r	Yukawa–Tsuno constant
$S_{i,j}$	overlap integral
S	entropy
ΔS_f	standard entropy of formation
ΔS_{tr}	standard entropy of transfer
S	selectivity
S	empirical solvation parameter
$\mathscr{S}$	empirical solvation parameter
S	symmetric
S_N, S_E	substitution (nucleophilic, electrophilic)
S	substrate (in enzymic reaction schemes)
SOH	a generalized protic solvent
SOMO	singly-occupied molecular orbital

syn-	stereochemical designation; on the same side (cf. anti-)
s	coefficient in nucleophilicity correlation (see *n*)
T	temperature
t	time
TFA	*trifluoroacetic acid*
Tos	*p*-toluenesulphonyl, Me——SO_2O—
t-Bu	tertiary butyl, $(CH_3)_3C$—
U	total internal energy
u	function in Bigeleisen equation
V	vibrational quantum number
V	volt
VB	valence bond
v	volume
v	velocity of reaction
w	work
w	parameter in Bunnett equation
X	an electron-donating (resonance) substituent, e.g. MeO—
X	empirical solvation scale
x	concentration, mole fraction
x	a fractional amount ($0 < x < 1$)
Y-	a generalized substituent
Y	empirical solvation scale
y	activity coefficient (molar units)
Z-	an electron-withdrawing (resonance) substituent, e.g. —NO_2
↷	notional movement of an electron-pair (note the arrow must be directed Nu:↷E)
↷	notional movement of a single electron
‡	pertaining to the transition state
*	pertaining to an electronically excited state
—↓↑—	spin-paired electrons
—↑—	unpaired electron
↔	resonance, symbol connecting VB contributing structures

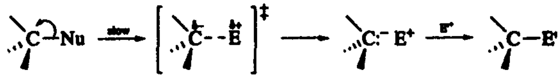
Mechanistic designations

A shorthand notation for the designation of reaction types is widely used in organic chemistry although it is not entirely systematic. In general, the symbol specifies the reaction as a substitution (S), addition (Ad) or elimination (E) followed as a subscript by the type of process—nucleophilic (N), electrophilic (E) or homolytic (H) and the molecularity of the slow step (1, 2 and sometimes 3). Other symbols include A (acid-catalysed), B (base-catalysed), Ar (aromatic) and cb (conjugate base); for carbonyl-type substitutions there are in addition, Ac (acyl–oxygen fission), Al (alkyl–oxygen fission). The following schemes are intended to be a quick guide to the essential features of various mechanistic types including their supposed transition states, enclosed in brackets and denoted by the sign (‡). Nu:⁻ and —E in structures are nucleofugic and electrofugic groups (i.e. leaving groups); the latter is usually —H. —X and —Z are electron-donating (+R) and electron-withdrawing (−R) substituents respectively, S stands for substrate (reagent) and SOH represents a protic (hydroxylic) solvent. The rate-determining step is also indicated by 'slow' for multistep reactions.

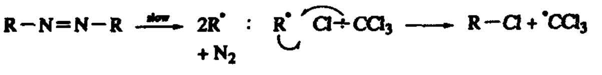
S_N1



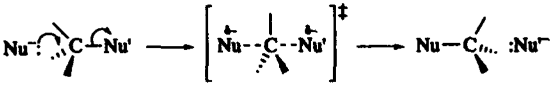
S_E1



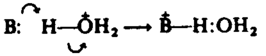
S_H1



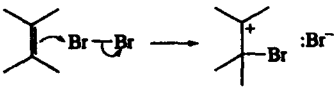
S_N2



This type of synchronous transfer is not limited to reactions at carbon, for instance:

