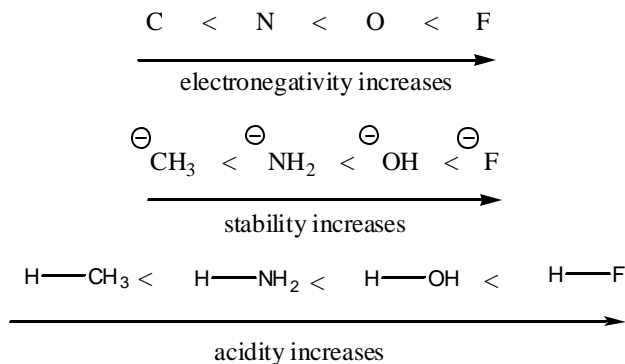


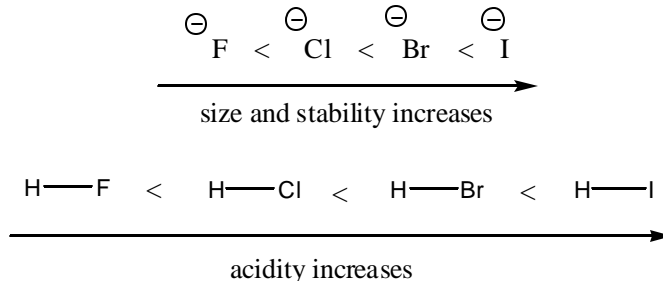
STRUCTURAL EFFECTS ON ACIDITY

THE UNDERLYING PRINCIPLE: THE DISSOCIATION OF AN ACID LEADS TO THE GENERATION OF THE CONJUGATE BASE, USUALLY NEGATIVELY CHARGED. ANY FACTOR LEADING TO THE STABILIZATION OF THE NEGATIVE CHARGE OF THE CONJUGATE BASE, WOULD FACILITATE DISSOCIATION, I.E. INCREASE THE ACID STRENGTH.

1. **Electronegativity:** The more electronegative an element is, the more easily does it bear a negative charge. From left to right in the periodic table electronegativity increases. The strength of the acid and stability of the conjugate base increase in the same direction.

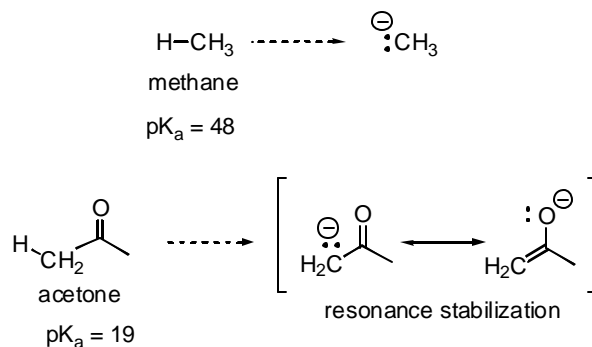


2. **Size of the anion:** The larger the anion, the more dispersed the negative charge, which leads to stabilization. Down the columns of the periodic table size increases. Acid strength and stability of the conjugate base increase in the same direction.

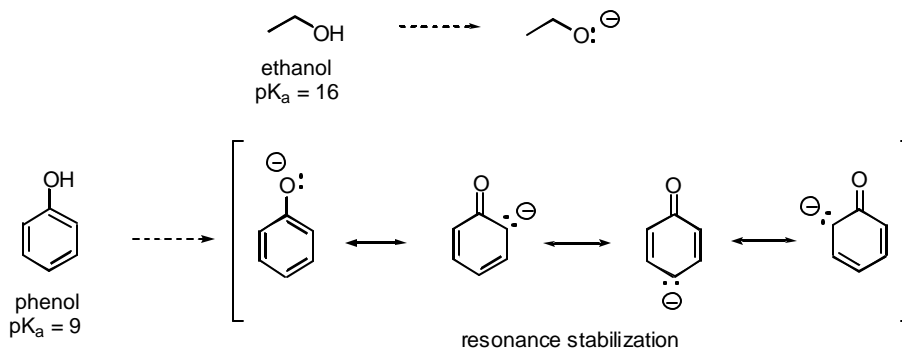


3. **Bond Strength** – the order of acidities in the hydrogen halide series can also be explained on the basis of the bond strength factor – the strength of the hydrogen – halogen bond decreases in direction from HF to HI. Thus it would be expected that the cleavage of this bond (i.e. dissociation) would be easiest for HI. HI would be expected to be the strongest acid of the four, as indeed it is.
4. **Resonance stabilization:** If the negative charge of the conjugate base can be distributed over a larger portion of the molecule (i.e. delocalized) via resonance, this leads to a significant stabilization of the conjugate base and thus to an increase of the acid strength.

Compare methane and acetone (in acetone one of the methane hydrogens is replaced by a CH₃CO-group):



Or compare ethanol and phenol:



5. **Hybridization:** Within the various modes of hybridization (sp^3 , sp^2 and sp) the percentage of s - and p -orbital participation varies. The percentage of s -orbital character is 50% for the sp -hybridization mode, 33% for the sp^2 hybridization mode and 25% for the sp^3 . Recall now, from the beginning of the course, the distribution of electron density in s -orbitals vs. p -orbitals. The density for s -orbitals is highest in the region closest to the nucleus, while for p -orbitals there is a node at the nucleus. The fact that the density of an s -orbital is highest at the nucleus would mean that there would be a much stronger electron-nucleus favorable interaction. This in its turn means that a negative charge in an s -orbital would be more stabilized than a negative charge in a p -orbital. Therefore, carbanions centered at sp -hybridized carbon atoms will be the most stable ones, followed by carbanions centered on sp^2 -hybridized carbons, followed by carbanions centered on sp^3 -hybridized carbons. But carbanions are the conjugate bases of hydrocarbons. Therefore, the corresponding hydrocarbons will follow the same order of acidity – the ones with triple bonds (sp -carbons) will be the most acidic, then sp^2 -carbons, finally sp^3 -carbons being the least acidic.

