Notes on
Organic acids and bases

NOWGONG GIRLS' COLLEGE
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NAGAON-ASSAM

By
Dr. Gangutri Saikia

Definition of acids and bases

In Bronsted-Lowry definition

An acid is a substance that donates a proton.

A base is a substance that accepts a proton.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{Conjugate base}}{Cl^-} + \underset{\text{Conjugate acid}}{H_3O^+}$$

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{Conjugate acid}}{NH_4^+} + \underset{\text{Conjugate base}}{{}^-OH}$$

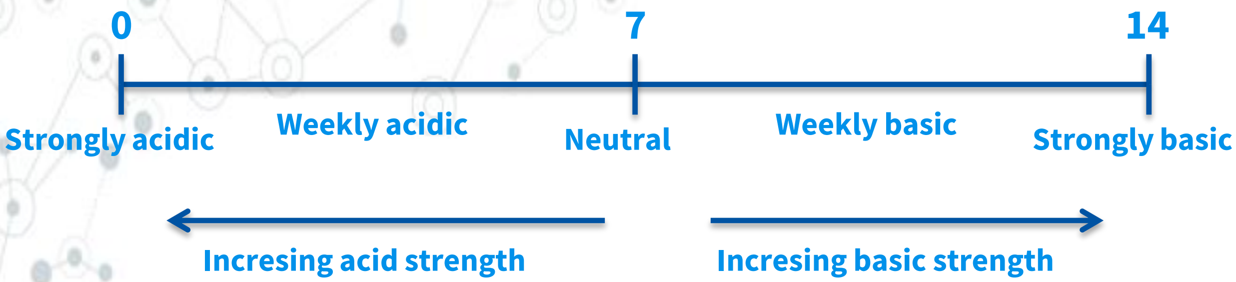
According to this definition, any substance that contains a hydrogen can potentially act as an acid, and any compound that contains a lone pair of electrons can act as base. Both an acid and a base must be present in a proton transfer reaction because an acid cannot donate a proton unless a base is present to accept it. Proton transfer reactions are often called acid-base reactions.

When a compound loses a proton, the resulting species is called its conjugate base. Thus Cl^- is the conjugate base of HCl, HO^- is the conjugate base of H_2O, and H_2O is the conjugate base of H_3O^+.

When a compound accepts a proton, the resulting species is called its conjugate acid. Thus NH_4^+ is the conjugate acid of NH_3, HCl is the conjugate acid of Cl^-, and H_2O is the conjugate acid of HO^-.

Acidity is a measure of how easily a compound gives up a proton. Basicity is a measure of how well a compound shares its electrons with a proton. A strong acid is one that gives up its protons easily. This means that its conjugate base must be weak because it has little affinity for the proton. Thus, ***the stronger the acid, the weaker its conjugate base.***

pH of a solution



pH is a measure of acidity of the solution. It does not tell us about the strength of the acid. pH of a solution varies with its concentration.

$$pH = -\log [H_3O^+]$$

Relative strength of acids and bases

The relative strength of acids & bases can be compared in terms of dissociation constant.

Strong acids dissociate completely while the weak acids do not.

$$AH + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_{eq} = \frac{[H_3O^+]\ [A^-]}{[AH]\ [H_2O]}$$

$$\text{Acidity constant, } K_a = K_{eq}\,[H_2O] = \frac{[H_3O^+]\ [A^-]}{[AH]}$$

$$pK_a = -\log K_a$$

The lower the value of pK_a, the larger the dissociation constant, stronger the acid.

$$[H_3O^+] = K_a \text{ X } \frac{[AH]}{[A^-]}$$

Taking negative logarithm on both sides,

$$pH = pK_a + \log \frac{[A^-]}{[AH]}$$

pK_a is a characteristic of a particular compound, it tell how readily the compound gives up a proton. At pH above pKa, the acid HA exists as A^-; at pH below the pK_a, it exists as undissociated HA.

