ORGANIC CHEMISTRY I

Organic chemistry I Organic chemistry of the basic hydrocarbon skeletons. The subject of organic chemistry. Chemical bonds and bonding in organic molecules. Hybridization of the carbon atom, bonding energy, bond length, polarity of the chemical bond. Inductive and mesomeric effects on the chemical bonds, conjugation. General criteria of chemical reaction - reaction kinetics, reaction profiles and mechanism. Activation energy and enthalpy of the reaction. Chemical nomenclature. Alkanes and cycloalkanes, their chemical nomenclature. Chain isomerie, conformation analysis of alkanes and cycloalkanes (with stress on cyclohexane ring). Fused cyclic systems. Newmann projection. cis-trans Isomerism of cycloalkanes. Radical reactions as typical reactions of this system. Summary of radical reactions. Optical activity and symmetry of molecules. Chiral molecules, conditions of chirality. Methods of space objects presentation. Enantiomers, optical activity, specific rotation and its measurement, optical purity, racemic mixture. Molecules with more than one stereocenter. Cahn, Ingold, Prelog rules. Nomenclature of enantiomers. Meso compounds. Resolution of enantiomers. Alkenes, stereochemistry of double bond, cis-trans and E-Z nomenclature. Addition reactions, their summary with attention to the stereochemistry and mechanism. Polymerizations.

ORGANIC CHEMISTRY I

Dienes and polyenes (cumulated, isolated, conjugated). Reactions of conjugated dienes, conditions and mechanism of 1,2- and 1,4-addition. Isoprenoides (monoterpenes, sesquiterpenes, di-, tri- and tetraterpenes, carotenes). Electronic spectra and relation between the structure and its spectrum. Pericyclic reactions - electrocyclic reactions, cycloaddition reactions, the rules of their realization, sigmatropic rearrangements. Akynes and their structure. Properties of the triple bond, addition reactions (electrophilic and nucleophilic additions), acidity of the hydrogen atoms bound on sp- carbon, pKa. The phenomenon of aromaticity and its properties. Nonbenzoid aromates (polycyclic aromates, annulenes, aromatic ions.} Mechanism of aromatic electrophilic substitution. Summary of electrophilic reactions, formation of electrophilic reagents. Effect of substituents on the reactivity and orientation. Hammet equation, sigma and rho constants. Ipso substitution. Nucleophilic substitution on the aromatic ring (SN1, SN2, elimination-addition mechanism). Conditions for addition reactions and reactions of oxidation. Substitution a other reactions on fused aromatic compounds.

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Chemical reaction and the theory

Every chemical reaction can be considered as reversible reaction

$$A + B \overset{K}{\rightleftharpoons} C + D \qquad K = \frac{[\,C\,]\,.\,[\,D\,]}{[\,A\,]\,.\,[\,B\,]}$$

For reactions taking place at constant pressure the equilibrium of the reaction is given by ΔG^o - standard change of Gibbs energy

$$\Delta G^o = \Delta H^o - T\,.\,\Delta S^o = -\ RT\,.\,\ln K$$

kde ΔH^o standard reaction enthalpy
ΔS^o standard reaction enthropy
T temperature
K equilibrium constant

Chemical reaction and the theory

For simple systems and reactions, in which the arrangement of atoms is not changing much during the reaction, then $\Delta S^o = 0$, and the equation is simplified

