3.2: Organic Acids and Bases and Organic Reaction Mechanism

3.2.1 Organic Acids

The acids that we talked about in General Chemistry usually refers to inorganic acids, such as HCl, H_2SO_4, HF etc. If the structure of the acid contains a “carbon” part, then it is an organic acid. Organic acids donate protons in the same way as inorganic acids, however the structure may be more complicated due to the nature of organic structures.

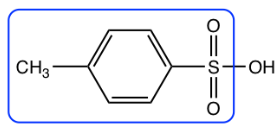
Carboxylic acid, with the general formula of R-COOH, is the most common organic acid that we are familiar with. Acetic acid (CH_3COOH), the ingredient of vinegar, is a simple example of a carboxylic acid. The K_a of acetic acid is 1.8×10^{-5}.

Another common organic acid is the organic derivative of sulfuric acid H_2SO_4.

sulfuric acid, H_2SO_4 **sulfonic acid, RSO_3H or $ArSO_3H$**

The replacement of one OH group in H_2SO_4 with a carbon-containing R (alkyl) or Ar (aromatic) group leads to the organic acid named “sulfonic acid”, with the general formula of RSO_3H, or $ArSO_3H$. Sulfonic acid is a strong organic acid with a K_a in the range of 10^6. The structure of a specific sulfonic acid example called *p* -toluenesulfonic acid is shown here:

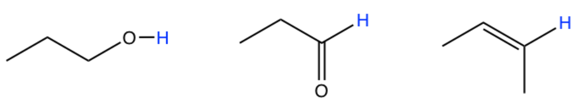
The common name is tosylic acid, and the circled part is known as the “**tosyl**” group, that is abbreviated as “**Ts**”. So the formula of tosylic acid can also be **TsOH**.



***p*-toluenesulfonic acid, TsOH**
(commond name: tosylic acid)

Figure 3.1a CH3C6H4SO3H Tosylic acid

Other than the acids mentioned here, technically any organic compound could be an acid, because organic compounds always have hydrogen atoms that could potentially be donated as H^+. Only a few examples are shown here with the hydrogen atoms highlighted in blue:



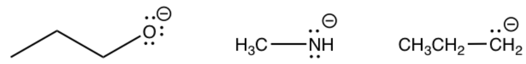
More examples of organic acids

Therefore, the scope of acids has been extended to be much broader in an organic chemistry context. We will have further discussions on the acidity of organic compounds in **section 3.3**, and we will see more acid-base reactions applied to organic compounds later in this chapter.

3.2.2 Organic Bases

While it is relatively straightforward to identify an organic acid since hydrogen atoms are always involved, sometimes it is not that easy to identify organic bases. According to the definition, a base is the species that is able to accept the proton. Organic bases may involve a variety of different structures, but they must all share the common feature of having ***electron pairs*** that are able to accept protons. The electron pairs could be lone pair electrons on a neutral or negative charged species, or π electron pairs. Organic bases could therefore involve the following types:

- Negatively charged organic bases: RO^-(alkyloxide), RNH^-(amide), R^-(alkide, the conjugate base of alkane). Since the negatively charged bases have a high electron density, they are usually stronger bases than the neutral ones.



Examples of negatively charged organic bases with lone pair electrons shown in the structure

Note: Keep in mind that the lone pairs are usually ***omitted*** in organic structures as mentioned before. For example, with the formula of CH_3NH^- given, you should understand that the N actually has two pairs of lone pair electrons (as shown in the above structure) and it is a base.

- Neutral organic bases, for example amine, C=O group and C=C group
  - Amine: RNH_2, R_2NH, R_3N, $ArNH_2$ etc (**section 2.3**). As organic derivatives of NH_3, which is an inorganic weak base, amines are organic weak bases with lone pair electrons on N that are able to accept the proton.

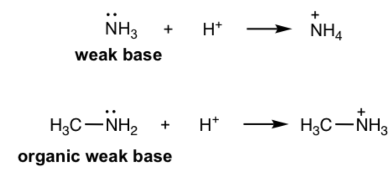


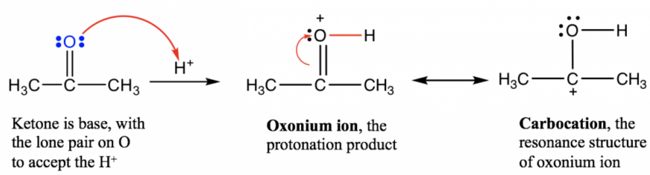
Figure 3.1b weak base and organic weak base

  - Functional groups containing oxygen atoms: carbonyl group C=O, alcohol R-OH, ether R-O-R. The lone pair electrons on O in these groups are able to accept the proton, so functional groups like *aldehyde, ketone, alcohol and ether are all organic bases*. It may not that easy to accept this concept at the first, because these groups do not really look like bases. However, they are bases according to the definition because they are able to accept the proton with the lone pair on the oxygen atom.

Adjust your thinking here to embrace the broader scope of acids and bases in an organic chemistry context.

Here, we will take the reaction between acetone and H^+ as an example, to understand the reaction deeply by exploring the **reaction mechanism,** and learn how to use the curved arrows to show it.

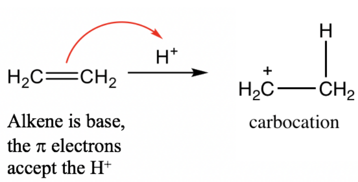
A reaction mechanism is the step-by-step electron transfer process that converts reactants to products. *Curved arrows* are used to illustrate the reaction mechanism. Curved arrows should always start at the electrons, and end in the spot that is receiving the electrons. The curved arrows used here are similar to those for resonance structures (**section 1.4**), but are not exactly same though. Please note that in resonance structures, the curved arrows are used to show how the electrons are transferred *within* the molecule, leading to another resonance structure. For mechanism purposes, there must be arrows that connect *between* species.



Notes for the above mechanism:

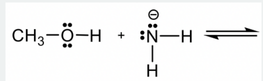
- For the acid-base reaction between C=O group and the proton, the arrow starts from the electron pair on O, and points to the H^+ that is receiving the electron pair. A new O-H bond is formed as a result of this electron pair movement.
- In this acid-base reaction, ketone is protonated by H^+, so this reaction can also be called the "**protonation of ketone**".
- The product of the protonation is called an "oxonium ion", which is stabilized with another resonance structure, carbocation.

  - Alkene (C=C): Although there are no lone pair electrons in the C=C bond of alkene, the π electrons of the C=C double bond are able to accept proton and act as base. For example:



Example: Organic acid and base reaction

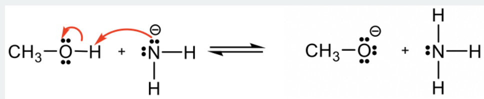
Predict and draw the products of following reaction and use curved arrow to show the mechanism.



Approach: If H^+ is the acid as in previous examples, it is rather easy to predict how the reaction will proceed. However, if there is no obvious acid (or base) as in this example, how do you determine which is the acid, and which is the base?

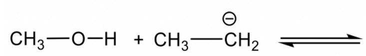
Methanol CH_3OH is neutral, and the other reactant, NH_2^-, is a negatively charged amide. The amide with a negative charge has higher electron density than the neutral methanol, therefore amide NH_2^-should act as base, and CH_3OH is the acid that donates H^+.

Solution:



Exercises 3.1

Predict and draw the products of following reaction and use curved arrow to show the mechanism.



Answers to Practice Questions Chapter 3