

10 Functional Groups of Organic Compounds

Organic Chemistry deals with compounds that are primarily based on the element carbon. Carbon atoms can be bonded through single, double, or triple bonds to other carbon atoms, forming chains, rings, polycycles, or other frameworks of virtually any sizes. They form stable bonds also to other elements, most often hydrogen, oxygen, and nitrogen but also sulfur, the halogens, and, less frequently, any of the other elements of the periodic table.

The diversity of structural possibilities of carbon compounds results in the fact that by now already more than 25 million organic compounds are known, which all differ in their physical and chemical properties. A certain classification of the compounds is therefore required.

Organic compounds can be classified according to a variety of criteria. For instance, naturally occurring compounds (natural products) can be distinguished from synthetic substances, toxic from non-toxic, and volatile from less volatile compounds, etc. From a chemical point of view it makes sense to classify substances on the basis of their chemical reactivities, which are closely connected to the functional groups contained in a molecule. For this reason we focus at the beginning of this course on the common functional groups of organic molecules.

The following experiments deal with the differentiation and identification of the most important functional groups of organic compounds. We will not go into the details of their chemical behaviors here; this will be done in the lecture courses. At this point we will focus in a first step on the acid–base properties of functionalized organic compounds, following up the concepts already taught before. In the subsequent experiments, specific reactivities of functional groups are used for their identification. The related chemical theory exceeds the scope of this course, and we do not ask you to understand it fully. For the sake of completeness, we nevertheless provide chemical explanations for the reactions performed with the several tests.

The individual experiments in Chapter 10 are:

- Experiment 10 A Acidity/Basicity of Organic Compounds
- Experiment 10 B Tests for Functional Groups
- Experiment 10 C Analysis of an Unknown Mixture

Experiment 10 A Acidity/Basicity of Organic Compounds

Objective

Important information about organic compounds and their functional groups can already be obtained by simple solubility tests. In Experiment 10 A, you will acquire a technique that allows you to quickly characterize unknown compounds and to classify them on the basis of their polarity and acid–base properties. You will become acquainted with a “solubility theory”, which you need as the basis to understand and apply the most common working-up procedure in Organic Chemistry — the extraction. You already separated two organic compounds by the extraction procedure (Experiment 5 A, CHE111/171), and here you learn more about the chemistry behind it. Additionally, you will recollect the most important functional groups that you already (might) have encountered in lecture courses or at high school.

Solubility of Organic Compounds

We have already dealt extensively with the solubility of chemical substances in CHE111/171. In Chapter 4 you were given a set of solubility rules for inorganic salts that allow the quick prediction of the solubility properties of a given inorganic compound. No comparable rules are available for organic compounds. In Organic Chemistry we primarily rely on the rule “*like dissolves like*”, which was already introduced in Experiment 4 B (see also table on the next page).

The following table shows that the hydrophobic/hydrophilic properties of an organic compound can be correlated rather directly to its functional groups. However, the total structure of a molecule is not considered in the table, and the indicated behaviors merely relate to the “local polarities” in the vicinity of the functional groups. This means, *e.g.*, that a carboxylic acid always contains a strongly polar and hydrophilic group that allows good interaction with water. However, the acid might also have a significant nonpolar (hydrophobic, lipophilic) hydrocarbon part so that the characteristics of the latter can dominate and dictate the overall properties of the substance. This is the case, *e.g.*, for fatty acids (*cf.* Experiment 11 E) that are sparingly soluble in water but very readily soluble in a variety of organic solvents, even in the very nonpolar hydrocarbons.

As a rule, most organic compounds are readily soluble in diethyl ether (Et_2O , frequently called just ether) and only sparingly in water. Exceptions from this rule are functionalized compounds with only a few carbon atoms (1 to about 5 C atoms, depending on the functional group), polyfunctionalized compounds, and organic salts. Some of them are poorly soluble in organic solvents but, as a rule, readily soluble in water instead.

class of substance	behavior	readily soluble in solv. of the type
hydrocarbons	↓	hydrocarbons, ethers
halogenated hydrocarbons		halogenated hydrocarbons
ethers		↓
amides		esters
esters		↓
nitro compounds		alcohols, dioxane, glacial acetic acid
nitrides		↓
ketenes		alcohols, water
aldehydes		↓
phenols		
amines		
alcohols		
carboxylic acids		
sulfonic acids		
salts	hydrophilic	water

On the basis of simple solubility tests, organic compounds can thus be classified roughly in three groups: in compounds that are soluble in water, compounds that are soluble in ether, and compounds that are soluble in both solvents. Thus, just the solubility of an organic compound in ether and water allows to draw first conclusions regarding its structure, albeit not very detailed ones:

readily soluble in	type of compound	solubility group
water and ether	• polar, small molecules ($\leq 5-6$ C atoms)	Group I
only water	• salts • very polar, small molecules	Group II
only ether	• nonpolar molecules • molecules with large nonpolar parts (in spite of polar groups being present)	Groups III–VIII

Acidity and Basicity of Organic Compounds

The acid and base properties of organic substances allow to modify their solubilities. An acidic compound can be converted into a salt by deprotonation; likewise, a basic compound can be converted to a salt by deprotonation. The salts of acids and bases are significantly more polar and, thus, distinctively more soluble in water (and less soluble in an organic solvent) than the uncharged acids and bases. Organic compounds with different acid/base strengths can often be converted selectively into the

corresponding salts by controlled deprotonation/protonation using differently strong bases or acids. This can be used to distinguish and separate them.