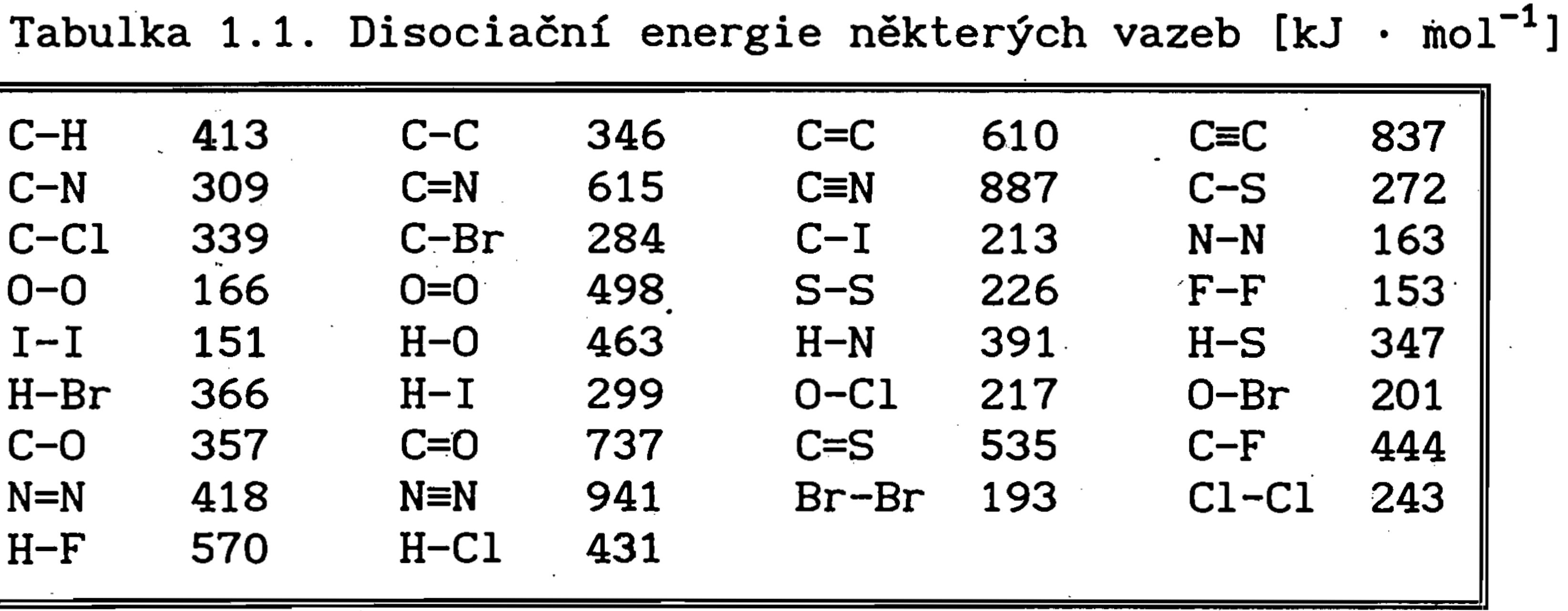
$$\boldsymbol{\Delta G^o = \Delta H^o = - RT \ln K}$$

Then based on the knowledge of $\boldsymbol{\Delta H^o}$ we can evaluate the equilibrium constant.

Heat of the reaction can be calculated when energy of split and formed bonds is known (consult the Table).

$$CH_3Br + H_2O \rightleftharpoons CH_3OH + HBr$$

Chemical reaction and the theory



Tabulka 1.1. Disociační energie některých vazeb [kJ · mol^{-1}]

C–H	413	C–C	346	C=C	610	C≡C	837
C–N	309	C=N	615	C≡N	887	C–S	272
C–Cl	339	C–Br	284	C–I	213	N–N	163
O–O	166	O=O	498	S–S	226	F–F	153
I–I	151	H–O	463	H–N	391	H–S	347
H–Br	366	H–I	299	O–Cl	217	O–Br	201
C–O	357	C=O	737	C=S	535	C–F	444
N=N	418	N≡N	941	Br–Br	193	Cl–Cl	243
H–F	570	H–Cl	431				

Energy of dissociation for several bond [kJ/mol^{-1}]

$$CH_3Br + H_2O \rightleftharpoons CH_3OH + HBr$$

During the reaction is split bond C-Br and O-H, they are formed bonds C-O and H-Br

+284 + 463 = + 747 kJ.mol^{-1} - 357+ (-366) = -723 kJ.mol^{-1}

To realize this reaction, we must add energy of +747 – 723 = + 24 kJ . mol^{-1}

reaction is endothermic

Chemical reaction and the theory

The value of ΔH^o at certain conditions is informing about equilibrium of the observed reaction, but information about the reaction rate is hidden.

$$CH_4 + 2\,O_2 \rightleftharpoons CO_2 + 2\,H_2O$$

$4 \,.\, 413 + 2.\, 166 = + 1984 \text{ kJ . mol}^{-1}$ $\qquad$ $2 \,.\, (- 737) + 4.\, (- 463) = - 3326 \text{ kJ . mol}^{-1}$

