

Supplemental Information for

“A Hierarchical Structure for an Organic Chemistry Course”

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1.0 Introduction

The Supplemental Information discusses the use of oxidation levels in organic reaction schemes. The schemes are more or less deformed by adapting them to the pages of the Word file. To read the Supplemental Information independently, it contains some repeating text, Scheme 1 and 3-D graph 1 of the main article. Note that NECA is the acronym for Neon Electron Configuration Analogy, the hierarchical structure for an organic chemistry course proposed in the main article. The Figures and Tables of the main article are included in a larger format at the end of the Supplemental Information. The call-out numbers for the cited literature do not refer to the main article.

2.0 Oxidation Levels in Organic Reaction Schemes

2.1. Introduction

In a traditional organic chemistry course, the name of most course modules refers to the main functional group of which reactions and mechanisms are discussed. The sequence of the course modules nearly follows the oxidation levels (OLs) of the functional group (attached) carbon(s). It is a good educational practice to explicitly communicate this knowledge to our audience in the form of a basic reaction scheme that presents an overview of the reaction landscape in a well structured way and that can be extended to a Basic Organic Reaction Knowledge Space (BORKS) and further on, to an overview of most reactions of the course. Three properties of the functional groups

are appropriate for this purpose: functional groups can be related to the periodic table [1], they can be classified by OL [2, 3, 4], and they are involved in acid-base reactions. These three properties make the scheme three-dimensional. Oxidation-reduction has been proposed for a logical characterization of organic structures as part of a three-dimensional reaction overview by type [5]. OLs are already used in reaction schemes [6].

Most courses introduce functional groups in introductory course modules. The functional groups can already be mastered in nomenclature and physical properties such as boiling points [7, 8] before the student meets them again in reactions and mechanisms. Therefore, at the 2s NECA subshell, the students are not really surprised that functional groups can be interconverted by means of reactions.

The BORKS is at best introduced in connection with the acid-base topic at the 2s NECA subshell. The BORKS consists of two parts: A basic reaction scheme (Reaction scheme 1) and how acid-base reactions can be connected to this scheme.

2.2. A Basic Organic Reaction Scheme

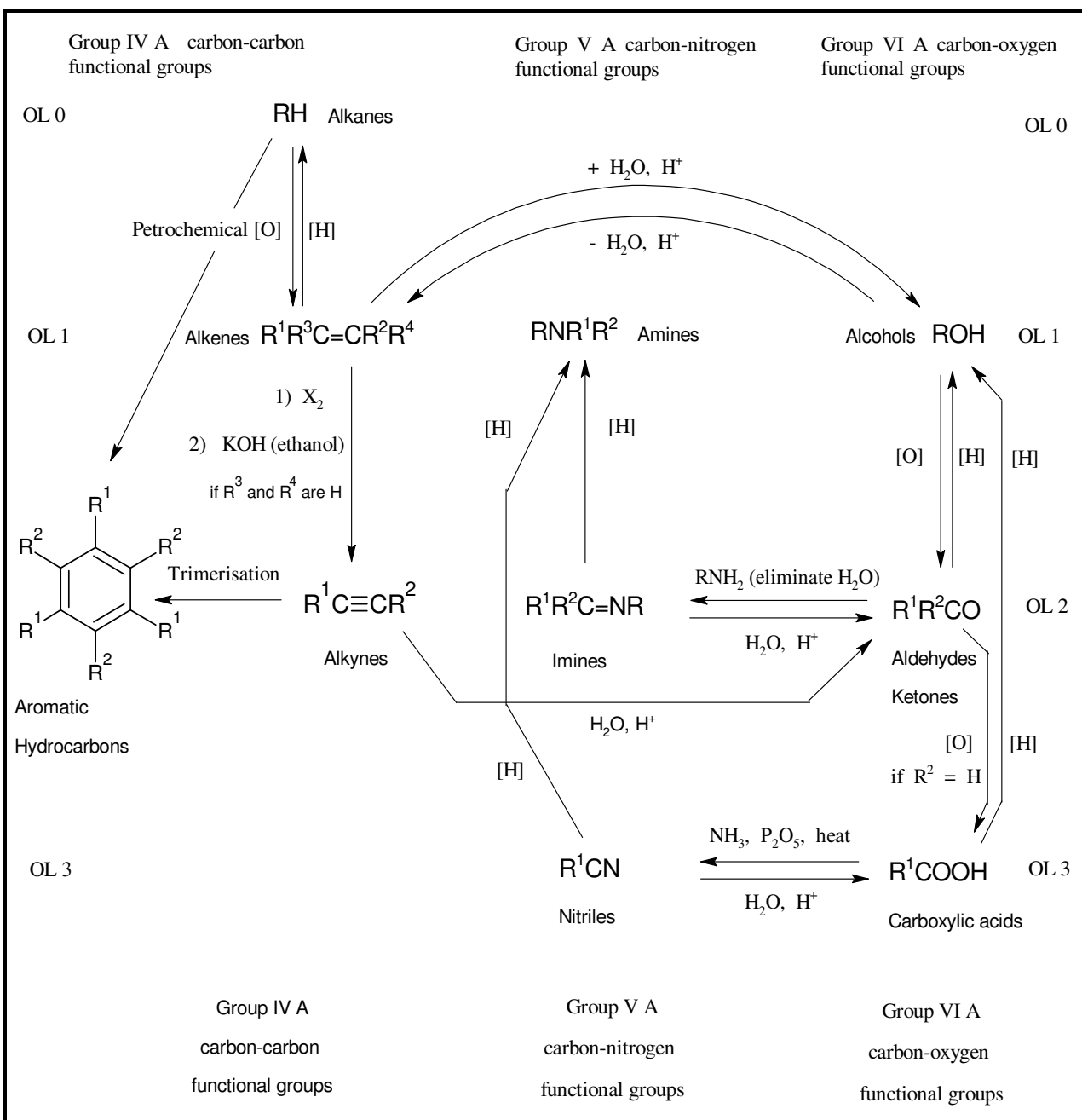
Reaction scheme 1 shows reactions for a selection of appropriate functional groups. The scheme is also appropriate for the functional groups of biomolecules. Very few of them are halogenated, which eliminates main group VII functional groups. Consequently, the basic functional groups are related to the main groups IV A, V A and VI A, which correspond to functional groups with carbon-carbon, carbon-nitrogen and carbon-oxygen bonds. These three bond types exist in single-, double- or triple bonds, except that carbon-oxygen cannot form triple bonds. However, carboxylic acids have three bonds from carbon to oxygen atoms. If a bond type exists in more than one functional group, then the most representative one is chosen. For example, alcohols are chosen instead of ethers. R^1 , R^2 , R^3 and R^4 are used to enumerate the R groups or to denote hydrogen.

The location of a functional group depends on two variables. The position of the most specific (hetero) atom of a functional group in the periodic table is the horizontal variable. The OL of a functional group (attached) carbon(s) is the vertical variable. These two variables do not determine the location of a functional group on a linear scale.

Abscissa and ordinate lines are omitted. Both variables are introduced for educational reasons. In the progress of the course and possibly also by consulting textbooks and/or internet information, students will gradually discover that neither of them is necessary in common reaction schemes.

The OL for the following functional group (attached) carbon(s) is: alkanes (OL 0), alkyl halides, alkenes, alcohols and amines (OL 1), alkynes, benzene, alkylbenzenes, aldehydes and ketones (OL 2), carboxylic acids and derivatives (OL 3).

Reaction scheme 1 extends the periodic table classification of the functional groups [1] (1s NECA shell) to an overview of organic reactions (2s NECA subshell). The reactions are not chosen by synthetic relevance, but because they are appropriate to form an easy and logical scheme to which other structures, other reactions and their mechanisms can be related. The functional groups at a given OL can be converted into each other without oxidizing or reducing agents. Redox reactions convert functional groups between different OLs. The redox reaction arrows accentuate the vertical dimension of the scheme. For the sake of simplicity, the scheme does not specify the necessary reactant(s) needed for the oxidation or reduction of a specific functional group. Specific reagents would only distract student's attention away from the purpose of the scheme. Therefore [O] and [H] are used to describe oxidizing and reducing reactants respectively. Not all the redox reactions can be obtained in both directions. Some reactions of Scheme 1 have side reactions such as the products of the carbocation rearrangements. Side reactions confront students with the shortcomings of Scheme 1 and the further on related schemes. A more comprehensive approach including reaction mechanisms will be necessary.