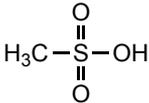
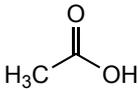
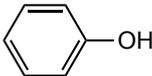
On the basis of different solubilities of organic compounds in neutral, basic, and acidic environments, we can easily distinguish between organic acids, bases, and neutral substances. Below, the functional groups that lead to acidic or basic properties of a compound are shortly introduced.

Organic Acids

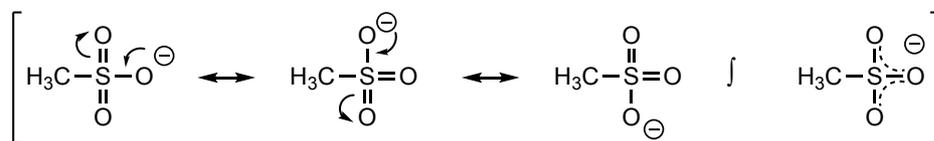
In principle, all compounds that bear at least one hydrogen atom are acids because they all can be deprotonated with a sufficiently strong base. In the proper sense, however, we only call a compound HA an acid when it relatively easily dissociates in aqueous environment to H^+ (H_3O^+) and the conjugate base (A^-) (see CHE111/171, Chapter 6); when its pK_a is smaller than that of water ($\text{pK}_a(\text{H}_2\text{O}) = 15.7$). A compound is the more acidic the better the anion formed by deprotonation is stabilized. The acidity of an XH compound accordingly increases within a period of the periodic table from the left to the right, with increasing electronegativity of X. More important than the stabilization of a anion by an electronegative element X, however, is its additional stabilization through resonance. Typical organic acids form resonance-stabilized anions as conjugated bases.

Compounds with Acidic OH Groups

The O–H bond of an OH functionality is polarized, and deprotonation should be readily possible. However, the most typical compounds with OH groups, the alcohols, do not belong to the organic acids despite the strongly electronegative character of the O atom. Their pK_a values usually lie about 1–3 units above that of water, and alcohols are accordingly just marginally dissociated in water. Typical organic acids with OH groups are sulfonic and carboxylic acids; phenols and 1,3-diketones (in the enol form, see below) are acidic as well, but to a considerably lesser degree.

compounds	pK_a	example	
sulfonic acids RSO_3H	< 0		$\text{pK}_a = -2.3$
carboxylic acids RCO_2H	< 5		$\text{pK}_a = 4.8$
phenols ArOH	10 ± 3 (approx.)		$\text{pK}_a = 10.0$

Sulfonic acids, carboxylic acids, and phenols are stronger acids than alcohols because the charges of the anions formed by dissociation (of the conjugate bases = sulfonates, carboxylates, and phenolates) are stabilized by resonance (= delocalization). The corresponding resonance formulas (= mesomeric forms or resonance structures) for a sulfonate are shown below:

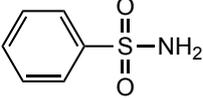
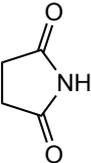


While the strongly acidic sulfonic acids dissociate in water almost completely, the considerably less acidic carboxylic acids dissociate only partially (cf. CHE111/171, Experiment 6 B), and the even less acidic phenols nearly do not dissociate at all. Accordingly, solutions of sulfonic acids in water show low pH values, those of carboxylic acids pH values somewhat below 7, and those of phenols do not react acidic at all.

Organic acids with pK_a values of ca. < 5 get fully deprotonated by relatively weak bases. Carboxylic acids usually dissolve as carboxylate salts in 0.5 M aqueous NaHCO_3 solutions. To fully deprotonate phenols, stronger bases are required. They normally dissolve as phenolates, however, in 0.5 M aqueous NaOH solution.

Compounds with Acidic NH Groups

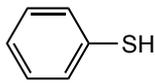
Nitrogen-containing compounds in low oxidation states are usually basic and, hence, release NH protons only reluctantly (see below). However, if the anions that are formed by deprotonation of the NH groups are well stabilized, NH compounds can also act as weak acids. The anions of the conjugate bases of sulfonamides and of imides are particularly well stabilized by resonance, so that the respective parent compounds are rather acidic.

compounds	pK_a	example	
sulfonamides $\text{RSO}_2\text{NHR}'$	10 ± 3		$\text{pK}_a = 10$
imides $(\text{RCO})_2\text{NH}$	10 ± 3		$\text{pK}_a = 9.7$

Sulfonamides and imides are comparable in their acidity to phenols, and, like them, are usually deprotonated by aqueous NaOH , but generally not by aqueous NaHCO_3 .