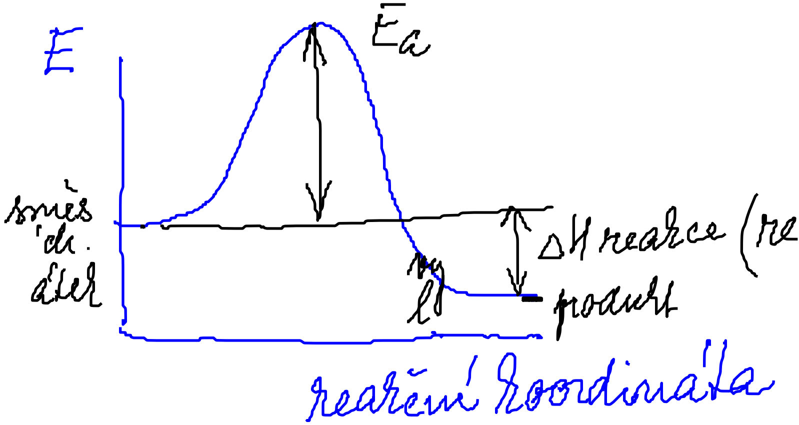
Exothermic reaction $\Delta H^o = - 1342 \text{ kJ . mol}^{-1}$

When we put together two components they are expected to react and according with the calculated equilibrium constant it is exothermic reaction, the reaction without any initiation is not able to proceed.

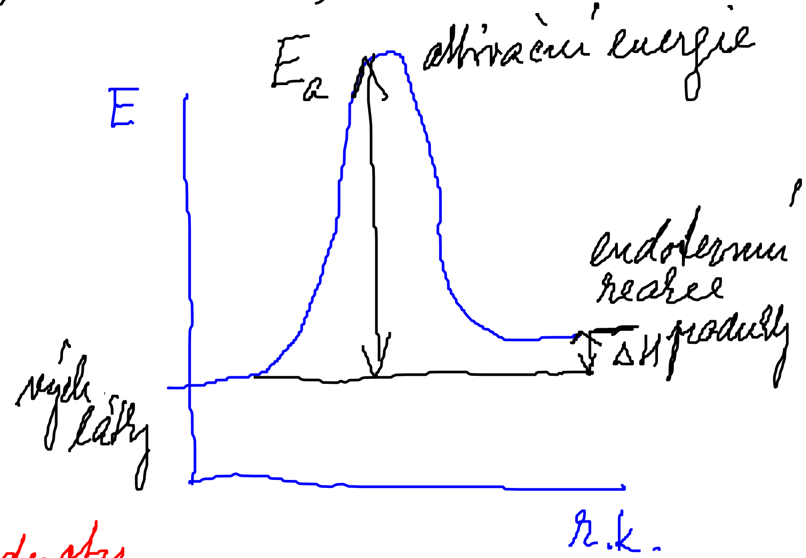
A certain energy must be supplied to overcome the energetic barrier, so called energy of activation **E_a**. Its value will influence the rate of reaction.

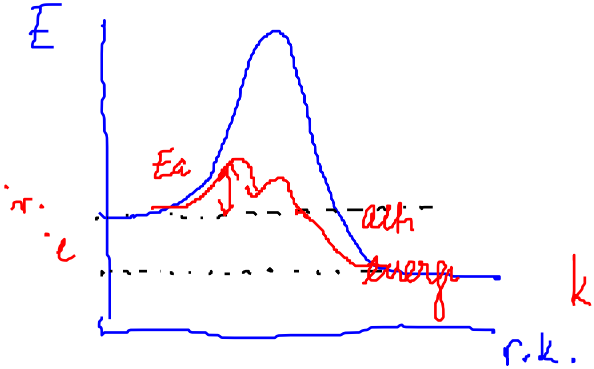
Chemical reaction and the theory

Energy diagram of chemical reacion.