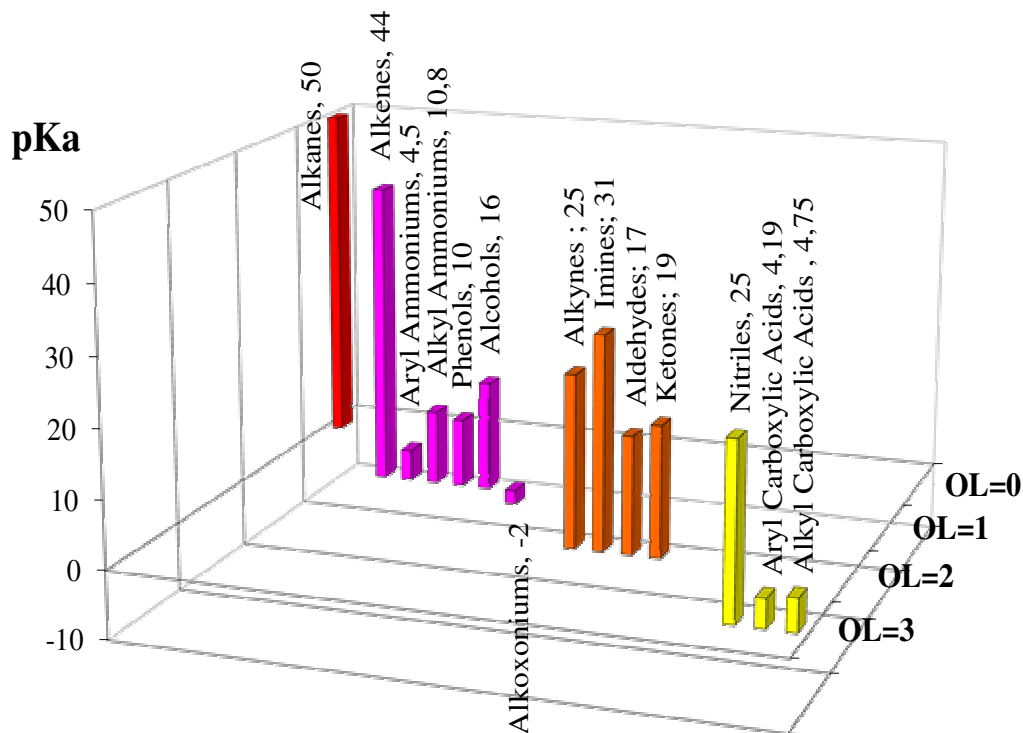
Reaction scheme 1. The 2s NECA subshell basic organic reaction scheme, which is ordered by periodic table connections and oxidation levels. Groups IVA, VA and VIA indicate the position of the most specific (hetero) atom of a functional group in the periodic table. R¹, R², R³ and R⁴ are used to enumerate the R groups or to denote hydrogen. The numbers 1) and 2) next to a reagent indicate consecutive reactions.

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2.3 The Basic Organic Reaction Knowledge Space

The periodic table group numbers and OLS are the x-y coordinates of Reaction scheme 1. The third dimension of BORKS is acid-base. Acid-base reactions convert the functional groups into ionic derivatives. The pK_a value of a functional group acid-base half-reaction determines the necessary acid or base strength for the corresponding reaction. The cationic derivatives are positioned in the positive direction of the z-axis and the anionic derivatives in the negative direction. Such a third dimension is not easily achieved and is therefore reduced to a mental exercise. An alternative is developed in Graph 1, which shows a 3-D graph corresponding to Reaction scheme 1 including the pK_a values [9, 10] of the functional groups in the z-dimension. Alkyl and aryl derivatives of some functional groups and the alkyloxoniums are included.

Reference 1 overviews also ionic derivatives of the functional groups and consequently reference 1 combines the x-axis (the periodic table connections) and z-axis (ionic formulas) of Reaction scheme 1. For students, reference 1 is the best introduction to the BORKS. The BORKS will cause no further problems to the students, if the acid-base reactions are discussed in detail in a previous course module. Acid-base in the z-dimension of the scheme is related to their applications. They are not intended to create a new functional group. They change the reactivity or solubility of a compound. The BORKS orientates the student in the possible overwhelming field of reactions. The next two sections show how this can be further developed. The mental process required from the students to relate other reactions and mechanisms to this scheme results in a coherent knowledge space on reactions and mechanisms.



Graph 1. A 3-D graph corresponding to Reaction scheme 1 including the pKa values of the functional groups.

2.4. Instructional aids and Extension of the Basic Reaction Scheme 1.

The condensed functional group formulas in Reaction scheme 1 will cause some problems to beginning students when they are faced to the functional group conversion reactions. It is not obvious to beginning students that for example ROH becomes R^1R^2CO in an oxidation reaction. Compared to the alcohol, the aldehyde/ketone shows an extra R-group and an extra carbon atom. Reaction scheme 2 helps students in that respect. There is a better structure correspondence in the conversion reactions. In the correspondent reactions, alcohols, amines and aldehydes/ketones show structure correspondent formulas. Each of these functional groups are presented by two formulas that are pooled together at near the same position in Reaction scheme 2 as in Reaction scheme 1. Reaction scheme 1 has the advantage of a rather easy overview. Reaction scheme 2 helps for the structural details in specific reactions. The

structural correspondent aldehyde/ketone product of the hydration of alkynes is located just below the Reaction scheme 1 aldehydes/ketones location. Consequently, OL 2 is broadened by a second row.

At best, the study of the interconversions are started for each OL separately. Combining the conversions at OL 1 respectively OL 2 in Reaction scheme 1 and 2 result in Reaction schemes 3 and 4. Reaction schemes 2, 3 and 4 are the instructional aids for Reaction schemes 1. Reaction scheme 3 already contains the particular structure related formulas of amines and alcohols for the redox reactions. The students must become aware, that the formula variants of the same functional group in the same and in subsequent reaction schemes are not exchangeable if the R^1 (and possibly also the R^2, \dots) have identical structures. For example R^1CH_2OH and $R^1(CH_2)_2OH$ are not identical if R^1 in both structures is H.

Thereafter, Reaction scheme 2 is used to show the redox conversions.

Reaction scheme 5 shows an extension of Reaction scheme 1 with alkyl halides, amides, carboxylates and esters but without arenes. OL 2 and OL 3 each show two rows. The alkyl halides are also present as reactants on the reaction arrows of two OL 3 functional groups. The horizontal location of some functional groups, such as amides and carboxylates, does not correspond anymore to their periodic table connection. The periodic table strictly related location of functional groups in reaction schemes is restricted to the basic organic reaction schemes and their instructional aids (Reaction schemes 1, 2, 3 and 4). Reaction scheme 6 is the instructional aid to introduce Reaction scheme 5.

2.5 An Overview of Most Reactions of the Course:

The Reaction scheme 1 Related Reaction Schemes

The 2s NECA subshell allows for a further overview of reactions by schemes based on OLs. The additional schemes are already advisable at the 2s subshell because the 1s shell and acid-base also promotes a total approach on functional groups, which means that the learning process integrates as many functional groups as possible in each 1s and 2s topic (nomenclature, physical properties, isomers, stereochemistry, acid-base ...). The additional schemes (Reaction schemes 7, 8 and 9) show how their functional groups are related to the basic Reaction scheme 1. They help the students to develop their knowledge space on reactions. In the additional schemes, the functional group formulas that connect to Reaction scheme 1 are in bold.