Compounds with Acidic SH Groups

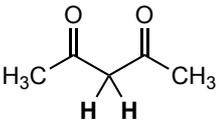
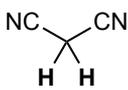
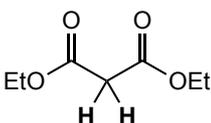
In principle, the acidity of XH compounds increases when X (within the same group) is of a higher period. Accordingly, SH compounds generally are more acidic than the analogous OH compounds. The pK_a values here are lower by about 4–7 units.

compounds	pK_a	example	
thiophenols ArSH	6.5 ± 3		$pK_a = 6.5$
thiols RSH	approx. 11	H_3C-SH	$pK_a = 10.5$

Thiophenols are often already deprotonated by $NaHCO_3$; thiols by $NaOH$ only.

Compounds with Acidic CH Groups

The CH bond is only slightly polarized *per se* and so the pK_a values of hydrocarbons are very high (e.g., ethane: $pK_a = 52$). In the vicinity of strongly electron withdrawing groups, however, H atoms bound to C atoms may become acidic. Possible electron withdrawing groups are, among others, nitro, carbonyl, nitrile, and carboxyl groups (according to decreasing CH activation). Whereas a single nitro group is sufficient to result a pK_a value of about 10 for the corresponding α -CH atoms, two carbonyl, nitrile, or carboxyl groups are required to achieve the same result (double activation).

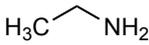
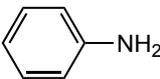
compounds	pK_a	example	
nitroalkanes R_2CHNO_2	10 ± 3	H_3C-NO_2	$pK_a = 10.2$
1,3-diketones $RCOCHR'COR$	9 ± 3 cyclic: as far as 5 ± 2		$pK_a = 9.0$
malononitriles $NCCHR CN$	11 ± 2		$pK_a = 12.9$
malonates $RO_2CCHR CO_2R$	13 ± 2		$pK_a = 11.3$

The acidity of the above compounds is due to the polarization of the CH bond as a consequence of the inductive (σ acceptor) effect of the NO_2 and the CO/CN groups, but, more importantly, due to the resonance stabilization of the anions of the deprotonated forms (π acceptor effect of the groups).

Organic Bases

All organic compounds that have functional groups with positions of high electron density, e.g., electron lone pairs, are potential bases. However, here we again consider as bases only those charge-neutral compounds that can be converted into salts by protonation in an aqueous environment. Thus, the compounds must be comparable or even stronger bases than water.

The strength of a base depends on two factors: on the availability of the electron lone pair and on the stabilization of the cation produced by protonation. The availability of the electron lone pair is closely related to its orbital energy. The higher the orbital energy is, the more reactive and, consequently, the more basic the electron pair is. Because the orbital energies decrease with increasing electronegativity of the elements, it is obvious that amines ($EN_N = 3.1$) must be more basic than alcohols ($EN_O = 3.5$). The basicity of *N*-containing organic compounds varies over a wide range, though, because the availability of the electron lone pair can be limited due to conjugation. Possible basic compounds that get fully protonated by 0.5 M aqueous HCl and, therefore, can often (but not always) be dissolved in water in form of their ammonium salts are alkyl amines (primary, secondary, and tertiary, cf. the table), aryl amines, and heterocyclic nitrogen compounds. Other *N*- (and *O*-) containing functional groups can also be protonated, if the acids used are sufficiently strong and sufficiently concentrated, e.g., conc. H_2SO_4 (see below).

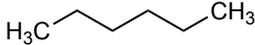
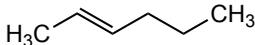
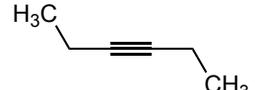
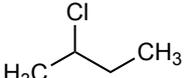
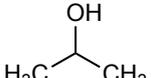
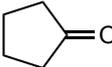
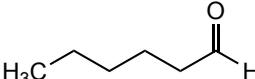
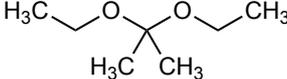
compounds	pK_b	example	
alkyl amines RNH ₂ (prim.) R ₂ NH (sec.) R ₃ N (tert.)	3.5 ± 1		$pK_b = 3.19$
aryl amines ArNH ₂	9 ± 3	 aniline	$pK_b = 9.27$
pyridine type	8 ± 3	 pyridine	$pK_b = 8.75$
pyrrole type	15 ± 3	 pyrrole	$pK_b = 15.0$