ΔH reakce (reakce je exotermní)





katalyzátor snižuje hodnotu aktivační energie (děj se rozdělí na několik dílčích přeměn)

a role of catalyst

Chemical reaction and the theory

$$A + B \overset{K}{\rightleftharpoons} C + D$$

$$v = \frac{d[C]}{dt} = \frac{d[D]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k\ .\ [A]\ .\ [B]$$

v	reaction rate
k	rate constant (reaction rate at concentration of components 1M)
t	time

Arrhenius equation

$$k = A\ .\ e^{-\frac{E_a}{RT}}$$

kde	e	is base of natural logarithm
	A	Arrhenius constant

CHEMICAL NOMENCLATURE

Struktura názvu:

Kmen-lokant-zakončení

Propan-2-ol

Lokant-prefix-kmen-zakončení

4-hydroxybutanal

2-amino-cyklohexanon

4-nitrobut-2-enová kyselina

Lokant, lokant-násobící prefix-kmen-zakončení

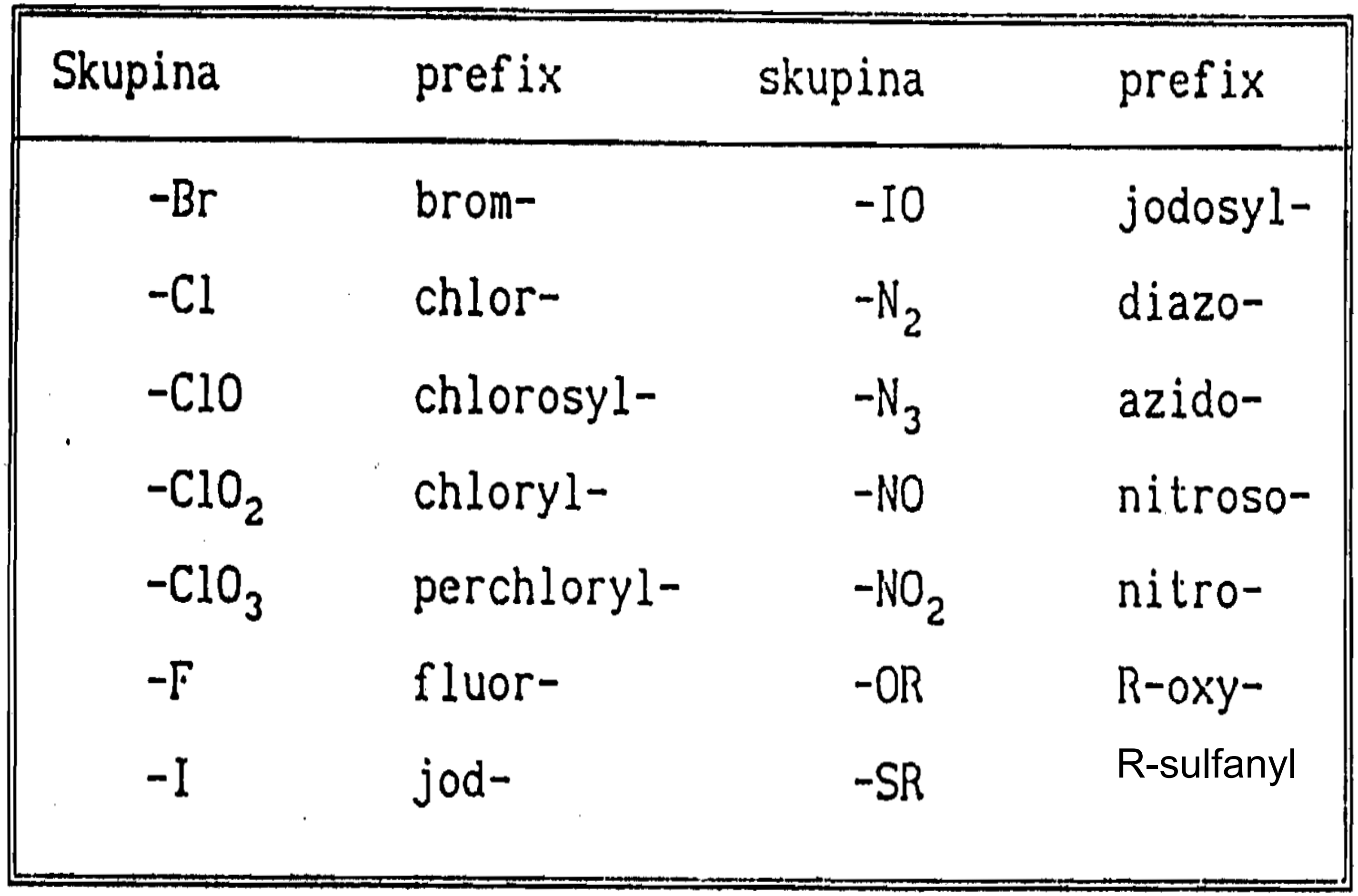
2,3-dimethyl-cyklopentankarboxylová kyselina