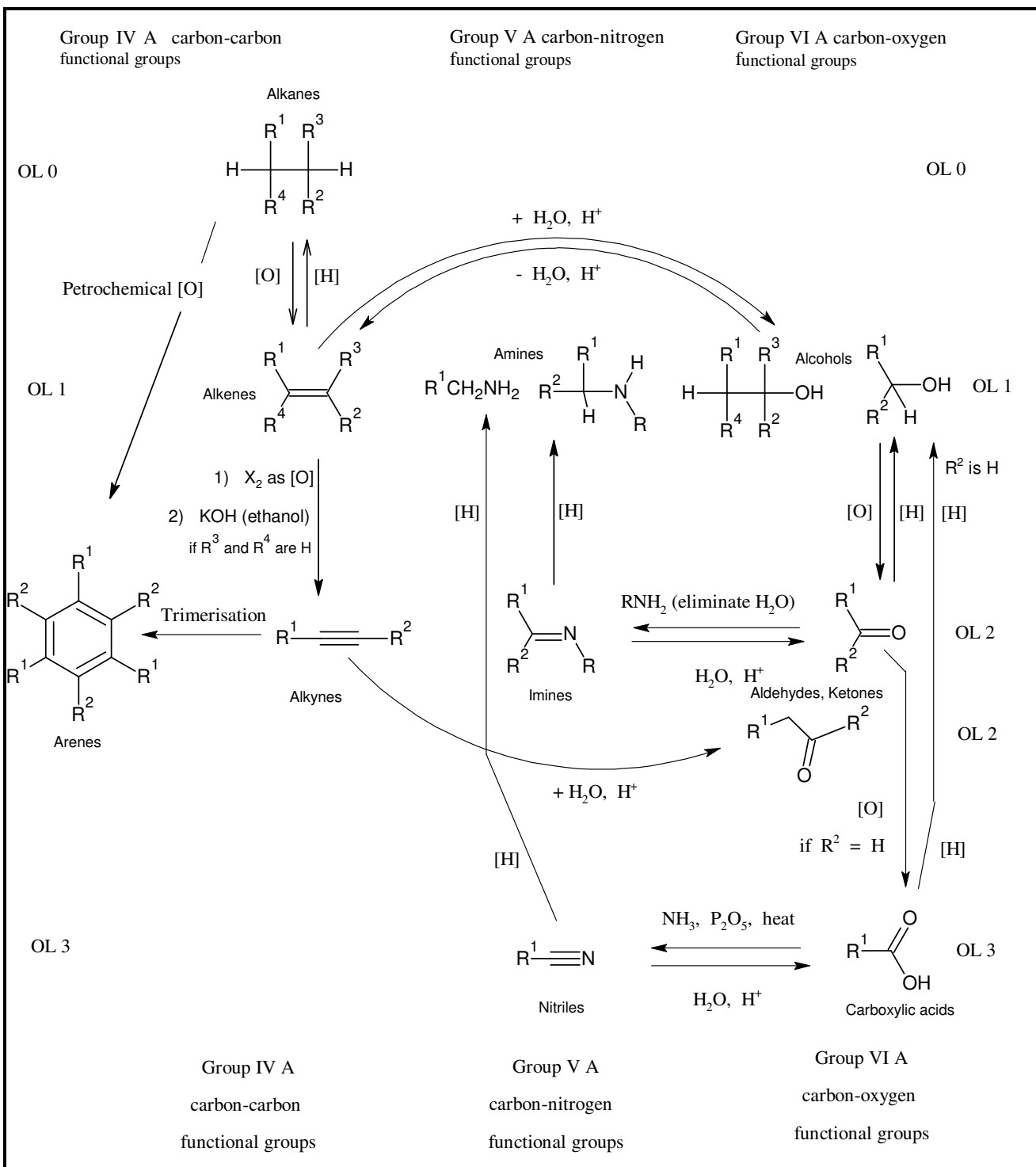
The alkyl halide reactions are further related to the basic Reaction scheme 1 by Reaction scheme 7. Reaction schemes 7, 8 and 9 show selected reactions according to OLs for respectively alkyl halides, benzene and carbonyls.

In Reaction scheme 7, the alkyl halides are concerned in OLs 0, 1 and 3. Reaction schemes 8 (benzene reactions) and 9 (carbonyl reactions) are concerned in OLs 2 and 3.

Reaction scheme 9 is an overview of selected carbonyl reactions. The carboxylic acids and their derivatives are at OL 3, which is split in three rows. Note the central position of R^1COZ in which Z can be NR^1R^2 , OH, O^- , OR, OCOR and X. If Z is OH, the central OL 3 formulas are carboxylic acids that are also OL 3 compounds in the basic Reaction scheme 1. If Z is OH, the two central located functional groups in bold font; the aldehydes/ketones and the carboxylic acids at respectively OL 2 and 3 connect Reaction scheme 9 to the basic Reaction scheme 1. The students can derive from Reaction scheme 9 that if Z in RCOZ is OH and with a (H^+) catalyst, the active formula is oxonium. Oxonium is also the active formula for aldehydes/ketones and (hemi)acetals/ketals if a H^+ catalyst is present. In the hydrolyze reactions at OL 3, Z is always OH or O^- (with a base as a catalyst).

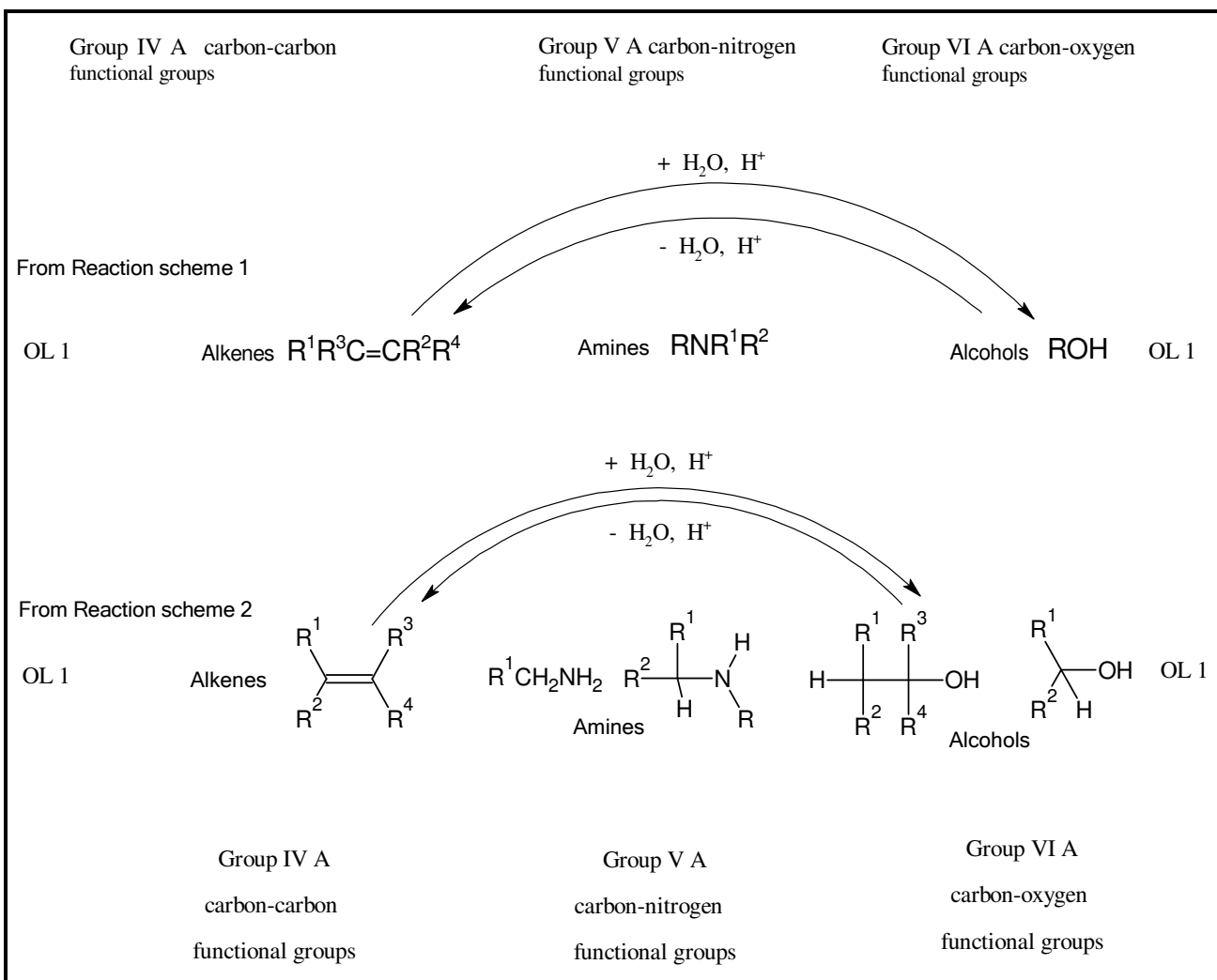
At this stage of the course, it is not strictly necessary that the students can derive reaction equations from the presented schemes. Although, the first step to achieve this goal may or must be done. It is also not yet possible that the student overview the whole presented reaction landscape. More important is that the students understand how these schemes are constructed, interconnected and how they find their way in them.