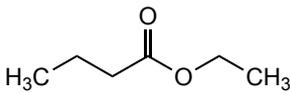
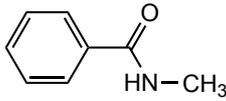
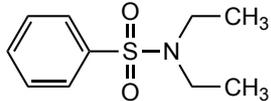
Neutral Substances

All organic compounds that are not converted, for the major part, to deprotonated or protonated forms in diluted aqueous HCl or NaOH solutions, respectively, are regarded as neutral substances. The classification “neutral substance”, however, does not mean

that such compounds do not react at all with acids or bases. They still may get protonated or deprotonated to small extents, forming reactive intermediates, and their acid/base properties become important in connection with acid- or base-catalyzed reactions (see later in this manual).

Moreover, many neutral substances can be completely protonated and deprotonated, respectively, in an anhydrous environment if very strong acids or very strong bases are used. For this reason, almost all *N*- and *O*-containing compounds (except for diaryl ethers and nitro compounds) as well as unsaturated hydrocarbons (except for aromatic compounds) can be converted to the conjugate acids by conc. H_2SO_4 . On the other hand, almost all carbonyl and carboxyl compounds can be deprotonated to the corresponding enolates by amide (= deprotonated amines) or other very strong bases. Typical neutral substance classes are compiled in the following table, with one example for each.

compounds	example	
alkanes	hexane	
alkenes	(<i>E</i>)-hex-2-ene	
alkynes	hex-3-yne	
aromatic hydrocarbons	benzene	
alkyl and aryl halides	2-chlorobutane (an alkyl halide)	
alcohols	propan-2-ol	
ethers	diethyl ether	
ketones	cyclopentanone	
aldehydes	hexanal	
acetals	2,2-diethoxypropane acetone diethyl acetal	

esters	ethyl butanoate butanoic acid ethyl ester	
amides	<i>N</i> -methylbenzamide	
<i>N,N</i> -disubstituted sulfonamides	<i>N,N</i> -diethylbenzene sulfonamide	

Solubility Groups, Solubility Tree

On the basis of their solubilities, organic compounds can be classified as follows:

Group I: soluble in water and ether.

Monofunctionalized, polar substances with neutral charge and up to about 5 C atoms. This group includes acidic, basic, and neutral compounds in sub-groups.

Group II: soluble in water; not or only sparingly soluble in ether.

Very polar substances of neutral charge containing several functional groups or organic salts. This group includes acidic, basic, and neutral compounds in sub-groups.

Group III: soluble in ether; not or only sparingly soluble in water and acid; readily soluble in weak or strong base.

Relatively *strong organic acids* ($\text{pK}_a \leq \text{ca. } 7-8$) with sufficiently large nonpolar structural parts: carboxylic acids with larger hydrocarbon residues and substituted electron-deficient phenols.

Group IV: soluble in ether; not or only sparingly soluble in water, acid, and weak base; readily soluble in strong base.

Weak organic acids (approx. $8 \leq \text{pK}_a \leq \text{ca. } 14$) with sufficiently large nonpolar structural parts: substituted electron-rich phenols, enols (dicarbonyl compounds), primary and secondary nitroalkanes, and *N*-mono/*N*-unsubstituted sulfonamides.

Group V: soluble in ether; not or only sparingly soluble in water and base; readily soluble in diluted acid.

Organic bases ($\text{pK}_b \leq \text{approx. } 15$, mostly *N*-containing compounds) with sufficiently large nonpolar structural parts: amines, aryl amines, and aromatic heterocycles.

Group VI-VIII: soluble in ether; not or only sparingly soluble in aqueous systems.

Neutral substances: little polar compounds that can be further classified due to their N/S content and their ability to be protonated by conc. H_2SO_4 (see below).

		pH of the original solution					
<p>H₂O</p> <p>pH-measurement with aqueous phase</p>	yes	Et ₂ O	yes	pH < 7	Group I carboxylic acids, small 1,3-diones (A) sulfonic acids (A) some phenols (A/wA)	polar, small molecules (up to about 5–6 C atoms)	
			no	pH > 7	amines (B)		
	no	NaHCO ₃	yes	pH ≈ 7	alcohols (N) aldehydes, ketones (N) esters, amides, nitriles (N)		
			no	pH < 7	Group II polycarboxylic acids (A) small 1,3-dicarbonyl comp. (wA) salts of amines (prot. amines) (wA) carboxylates (deprot. carboxylic acids) (B)		
	yes	NaOH	yes	pH > 7	tetrasubst. ammonium salts (N) sugars, polyols (N) amino acids (A, B, N)		salts and very polar, small molecules
			no	pH ≈ 7	Group III carboxylic acids (A) some phenols (A/wA)		
	no	HCl	yes	pH ≈ 7	Group IV phenols (wA) enols (larger 1,3-dicarbonyl comp.) (wA) nitro alkanes (α-H-atom) (wA) sulfonamides (wA)		nonpolar molecules and nonpolar parts (dispite polar groups being present)
			no	pH > / ≈ 7	Group V amines (B) aromatic N-heterocycles (wB)		
no	HCl	yes	pH ≈ 7	Group VI aromatic nitro compounds (N) amides, nitriles (N) N,N-disubstituted sulfonamides (N)	nonpolar molecules and nonpolar parts (dispite polar groups being present)		
		no	pH ≈ 7	Group VII alkenes, alkynes (N) alcohols, ethers (N) aldehydes, ketones (N) esters (N)			
				Group VIII saturated hydrocarbons (N) aromatic hydrocarbons (N) alkyl and aryl halides (N) diaryl ethers (N)	molecules with larger nonpolar parts (dispite polar groups being present)		