Afix-lokant-prefix-lokant-prefix-kmen-zakončení

Skupina	**Vzorec**	**Předpona**	**Přípona**
Kationty	(+)	-onin-	-onium -ium
Karboxylové kyseliny	-COOH -(C)OOH	karboxy- ---	-karboxylová kyselina -ová kyselina
Sulfonové kyseliny	$-SO_2-OH$	sulfo-	-sulfonová kyselina
Anhydridy	-CO-O-CO- -(C)O-O-(C)O-	--- ---	-karboxanhydrid -anhydrid (anhydrid ...ové kyseliny)
Soli	$-COO^-M^+$ $-(C)OO^-M^+$	--- ---	(kation)-...karboxylát (kation)-...-oát (kation)-...-át
Karboxyláty	$-COO^-$	karboxylato-	-karboxylát
Sulfonáty	$-SO_2-O^-$	sulfonato-	-sulfonát
Estery karb. kys.	-COOR -(C)OOR	R-oxykarbonyl ---	R-….karboxylát R-….-oát (R-ester ...ové kyseliny)
Acylhalogenidy = halogenidy karbox. kys.	-CO-halogen -(C)O-halogen	halogenkarbonyl ---	-karbonylhalogenid -oylhalogenid (halogenid ...ové kyseliny)
Amidy	$-CO-NH_2$ $-(C)O-NH_2$	karbamoyl- ---	-karboxamid -amid (amid ...ové kyseliny)
Hydrazidy	$-CO-NH-NH_2$ $-(C)O-NH-NH_2$	--- ---	-karbohydrazid -ohydrazid
Imidy	-CO-NH-CO-	---	-dikarboximid