The 2s NECA subshell terminates with a study of specific oxidation and reduction reactions including their corresponding reactants.

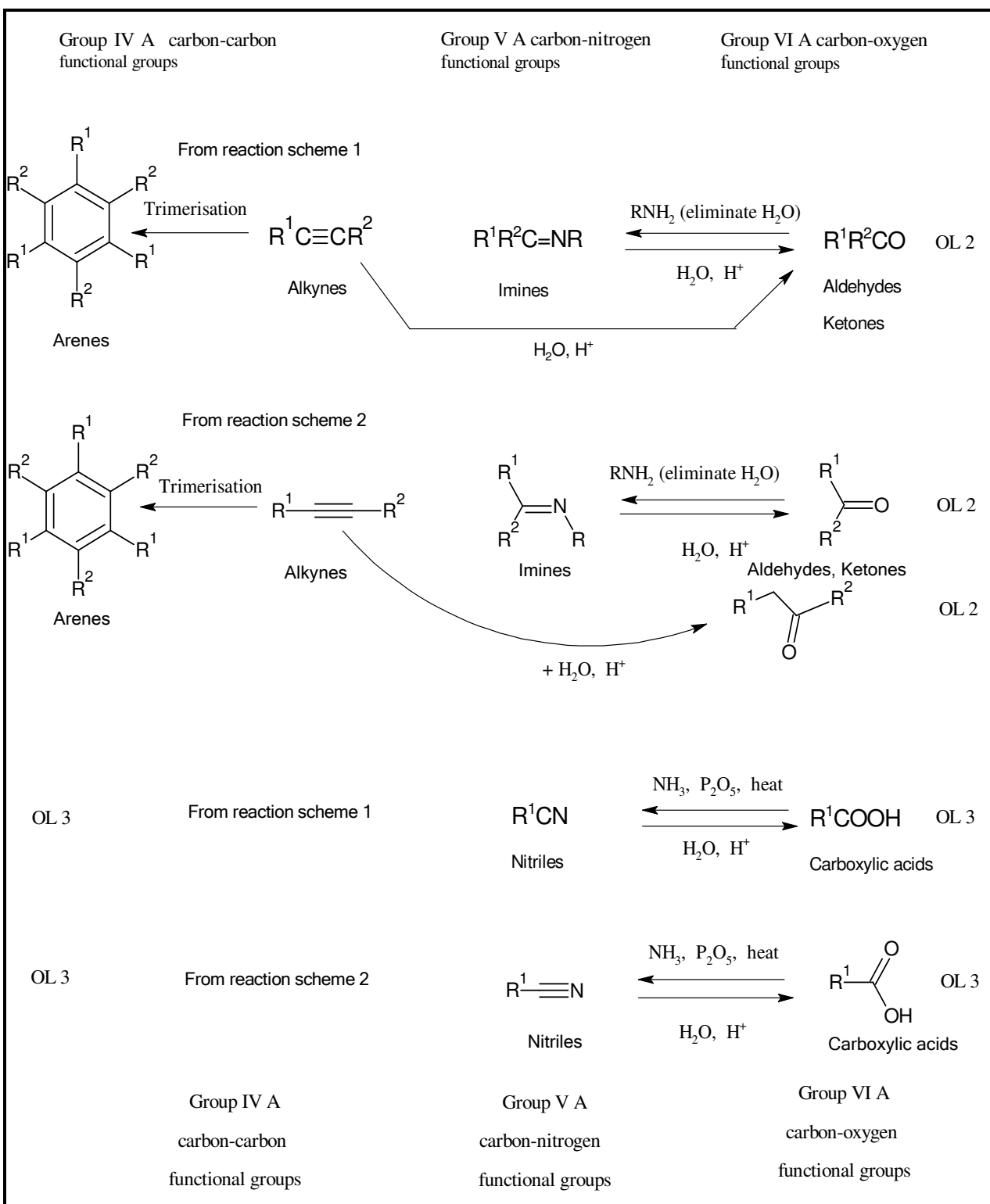


Reaction scheme 2. A Reaction scheme 1 variant that has a clearer correspondence in formula structure between conversed functional groups.

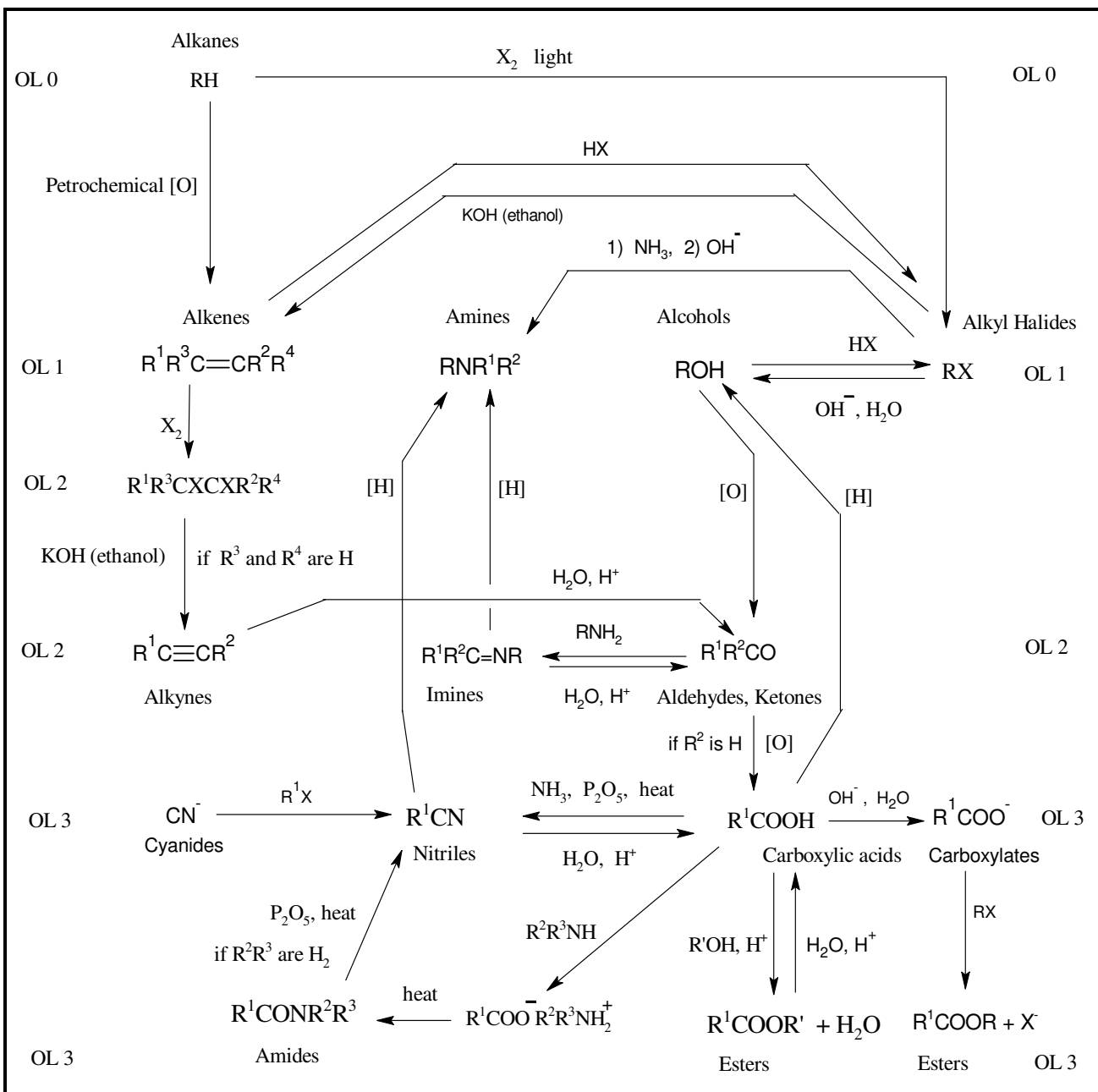
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Reaction scheme 3. Instructional aid for oxidation level 1.

