

# FACTORS AFFECTING BRONSTED-LOWRY ACIDITY - II

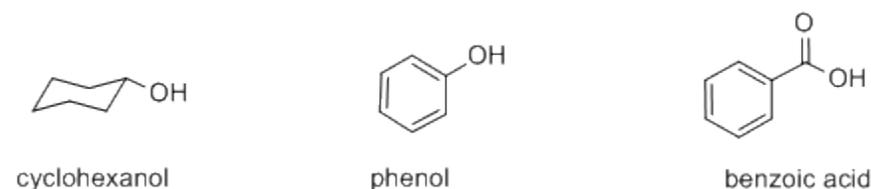
## DISTAL FACTORS :

Sometimes there are factors farther away from the proton that affect Bronsted acidity. In addition to considering the atom to which the proton is directly attached, we may need to consider other parts of the molecule to understand anion stability.

A first factor to consider is delocalization due to conjugation. In Lewis structure terms, that means resonance. Delocalization of charge is stabilizing, so if a negative charge can be distributed across multiple atoms via resonance, a conjugate base will be more stable.

- resonance can delocalize negative charge and stabilize an anion.
- a more stable conjugate base forms more easily. A Bronsted acid will give up a proton more easily if it gives rise to a stable conjugate base.

Many organic compounds contain hydroxyl or OH groups, some of which are acidic and some of which are not. Three kinds of compounds containing this group are alcohols, phenols and carboxylic acids. Examples of these functional groups include cyclohexanol, phenol and benzoic acid.



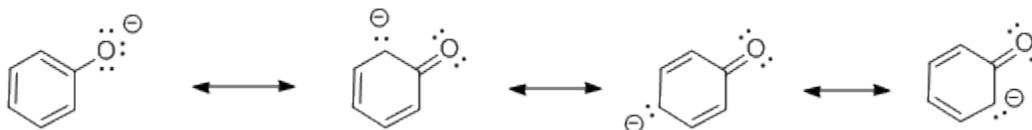
**Figure AB12.1.** Cyclohexanol, phenol and benzoic acid.

Cyclohexanol is an alcohol. An alcohol contains an OH group connected to a tetrahedral carbon.

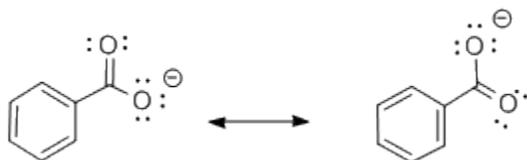
Phenol is slightly different; it contains an OH group connected to a trigonal planar carbon that is part of an aromatic ring. Aromatic rings are cyclic groups of atoms, usually carbons, with delocalized pi bonding all around the ring. Benzene is the most common example of an aromatic ring. It is a ring of six carbons and all of the carbons are trigonal planar. In the Lewis structure, it is drawn with alternating single and double bonds between the carbons.

Benzoic acid contains a very different functional group in which the OH is connected to a carbonyl. A carbonyl is a carbon-oxygen unit with a double bond, C=O. The carbon in a carbonyl is trigonal planar, as in a phenol, but the presence of the double bond to oxygen makes a big difference.

Cyclohexanol has a pKa of about 18. It is less acidic than water. It can give up a proton, but the proton is much more likely to be bound to the oxygen than dissociated. Phenol has a pKa of about 9 and is considered mildly acidic. Benzoic acid has a pKa of about 5; its acidity is similar to hydrofluoric acid, although not nearly as acidic as other hydrogen halides.



**Figure AB12.2.** The anion resulting from deprotonation of phenol.



**Figure AB12.3.** The anion resulting from deprotonation of benzoic acid.

Comparing the conjugate bases of cyclohexanol, phenol and benzoic acid reveals some differences.

- In cyclohexanol, the anion formed by loss of a proton is localized on the oxygen. There is no resonance stabilization.
- In phenol, the anion formed by loss of a proton is delocalized. Resonance structures show the negative charge can be shared between the oxygen atom and three of the carbons in the benzene ring.
- In benzoic acid, the anion is also delocalized. This time the negative charge is shared between two different oxygen atoms.

Resonance delocalization plays a clear role in stabilizing the conjugate base formed after loss of a proton. Despite the similar bond polarity in cyclohexanol and phenol, the proton is much more tightly bound in cyclohexanol. The greater stability of the

phenolate anion compared to the cyclohexanoxide anion makes it easier to remove a proton from phenol than cyclohexanol.

- The atoms onto which the charge is delocalized still plays a major role in determining stability. Delocalization onto an additional oxygen atom may be more stabilizing than delocalization onto several carbons.

Source : <http://employees.csbsju.edu/cschaller/Principles%20Chem/acidity/acid%20distal.htm>