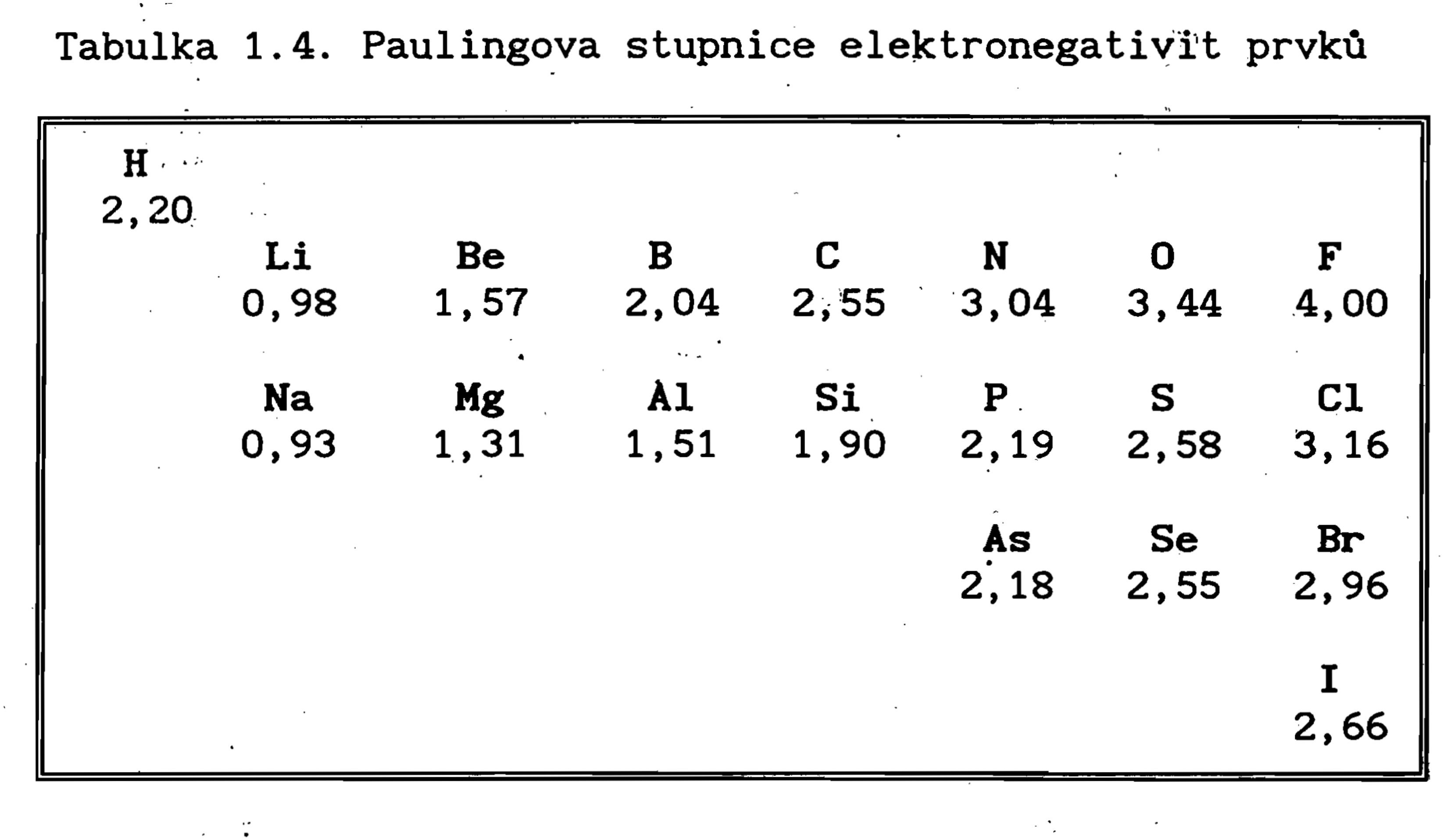
– halogenidy karbox. kys.	-(C)O-halogen	---	-oylhalogenid (halogenid ...ové kyseliny)
Amidy	-CO-NH$_2$	karbamoyl-	-karboxamid
	-(C)O-NH$_2$	---	-amid (amid ...ové kyseliny)
Hydrazidy	-CO-NH-NH$_2$	---	-karbohydrazid
	-(C)O-NH-NH$_2$	---	-ohydrazid
Imidy	-CO-NH-CO-	---	-dikarboximid
	-(C)O-NH-(C)O-	---	-imid
Nitrily	-C≡N	kyan-	-karbonitril
	-(C)≡N	---	-nitril, -nitril
Aldehydy	-CHO	formyl-	-karbaldehyd
	-(C)HO	oxo-	-al
Ketony	>C=O	oxo-	-on
Alkoholy, fenoly	-OH	hydroxy-	-ol
Alkoholáty, fenoláty	-O$^-$	oxido-	-olát
Thioly	-SH	sulfanyl-	-thiol
Thioláty	-S$^-$	-sulfido	-thiolát
Aminy	-NH$_2$	amino-	-amin
Iminy	=NH	imino-	-imin
Hydraziny	-NH-NH$_2$	hydrazino-	-hydrazin
Ethery	-OR	R-oxy	---
Sulfidy	-SR	R-sulfanyl (dříve: R-thio)	---
Halogensloučeniny	-X	halogen-	---
Nitrosloučeniny	-NO$_2$	nitro-	---

CHEMICAL NOMENCLATURE



Skupina	prefix	skupina	prefix
-Br	brom-	-IO	jodosyl-
-Cl	chlor-	$-N_2$	diazo-
-ClO	chlorosyl-	$-N_3$	azido-
$-ClO_2$	chloryl-	-NO	nitroso-
$-ClO_3$	perchloryl-	$-NO_2$	nitro-
-F	fluor-	-OR	R-oxy-
-I	jod-	-SR	R-sulfanyl

BONDING IN ORGANIC MOLECULES



Tabulka 1.4. Paulingova stupnice elektronegativit prvků

H							
2,20							
	Li	**Be**	**B**	**C**	**N**	**O**	**F**
	0,98	1,57	2,04	2,55	3,04	3,44	4,00
	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
	0,93	1,31	1,51	1,90	2,19	2,58	3,16
					As	**Se**	**Br**
					2,18	2,55	2,96
							I
							2,66