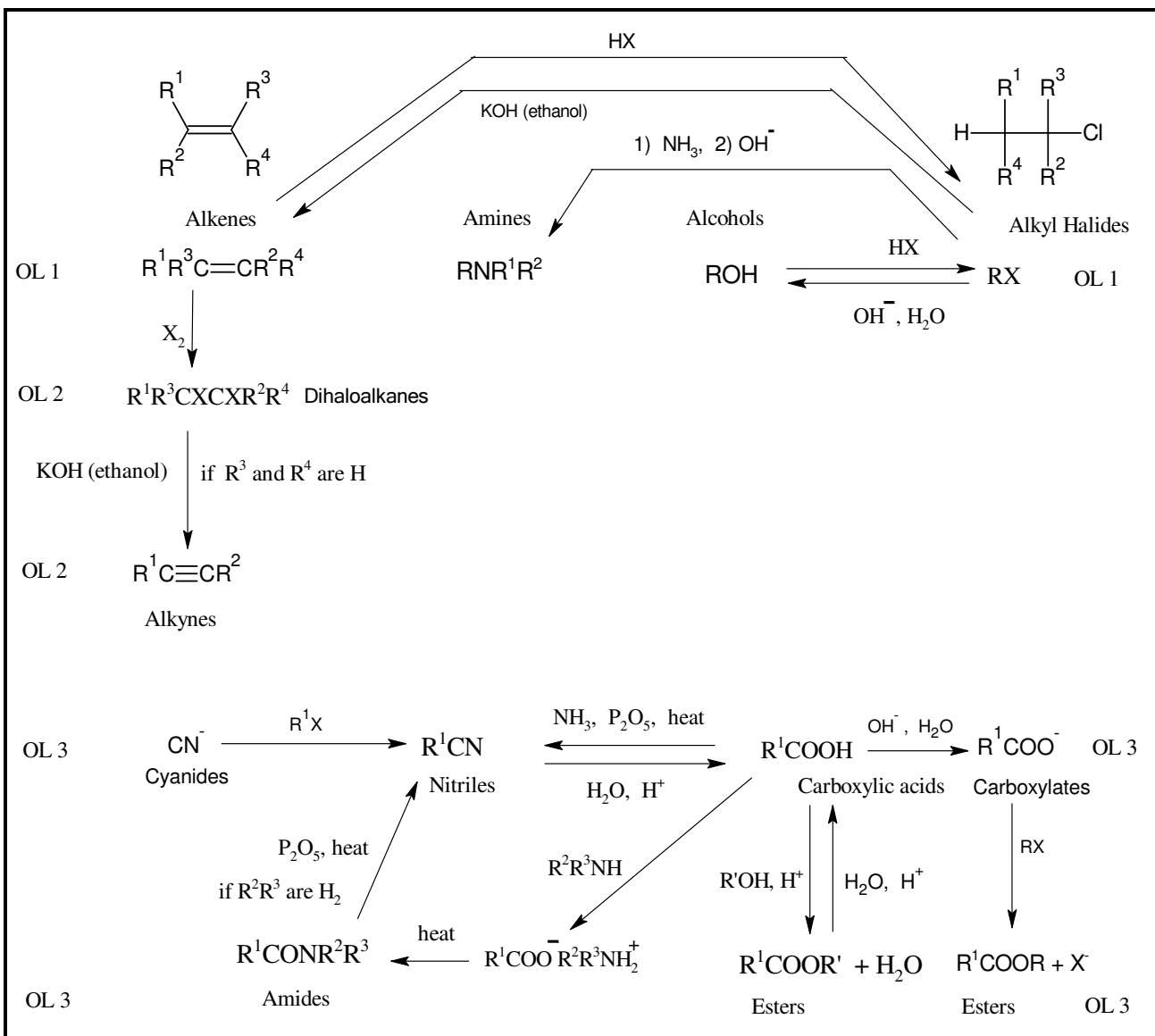


Reaction scheme 4. Instructional aid for oxidation levels 2 and 3.

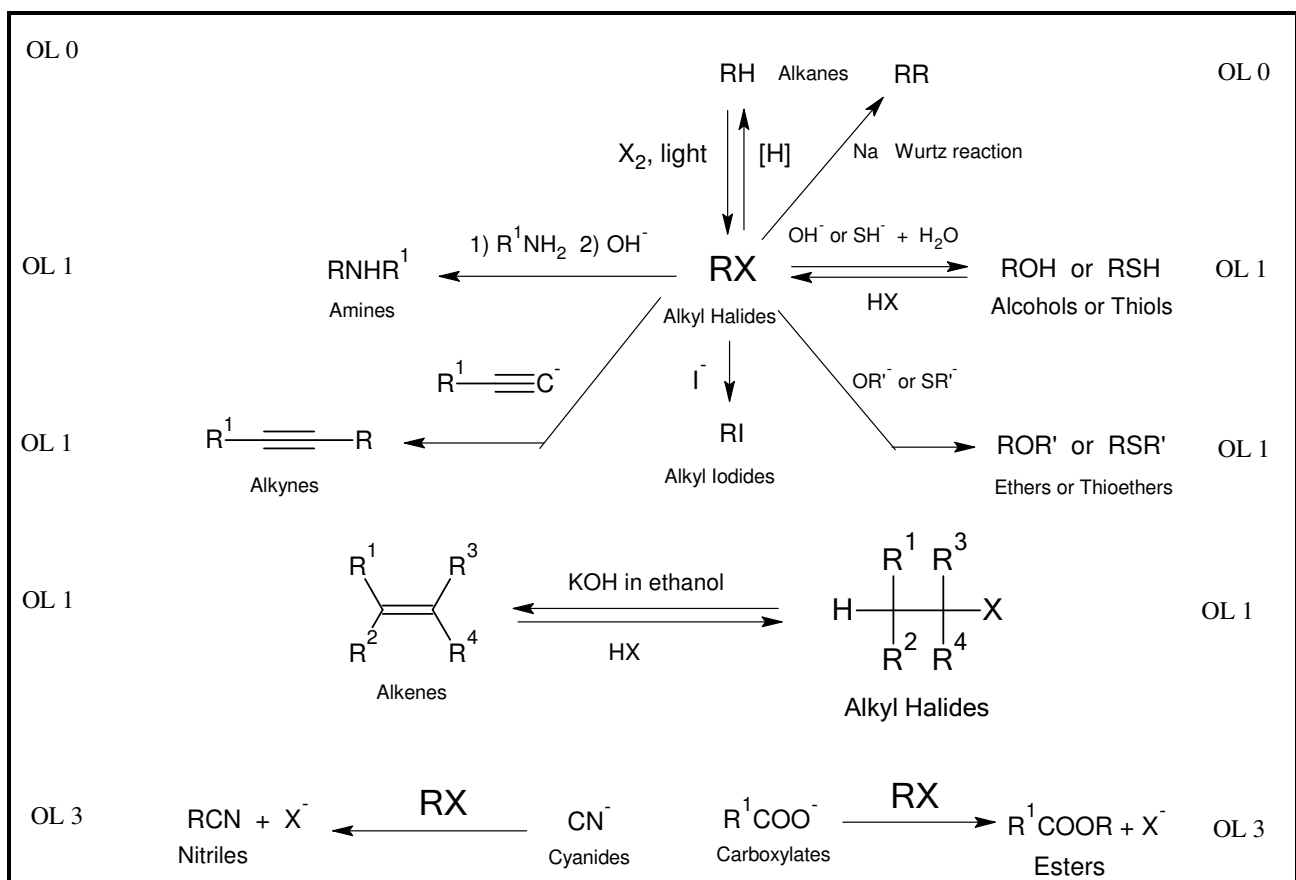


Reaction scheme 5. An extension of Reaction scheme 1 with alkyl halides, carboxylates, esters and amides but without arenes.