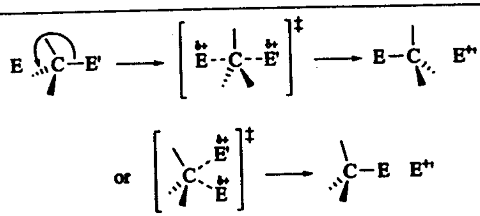


S_N2 reaction at H

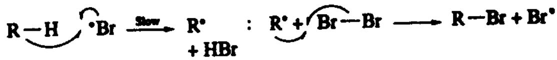


S_N2 reaction at Br

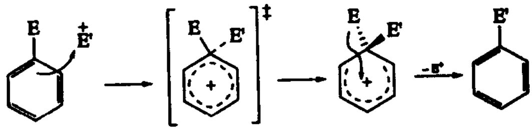
S_E2



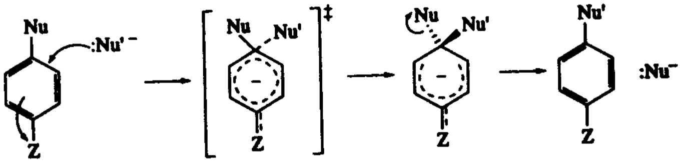
S_H2



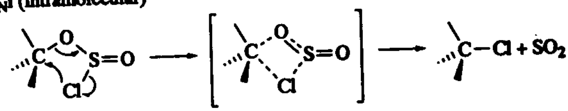
S_E2Ar



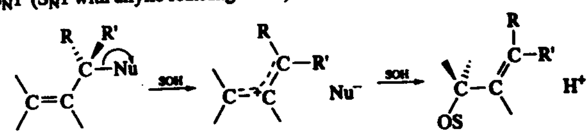
S_N2Ar



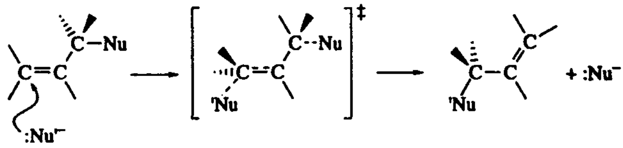
S_Ni (intramolecular)



S_N1' (S_N1 with allylic rearrangement)



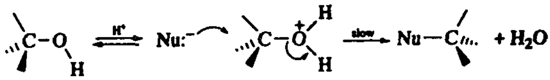
S_N2' (S_N2 with allylic rearrangement)



$S_{RN}1$, $S_{RN}2$; 1-electron reduction followed by S_N1 or S_N2 sequences
$S_{ON}1$, $S_{ON}2$; 1-electron oxidation followed by S_N1 or S_N2 sequences

A–S_N2

A–S_N2



A1 (hydrolytic processes)

$$S + H-\overset{+}{B} \rightleftharpoons S\overset{+}{H}:B$$

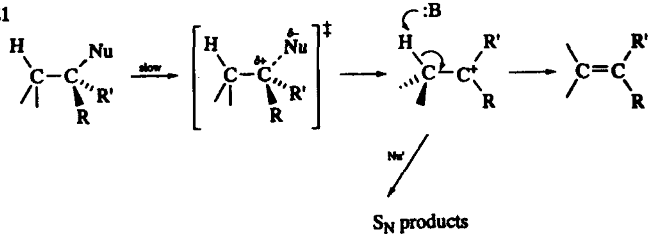
$$S\overset{+}{H} \xrightarrow{\text{slow}} \text{products}$$

A2 (hydrolytic processes)

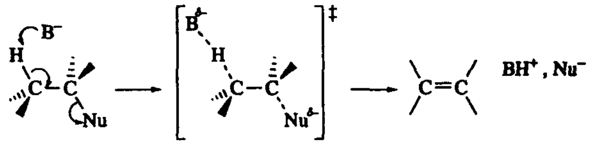
$$SH^+ + H_2O \xrightarrow{\text{slow}} \text{products}$$

Eliminations:

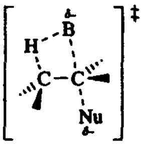
E1



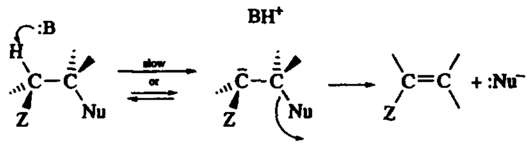
E2 (E2H)



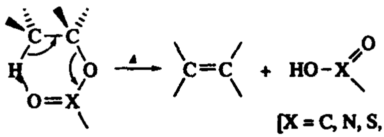
E2C is like E2H but the ‘soft’ base interacts both with C and H



Elcb

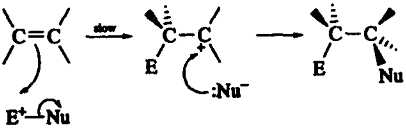


E_i

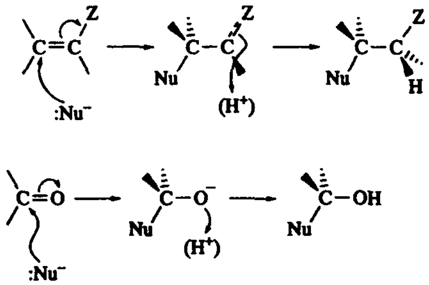


[X = C, N, S, Se]

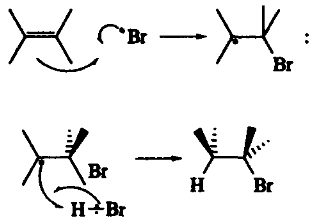
Additions:
Ad_E2



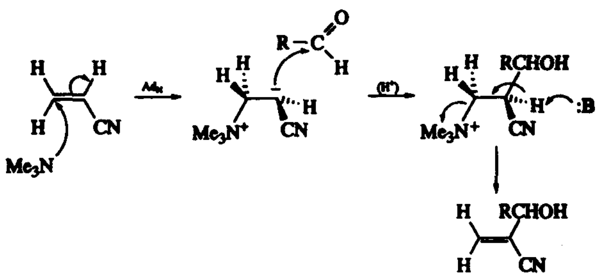
Ad_N2



Ad_H2



Ad–E: a sequence of addition followed by elimination, the net result being substitution



E–Ad: a sequence of elimination followed by addition resulting in substitution. See arynes (Section 10.5.3).