A = acid, wA = weak acid
 B = base, wB = weak base
 N = neutral substance

Classification of the Neutral Substances

The neutral substances can be sub-classified into the Groups VI–VIII. For this, the samples are analyzed qualitatively for their content of N and S (Group VI), and the N/S-free compounds are further classified into the groups VII (can be protonated by conc. H_2SO_4) and VIII (inert toward conc. H_2SO_4):

Group VI: not or only sparingly soluble in water, diluted acid, or base; often soluble in ether; contains N and/or S.

Neutral substances with N- and/or S-containing functional groups and sufficiently large nonpolar residues.

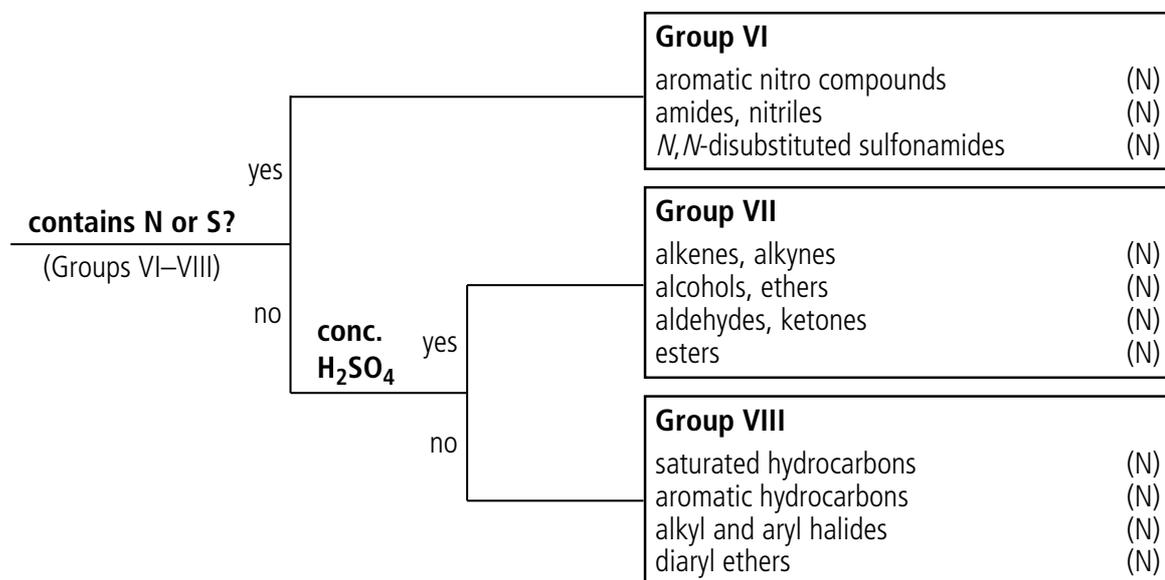
Group VII: not or only sparingly soluble in water, diluted acid, or base; often soluble in ether; contains neither N nor S; soluble in conc. H_2SO_4 .

Neutral substances containing O, double, and/or triple bonds that can be protonated by conc. H_2SO_4 (mostly with decomposition!).

Group VIII: not or only sparingly soluble in water, diluted acid, or base; often soluble in ether; contains neither N nor S; insoluble in conc. H_2SO_4 .

Neutral compounds that are inert even towards strong acid.

The “solubility tree” is supplemented, thus, as follows:



To analyze the sample for nitrogen and sulfur (and halogens), the compound is fused with sodium. N-containing compounds produce CN^- in the sodium fusion, S-containing compounds produce S^{2-} (and SCN^- , if also N is contained), and halogen-containing substances produce the corresponding halides. The anions can then be identified specifically as learned in CHE111/171, Experiment 9 C.

Preparative Tasks to Experiment 10 A

1. Indicate for each of the substances of the following list (= possible compounds you might receive in Experiment 10 A) the functional group(s).
2. Assign them to the Groups I–VIII (incl. subgroups) as far as possible.