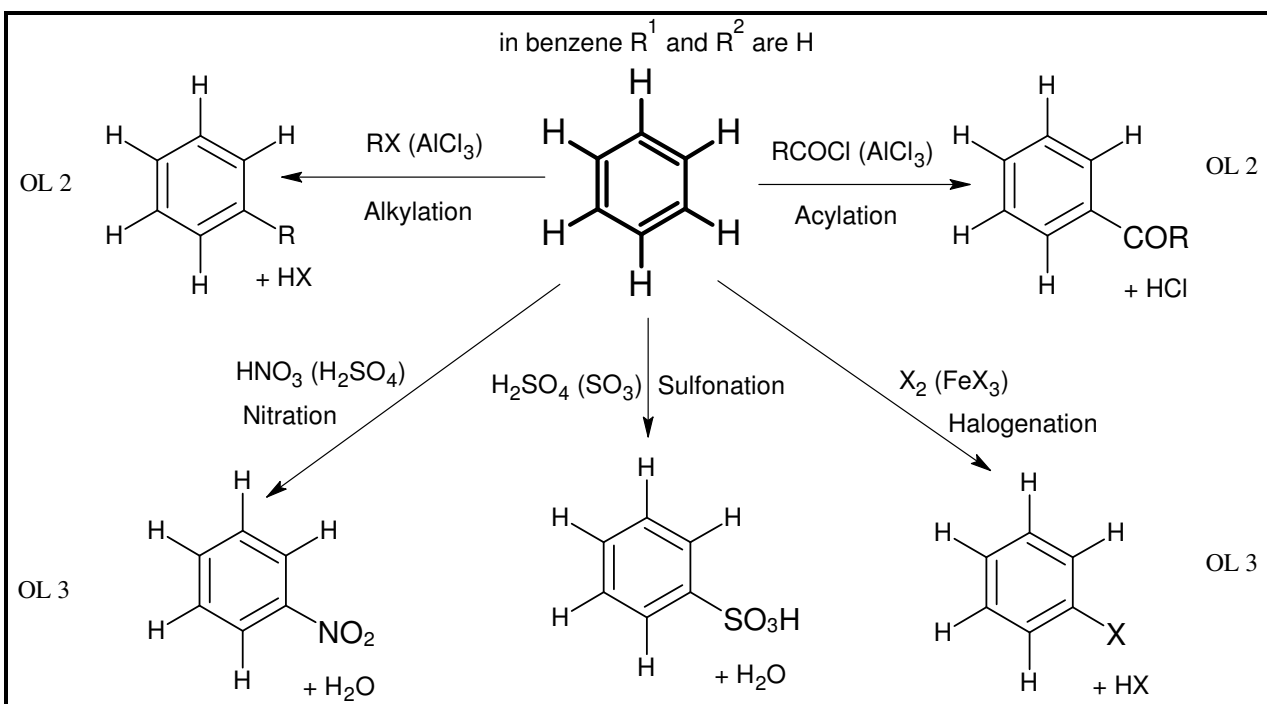
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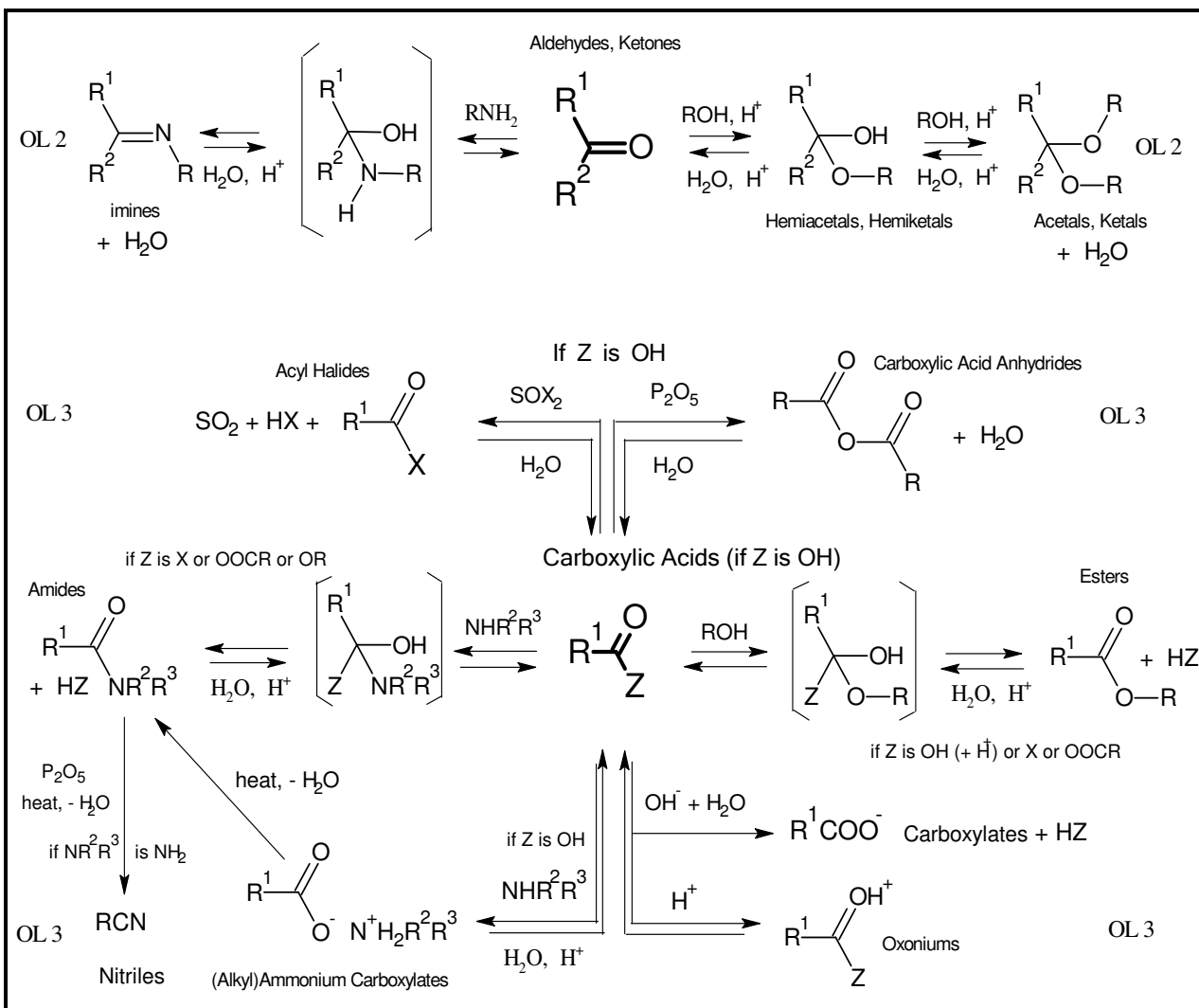
Reaction scheme 6. Instructional aid for Reaction scheme 5.



Reaction scheme 7. An overview of selected alkyl halide reactions according to oxidation levels.



Reaction scheme 8. An overview of selected substitution reactions on benzene according to oxidation levels.



Reaction scheme 9. An overview of selected carbonyl reactions according to oxidation levels

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3.0. Addendum: Oxidation Levels of Functional Group (Attached) Carbon(s)

For functional groups containing heteroatom(s), the OL is identical to the number of bonds from carbon to hetero atoms³. The OL of the carbons in alkanes is 0.

More generally, the OL is the number of carbon-carbon pi-bonds to the intended carbon increased by the number of bonds from that carbon to hetero atoms. For example, the carboxylic carbon in acetic acid has three carbon-oxygen bonds, but no carbon-carbon pi-bonds to it. Its OL is 3 and is denoted as OL 3. The OL of vinyl chloride is 2, the intended vinyl chloride carbon has a pi-bond and a hetero atom bond to it.

