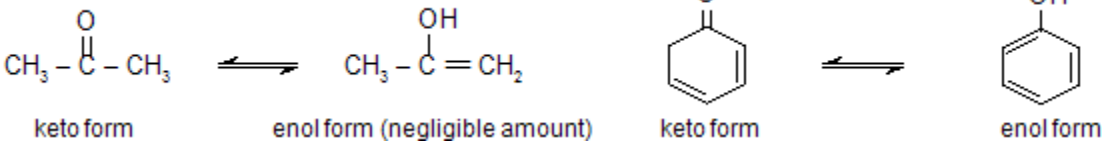
TAUTOMERISM

(v) Tautomerism

Tautomerism may be defined as the phenomenon in which a single compound exists in two readily interconvertible structures that differ markedly in the relative position of at least one atomic nucleus, generally hydrogen. The two different structures are known as tautomers of each other.

Sometimes the term tautomerism is also called as **desmotropism** (Greek *desmos*-bond; *tropos*-turn), since the interconversion of the two forms involves a change of bonds or **dynamic isomerism** as the two forms are in dynamic equilibrium with each other. Other names for tautomerism are kryptomerism, allelotropism or merotropy; however, tautomerism is the most widely accepted term.

There are several types of tautomerism of which *keto-enol tautomerism* is the most important. In this type, one form (tautomer) exists as a ketone while the other exists as an enol. The two simplest examples are of acetone and phenol.



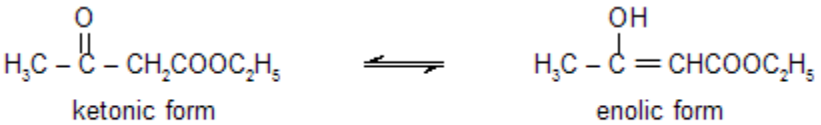
keto form — enol form (negligible amount) — keto form — enol form

However, the most widely studied example of keto-enol tautomerism is that of acetoacetic ester (ethyl acetoacetate).

keto form (92.3 %) — enol form (7.7 %)

The two forms are readily interconvertible by acid or base catalysts, and under ordinary conditions surface of the glass is sufficient to catalyse the interconversion. The exact composition of the equilibrium depends upon the nature of the compound, solvent, temperature, etc. *The conversion of a keto form into enol from is known as* **enolisation.** The two forms of acetoacetic ester have been isolated under suitable conditions.

Keto-enol tautomerism in acetoacetic ester is proved by the fact that under ordinary conditions the compound gives the properties of the ketonic group as well as that of the enolic group.



ketonic form — enolic form

(note the presence of a ketonic group) — (note the presence of a double bond and acidic –OH group)

Note that in *all the examples of keto-enol tautomerism the two isomeric forms are interconvertible by*

the migration of a proton from one atom (carbon) to the other with the simultaneous shifting of bonds

Distinction of tautomerism from resonance :

The tautomeric forms are quite chemically distinct entities and can be separated (in suitable cases e.g. acetoacetic ester) and characterised. On the other hand, resonating forms differ only in the distribution of electrons and can never be separated from one another since neither of them has any real existence. The important differences between resonance and tautomerism can be summarised as below.

1. Tautomerism involves a change in the position of atom (generally hydrogen), while resonance involves a change in the position of the unshared or
π electron
only.
2. Tautomers are definite compounds and may be separated and isolated. Resonating structures are only imaginary and can't be isolated.
3. The two tautomeric forms have different structures (i.e. functional groups). The various resonating structures have the same functional group.
4. Tautomers are in dynamic equilibrium with each other, resonating structures are not in dynamic equilibrium.
5. Tautomerism has no effect on bond length, while resonance affects the bond length (single bond is shortened while the double bond becomes longer).

6. Tautomerism does not lower the energy of the molecule and hence does not play any role in stabilising the molecule, while resonance decreases the energy and hence increases the stability of the molecule.

7. Tautomerism is indicated by ' $\rightleftharpoons$ ' while resonance by '$\longleftrightarrow$'.

8. Tautomerism can occur in planar as well as non-planar molecules, while resonance occurs only in planar molecules.