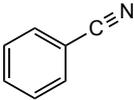
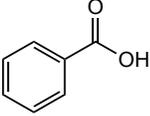
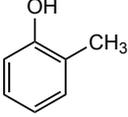
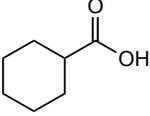
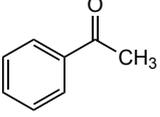
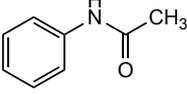
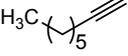
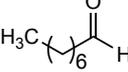
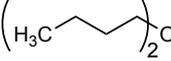
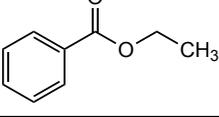
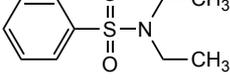
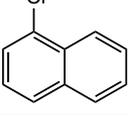
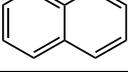
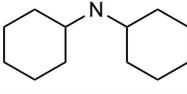
Specify those compounds you cannot unambiguously assign on the basis of the given criteria. You shall discuss these compounds specifically with the teaching assistants during the introductory meeting for Experiment 10 A and you have to make sure that you finally have all the correct assignments (this is crucial for the experiment!).

List of the Compounds for Analysis in Experiments 10A and 10B

(sorted according to their chemical formulas)

formula	name	structure	hazard pict	grp
$C_2H_2O_4$	oxalic acid (ethanedioic acid)			
$C_2H_3ClO_2$	chloroacetic acid (chloroethanoic acid)			
C_2H_3N	acetonitrile (methyl cyanide)	$H_3C-C\equiv N$		
$C_2H_3NaO_2$	sodium acetate (sodium ethanoate)			
$C_2H_4O_2$	acetic acid (ethanoic acid)			
C_2H_6O	ethanol	H_3C-CH_2-OH		
$C_2H_8N_2$	ethylenediamine	$H_2N-CH_2-CH_2-NH_2$		
C_3H_6O	acetone (propanone)			
C_3H_6O	allyl alcohol (propenol)			
C_3H_6O	propionaldehyde propanal			
$C_3H_7NO_2$	L-alanine			
CH_3NO_2	nitromethane	H_3C-NO_2		
C_3H_8O	isopropanol (propan-2-ol)			

formula	name	structure	hazard pict	grp
C ₄ H ₄ O ₄	fumaric acid (<i>(E)</i> -butenedioic acid)			
C ₄ H ₉ Cl	chlorobutane (butyl chloride)			
C ₄ H ₉ Cl	2-chlorobutane (<i>sec</i> -butyl chloride)			
C ₄ H ₉ Cl	<i>tert</i> -butyl chloride (2-chloro-2-methylpropane)			
C ₄ H ₁₁ N	diethylamine			
C ₄ H ₁₂ ClN	tetramethylammonium chloride			
C ₅ H ₁₂ O	2-methylbutan-2-ol (<i>tert</i> -pentanol)			
C ₆ H ₅ NO ₂	nitrobenzene			
C ₆ H ₇ NO ₂ S	benzene sulfonamide			
C ₆ H ₈ O ₂	cyclohexa-1,3-dione			
C ₆ H ₁₀	cyclohexene			
C ₆ H ₁₀ O	cyclohexanone			
C ₆ H ₁₂	cyclohexane			
C ₆ H ₁₂ O	cyclohexanol			
C ₆ H ₁₂ O ₆	D-glucose			
C ₆ H ₁₄ O	hexanol			
C ₆ H ₁₅ N	triethylamine			
C ₆ H ₁₆ ClN	triethylamine hydrochloride			

formula	name	structure	hazard pict	grp
C ₇ H ₅ N	benzonitrile (phenyl cyanide)			
C ₇ H ₆ O ₂	benzoic acid			
C ₇ H ₈ O	<i>o</i> -cresol (2-methylphenol)			
CHO	cyclohexane carboxylic acid			
C ₈ H ₈ O	acetophenone (methyl phenyl ketone)			
C ₈ H ₉ NO	acetanilide (<i>N</i> -phenylacetamide)			
C ₈ H ₁₄	oct-1-yne			
C ₈ H ₁₆ O	octanal			
C ₈ H ₁₈ O	dibutylether			
C ₈ H ₁₉ N	octylamine			
C ₉ H ₁₀ O ₂	ethyl benzoate			
C ₁₀ H ₁₅ NO ₂ S	<i>N,N</i> -diethylbenzene sulfonamide			
C ₁₀ H ₇ Cl	1-chloronaphthalene			
C ₁₀ H ₈	naphthalene			
C ₁₂ H ₂₃ N	dicyclohexylamine			

Experimental Instructions

Problem

You will receive four unknown compounds, about 10 g of each, from the substances given in the table on p. 32ff. You have to characterize these four compounds on the basis of solubility tests and, where appropriate, by sodium fusion and tests for nitrogen, sulfur, and halogens. Finally the compounds have to be assigned to the Groups I–VIII.