Alternatively, the OL is determined by half of the difference in oxidation state between the intended functional group carbon(s) and the corresponding alkane carbon(s). For example, the oxidation state for a carboxylic carbon is +3 and the oxidation state of an ethane carbon is -3, the difference is 6 and the OL is 3. By this rule, the alkenes and alkynes functional carbons obtain a mean OL. The OL of an individual carbon of a multiple carbon-carbon bond is also its difference in oxidation state to the oxidation state of the corresponding alkane carbon. Electronegative atoms on multiple carbon-carbon bonds ask for an appropriate larger or branched corresponding alkane. For example, the corresponding alkane carbon for the carbon of the carbon-halogen bond in vinyl chloride is the methylene of propane. The OL of a benzene carbon (OL 2) is the same as the OL of the corresponding alkyne carbon. Note that benzene can be regarded as a trimer of ethyne.

4.0. Abbreviations

BORKS	Basic Organic Reaction Knowledge Space
OL(s)	Oxidation Level(s)
NECA	Neon Electron Configuration Analogy

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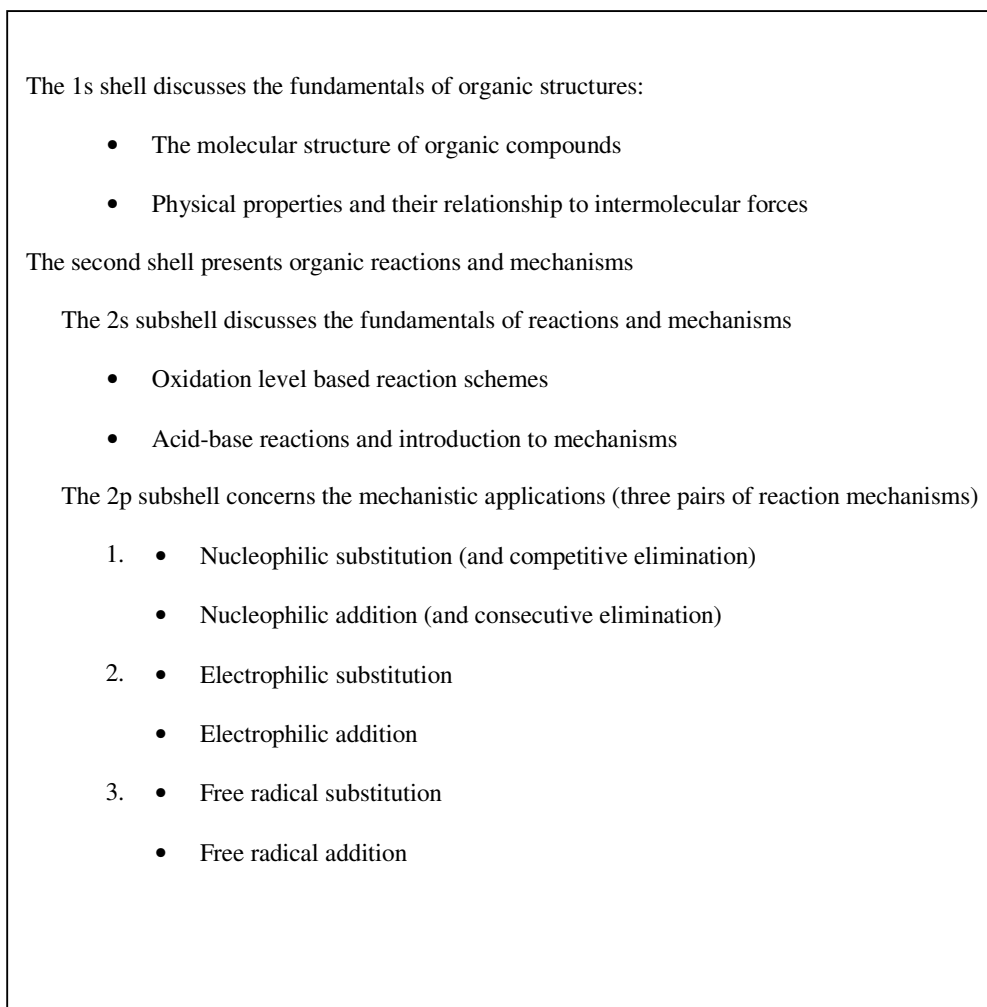
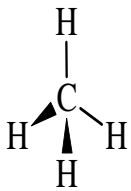
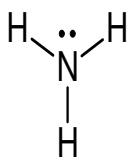
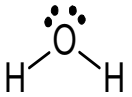

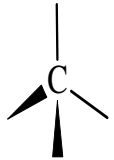
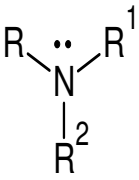
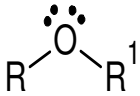

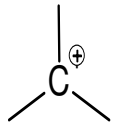
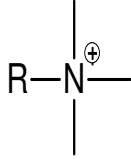
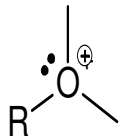
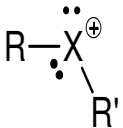
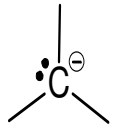
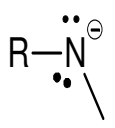

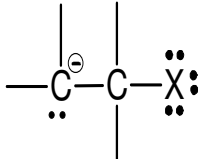


Fig. 1. The Neon Electron Configuration Analogy (NECA)
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Table 1. Single bonded functional group classes and their ionic forms in relation to the periodic table.

Group IVA	Group VA	Group VIA	Group VIIA
			
 <p>RH (Cyclo)Alkanes</p>	 <p>Amines RNR^1R^2 primary: RNH_2 secondary: $RNHR'$ tertiary: RNR''</p>	 <p>ROR^1 ROH R^1 is H and if R is (cyclo)alkyl: Alcohols if R is aryl: Phenols if R is 1-alkenyl: Enols ROR' R^1 is R': Ethers</p>	 <p>(Cyclo)Alkyl and Aryl Halides</p>
 <p>Carbocations</p>	 <p>Ammoniums</p>	 <p>Oxoniums</p>	 <p>Haloniums</p>
 <p>Carbanions</p>	 <p>Amine Anions</p>	 <p>if R is (cyclo)alkyl: Alkoxides if R is aryl: Phenoxides if R is 1-alkenyl: Enolates</p>	 <p>Beta Anions</p>

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Table 2. Related Properties for Selected Compounds of the Compared Homologous Series