$$pH > pK_a \qquad\qquad pH < pK_a$$

$$pH - pK_a = +ve \qquad\qquad pH - pK_a = -ve$$

$$\Rightarrow \log \frac{[A^-]}{[AH]} = +ve \qquad\qquad \Rightarrow \log \frac{[A^-]}{[AH]} = -ve$$

$$\text{i.e. } [A^-] > [AH] \qquad\qquad \text{i.e. } [A^-] < [AH]$$

Factors affecting acid strength or pK_a values

1. Intrinsic stability of the conjugate base- Acid strength is determined by the stability of the conjugate base that is formed when the acid gives up its proton- the more stable the base, the stronger its conjugate acid. A stable base is one that readily bears the electrons it formerly shared with the proton which means it is less apt to share those electrons with a proton.

Stability can arise by having the negative charge on an electronegative atom or by spreading the charge over other groups.

(a) If we compare the acidity of CH_4, HF, H_2O and NH_3, **the order of relative acidity is: $CH_4 < NH_3 < H_2O < HF$**.

The elements, C, N, O and F are all about the same size, but they have different electronegativity, which increases across the row from left to right: C < N < O < F. The more electronegative atom is better able to bear its negative charge. So, stability of the conjugate bases follows the order: $CH_3^- < {}^-NH_2 < HO^- < F^-$.Therefore, the relative acidity follows the order $CH_4 < NH_3 < H_2O < HF$.

2. Bond strength of the acid- Greater the bond strength, the stronger the acid.

Weak A—H bond make stronger acid. (b) If we compare the acidity of HF, HCl, HI and HBr, **the order of relative acidity is: HF < HCl < HBr < HI**.

This is due to weakening bond strength on descending the group. When comparing the atoms, all are in different sizes. As the halide ion increases in size , its stability increases because its negative charge is spread over a larger volume of space. Therefore, HI is the strongest acid of the hydrogen halides.

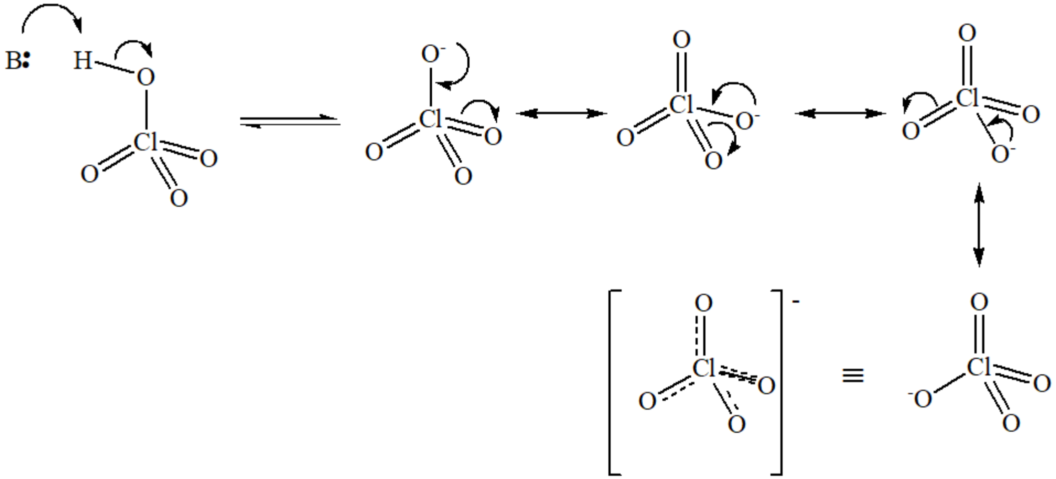
Moving across a row of the periodic table, the orbitals have approximately the same size so it is the electronegativity of the element that determines the stability of the base.

Moving down a column of the periodic table, the size of the orbitals increases, so electron density decreases. The less the electron density, the more stable the conjugate base, and the stronger the acid.

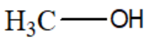
3. The solvent- The better the solvent is at stabilising the ions formed, the easier it is for the reaction to occur.