Accessories

Combustion tubes, Et₂O, aqueous solutions of HCl (0.5 M), NaHCO₃ (0.5 M), NaOH (2 M), AgNO₃ (0.5 M), Na₂[Fe(CN)₅NO] (1 M, sodium nitroprusside), FeSO₄·7 H₂O (pure, solid), Na (pure, solid, under oil), H₂SO₄ (2 M), HNO₃ (2 M).

Safety Instructions

Be aware that you usually do not know anything about the safety risks connected to unknown compounds. Most of the samples provided in this practical course are harmless, but some are not (especially in concentrated form)! Therefore, always handle all of your samples, particularly if you do not know what they are, as if they were dangerous substances: Avoid skin contact and inhalation of the vapors. (Hence, what do you do in practice?)

Elemental Na reacts violently and exothermically with H₂O or O₂, producing corrosive NaOH and H₂ gas. The latter can ignite spontaneously in this exothermic reaction. Therefore, always keep Na stocks well protected under a layer of oil and prevent that elemental Na can come in contact with H₂O. Always work in the fume hood, with the sash closed as far as possible.

Preliminary Remarks

The results of chemical tests are not always easily assessed. You probably made this experience already with the Experiments 9 in CHE111/171. As a general rule, only “positive test results” (e.g., the observation of a reaction typical for a functional group) are really significant. “Negative results” (e.g., the absence of a reaction that normally is typical for a functional group) do not allow unambiguous interpretation. Chemical reactions often are complex and can be affected by many

parameters that are not completely known — e.g., by the presence of contaminants, the effective concentrations of the reaction partners, etc. Therefore, consider “negative results” as indications at best, but never as proof.

Procedure

Solubility Tests 1

Measure the pH of the solutions, emulsions, or suspensions you have obtained upon mixing the samples with pure H₂O, and add this information into your table.

Test the solubility of each compound individually in each of the 5 solvents:

H₂O, aq. solutions of NaOH (2 M), NaHCO₃ (0.5 M), HCl (0.5 M), and Et₂O

Start for each sample with H₂O. Add 10 drops of the liquid substance (or the amount that fits on the tip of a spatula of the pulverized solid substance, about 20–50 mg) into a small test tube. Then add some drops of H₂O and shake thoroughly. Draw a sample of the solution with a glass rod, and dip it onto a small strip of pH indicator paper, and record the pH value of the solution into the notebook. If the sample has not completely dissolved, add dropwise more of the solvent (to max. 0.5 mL) while you shake and observe the dissolving progress (enter your observations into a table).

Proceed likewise with the other solvents, without measuring the pH values of the solutions (why?)

Readily soluble compounds dissolve immediately within the first drops of solvent; insoluble compounds do not dissolve even in 0.5 mL. For many compounds, the solubility lies somewhere in-between.

At this point it must be noted that not all salts of organic compounds are readily soluble in water. It is possible that acid–base reactions deliver salts that are not readily soluble (contrary to what we expect). Since we take the water solubility of a sample in basic or acidic medium just as measures to recognize whether or not a deprotonation or protonation had occurred, direct observation of a chemical reaction (e.g., the observation of a precipitate forming) can be taken as a “positive test result” as well!

When you have the impression that a substance dissolves more readily in acid or in base than in pure water, you may confirm this observation by neutralization of the solution. If the amount of solvent is not too high, the dissolved material

should precipitate again in its original form upon neutralization, which can be observed as cloudiness (or the formation of a precipitate or second phase).

Preliminary Evaluation

Assign each of your sample compounds to the Groups I, II, III, IV, V, or (VI–VIII.) Confirm your results with your teaching assistant before proceeding.

For some of the samples, the classification might not be unambiguous. Make sure that you discuss these cases with your teaching assistant and that your teaching assistant confirms the correct assignment (or decides, to which group you have to assign the sample). It is decisive for the next steps that you know to which group your compound belongs!

Assignment of Group VI: Sodium Fusion and Detection of Nitrogen, Sulfur, and Halogen

To fine-assign the compounds you have collectively assigned to the Groups VI–VIII (only these!), you have to analyze them for their N and/or S content (assignment of Group VI). For this purpose, sodium fusion and subsequent anion analysis is performed.

Sodium Fusion

The sodium fusion experiment is not suited for very volatile compounds. Do not perform it with low boiling liquids that usually are also of low viscosity.