Homologous Series	Alkyl C-0		Alkyl C-1		Alkyl C-2		Alkyl C-4		Alkyl C-6		Alkyl C-8		Mean A_{incr} $10^{-6} \text{ m}^3 \text{ mol}^{-1}$	Mean μ D
	BP _{incr} K	BP °C	BP _{incr} K	BP °C	BP _{incr} K	BP °C	BP _{incr} K	BP °C	BP _{incr} K	BP °C	BP _{incr} K	BP °C		
n-Alkanamides	458	205	395	213	309	221	236	236	182	251	141	267	8,7	3,78
n-Alkanoic Acids	353	101	300	118	230	141	187	186	154	223	129	255	6,3	1,67
n-Alkanoic Anhydrides					229	140	171	170	131	200	102	228	11,0	3,20
1-Nitro-n-alkanes			284	101	203	114	148	147	110	179	84	210	5,8	3,56
Di-n-alkyl Disulfides					198	110	155	154	125	194	100	226	16,1	2,02
n-Alkanenitriles	278	26	264	82	186	97	142	141	116	185	99	224	4,4	3,85
n-Alkanoyl Chlorides			233	51	169	80	129	128	105	174	90	215	10,5	2,50
n-Alkan-1-ols	353	100	248	65	167	79	118	117	89	158	69	195	1,6	1,67
1-Iodo-n-alkanes	217	-35	225	42	161	72	131	131	112	181	100	226	13,0	1,84
Methyl n-Alkanoates			214	32	146	57	103	102	82	151	67	193	6,4	1,74
n-Alkan-2-ones					145	56	103	102	83	152	70	195	4,8	2,71
n-Alkanals	232	-21	203	21	137	49	104	103	84	153	65	191	5,0	2,57
1-Bromo-n-alkanes	186	-67	186	4	127	38	102	102	86	155	75	201	7,8	2,04
Di-n-alkyl Sulfides					126	37	93	92	73	142	60	186	8,0	1,54
n-Alkane-1-thiols	192	-61	189	6	124	35	99	99	82	151	73	199	8,0	1,51
1-Amino-n-alkanes	219	-33	176	-6	105	17	78	78	62	131	54	180	3,5	1,30
1-Chloro-n-alkanes	168	-85	159	-24	101	12	79	78	66	135	56	182	4,9	1,97
n-Alkyl Ethynes	169	-84	159	-23	97	8	72	71	56	125	48	174	7,2	0,81
n-Alkyl Ethenes	149	-104	135	-47	82	-6	64	63	52	121	45	171	8,9	0,41
Di-n-alkyl Ethers					66	-23	35	35	22	91	16	142	2,0	1,24
1-Fluoro-n-alkanes	273	20	104	-78	51	-38	33	33	23	92	17	143	-0,1	1,90
n-Alkanes BP (°C)	-252,5		-182,5		-88,6		-0,5		69,0		125,7			
n-Alkanes BP (K)	20,7		90,7		184,6		272,7		342,2		398,9			
n-Alkanes A ($10^{-6} \text{ m}^3 \text{ mol}^{-1}$)	1,8 ^a		6,5 ^a		11,2 ^a		20,5 ^a		29,9		39,2			
In the n-Alkanes, Alkyl C-0 corresponds to H ₂	BP is boiling point incr is increment				μ is dipole moment D is Debye unit				A is molar refractivity				^a is an extrapolated value	

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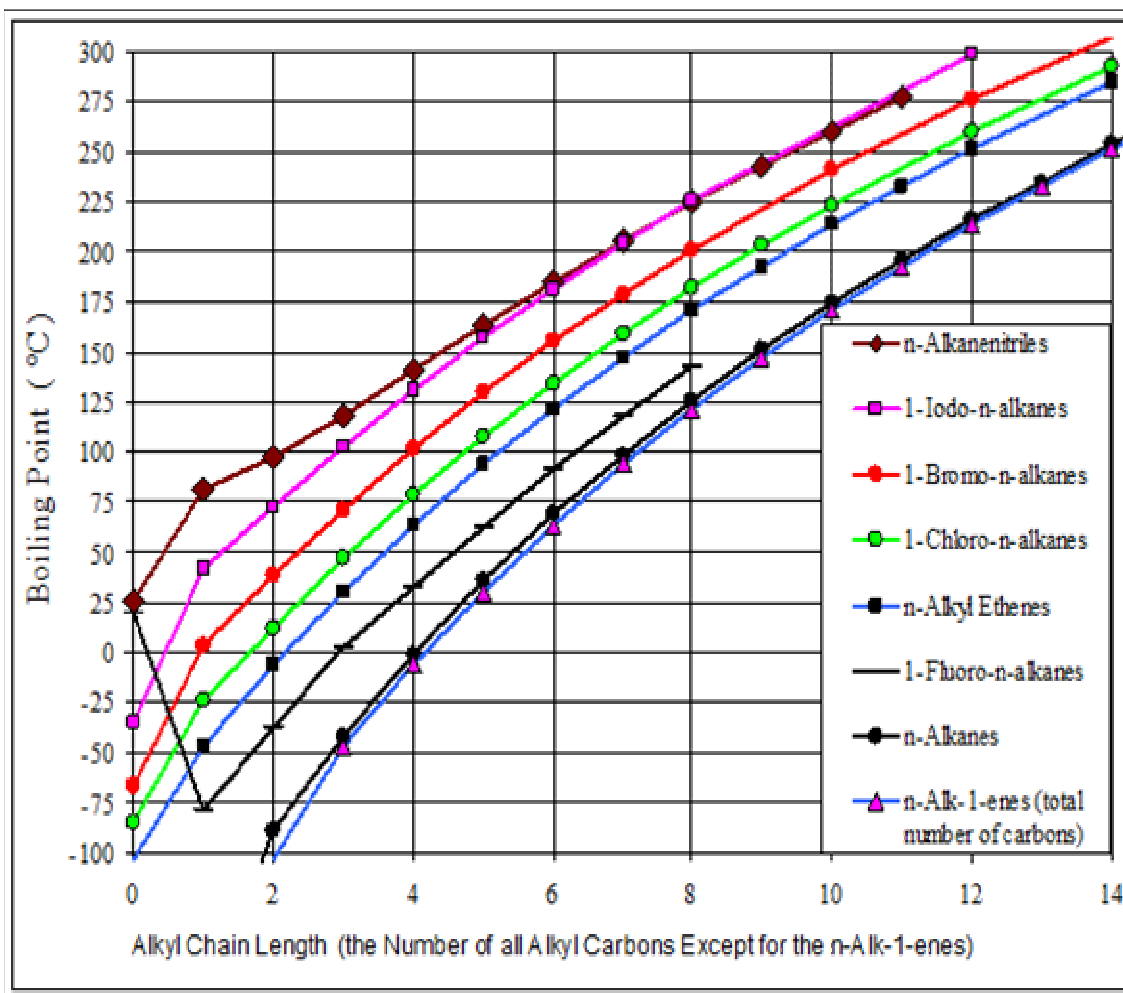


Figure 2. Overview of Some Boiling Point Curves

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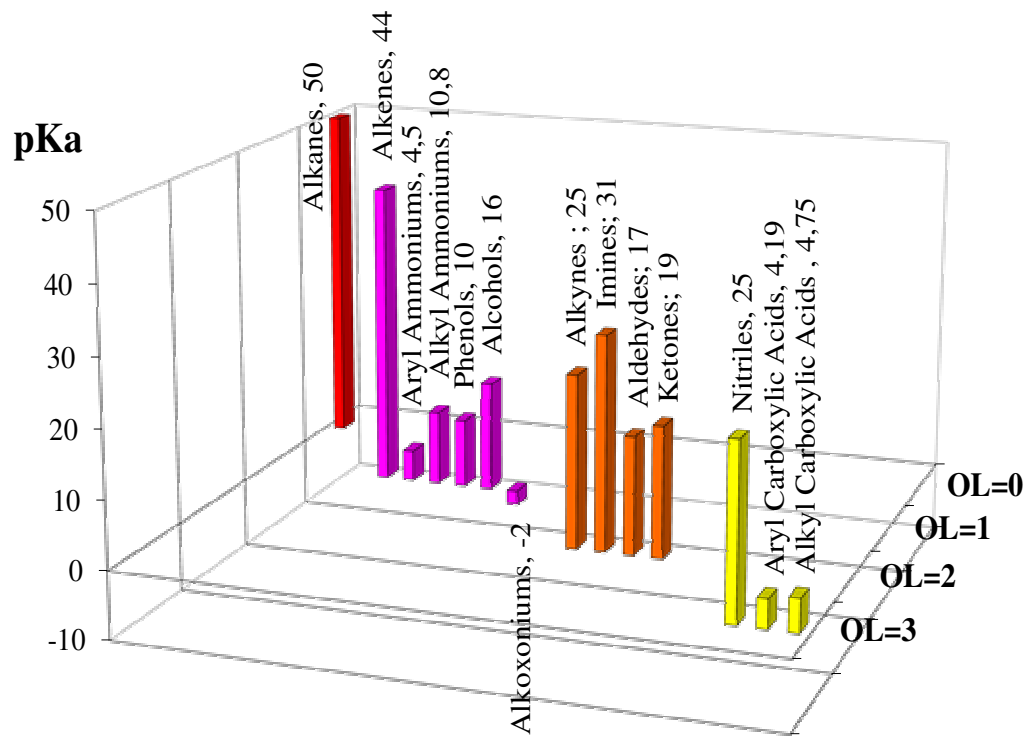


Fig. 4. A 3-D graph corresponding to Reaction scheme 1 showing the pKa values of the functional groups.