(c) The acidity order: $HClO_4$ > $HClO_3$ > $HClO_2$ > HClO

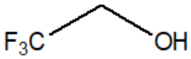
As one proton is removed , we end up with a negative charge on oxygen. For HClO, -ve charge is localised on one oxygen. With each successive oxygen, the charge can be delocalised and this makes the anion more stable.



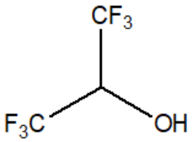
It is not necessary for a group to be conjugated in order to spread the negative charge. Any group that withdraw electron s will help stabilise the conjugate base and so increase the acid strength.



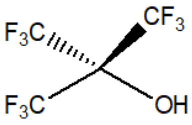
pK_a 15.5



pK_a 12.4



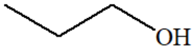
pK_a 9.3



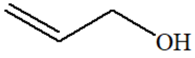
pK_a 5.4

(c) Hybridisation also affects the pK_a

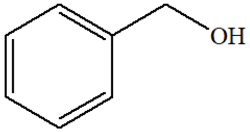
The hybridisation of the orbital from which electron is removed can also affect the pK_as. The more s character an orbital has, the more tightly it held onto its electrons. Hence the anions derived from these are increased in stability.



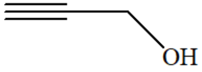
pK_a 16.1



pK_a 15.5



pK_a 15.4



pK_a 13.5

The more stabilised the conjugate base A^-, stronger is the acid. Ways to stabilise include:

✓ Having the charge on an electronegative element.

✓ Delocalising the –ve charge over other atoms.

✓ Spreading out the charge over electron withdrawing groups by polarisation of sigma bond.

✓ Having the –ve charge in an orbital with more s character.

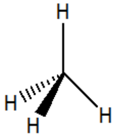
✓ Becoming aromatic.

The order of stability of conjugate bases-

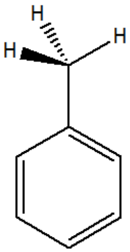
$CH_3CH_2O^- \quad < \quad CH_3COO^- \quad < \quad CH_3SO_3^-$

The order of acid strength-

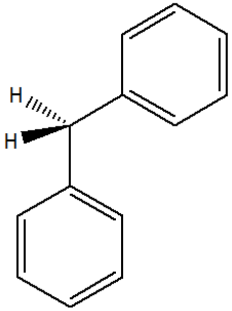
$CH_3CH_2OH \quad < \quad CH_3COOH \quad < \quad CH_3SO_3H$



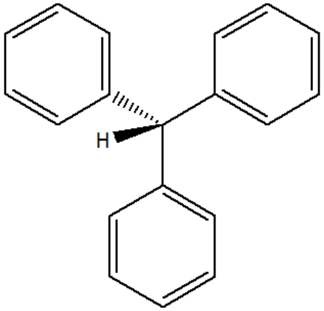
pK_a = 48



pK_a = 40



pK_a = 33



pK_a = 32

Factors affecting base strength

1. The more stable the base, the weaker it is.

2. The more available electrons are, the stronger it is. So, the –vely charged molecule is more basic compared to the neutral one.

3. A compound in which –ve charge is delocalised is less basic than the one with more concentrated and localised charge.

4. An important factor in determining the strength of a base is on which element the lone pair is on. The more electronegative the element the tighter it keeps hold of its electrons and so less available they are to accept a proton and weaker is the base.

5. Any substituent which increases the electron density on the atom will make the lone pair more available for protonation, thus increases the basicity. Conversely, any substituent that withdraws electron density from the donating atom makes it less basic.

6. The other factor which influences the basicity is the stabilisation of the resultant +ve charge formed on protonation. The resultant +ve charge can be stabilised by solvation. Each H attached to the donating atom will be H-bonded with solvent water and this helps to stabilise the charge.

Effects that decrease the electron density on the donating atom-

1. If the donating atom is attached to an electron withdrawing group.

2. The lone pair is on sp or sp^2 hybridised orbital.

3. The lone pair is conjugated with an electron withdrawing group.

4. The lone pair is involved in maintaining aromaticity of the molecule.