Add some liquid sample (to a height of about 5 mm, by dipping the pipette completely to the bottom of the tube and avoiding spills on the tube wall) or some solid sample (20–30 mg) into a combustion tube. Hold the tube with the crucible tongs slightly inclined, and introduce a freshly cut piece of Na (about 4×1×1 mm) into it with tweezers so that it lies about 5 mm above the substance. Then heat the Na in the tube, which is still kept inclined, with a small sharp flame of your *Teclu* burner to melting — avoid heating your sample too strongly. Allow the liquid metal to flow into the sample to react with it (often violently). Heat the Na and the substance until the glass tube becomes red by heat and the sample got charred. Drop the still hot tube into a test tube with about 10 mL of deionized H₂O, where the combustion tube should break into pieces. Shake shortly to dissolve the Na salts, filter off the solution (= sodium fusion solution); if appropriate, rinse the test tube with 2–3 mL of H₂O and supplement the sodium fusion solution with it.

Attention: There might be some unreacted Na left in the combustion tube that will violently react with the water. Therefore, perform this experiment with the appropriate care in the fume hood, with the sash pulled down. Never keep any organic solvent in the immediate proximity of your experiment!

Heat the fusion tube and crush it by dipping it into a test tube with H₂O also when the sodium fusion failed. It is crucial to destroy any remaining, highly reactive elemental sodium under controlled conditions to avoid accidents.

Organic compounds that contain N form upon sodium fusion CN⁻ (particularly amides, imides, imines — to a lesser extent alkyl amines and their ammonium salts). Organic compound with S-content form S²⁻ and those with halogen-content Hal⁻. The several ions can be detected by specific test reactions:

Detection of Nitrogen (Lassaigne Test for CN⁻)

Add a small amount of FeSO₄·7 H₂O (tip of the spatula; about 20 mg) to 1 mL of the sodium fusion solution and heat the mixture. The iron(II) salt dissolves, the color of the solution turns yellow to dark green, and iron hydroxides precipitate. Acidify the mixture with a few drops of 2 M H₂SO₄. In the presence of CN⁻, *Prussian blue* forms Fe(III)[Fe(III)Fe(II)(CN)₆], a deeply blue complex salt. You can easily observe the formation of this compound when you give some drops of the thoroughly shaken solution onto a filter paper. Attention: the *Lassaigne* test is not very reliable! It frequently gives only very small amounts (or even none) of the expected colored species, particularly if aliphatic amines and their hydrochlorides are analyzed! Thus, do not overrate a negative result!

Fe(II) is oxidized in parts to Fe(III) by atmospheric oxygen (cf. Part 1).

Detection of Sulfur

Add some drops of 1 M aq. sodium nitroprusside (Na₂[Fe(CN)₅NO]) to 0.5 mL of the sodium fusion solution. A purple-violet color shows the presence of S²⁻.

The NO⁺ of the prusside reacts with S²⁻ to NOS⁻ (sulfur analog of NO₂⁻), and the purple colored complex anion [Fe(CN)₅NOS]⁴⁻ is formed.

Detection of Chloride (and other Halides)

To decide to which of the three groups VI–VIII your sample belongs, the knowledge of its halogen-content is not necessary. However, having the sodium fusion solution at hand, the additional information can be useful as a further characteristic of the product. For halogen detection:

Acidify 0.5 mL of the sodium fusion solution with 2 M HNO_3 , and, in case you have detected N or S, boil the solution in the fume hood to expel HCN (prussic acid!) and/or H_2S . Then add several drops of 0.5 M AgNO_3 . The formation of a colorless precipitate indicates the presence of a halide — in our case this would be Cl^- . (For the differentiation of Cl^- , Br^- , and I^- cf. Experiment 9 C, CHE111/171)

Assignment of Groups VII and VIII

To assign the remaining compounds to the Groups VII or VIII, their solubility in conc. H_2SO_4 is investigated.

Thus, place 5 drops of the liquid substance (or the amount that fits on the tip of a spatula; about 20–50 mg of the pulverized solid substance) into a small test tube, and then add dropwise conc. H_2SO_4 to your sample. Shake carefully and observe dissolution (\rightarrow group VII) or other effects. It is important to know that apart from protonation also other reactions might occur under the strongly acidic conditions (most often subsequent reactions with the protonated species). These reactions are often irreversible. Significant changes of color indicate reactions and, therefore, the presence of functional groups. The respective sample is then also assigned to group VII.

Attention: conc. H_2SO_4 is aggressive and highly corrosive. Avoid contact with skin. In case of spilling, dilute immediately with cold water. After the experiment, pour the content of the test tube into an excess of water to dilute the H_2SO_4 to a non-hazardous concentration.

Collection

You will need the remaining part of your samples for Experiment 10 B!

Collect all waste solutions in the provided waste container; they will be disposed of properly by us.

Evaluation

In the laboratory notebook: assign your compounds to the Groups I–VIII (incl. subgroups) and characterize them as far as possible (e.g., contains halogen). Ask the teaching assistants for confirmation of your results before you leave the laboratory!

List for each of your samples those substances from the table given on p. 32ff that are, based on your acquired information, possible candidates for your unknowns. This information is important for the next experiment!