



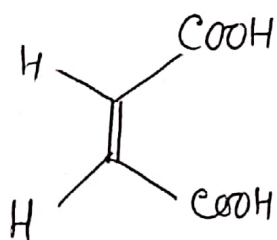
$$K_a = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

more the K_a value, more is the acidity.

Gain $pK_a = -\log K_a$

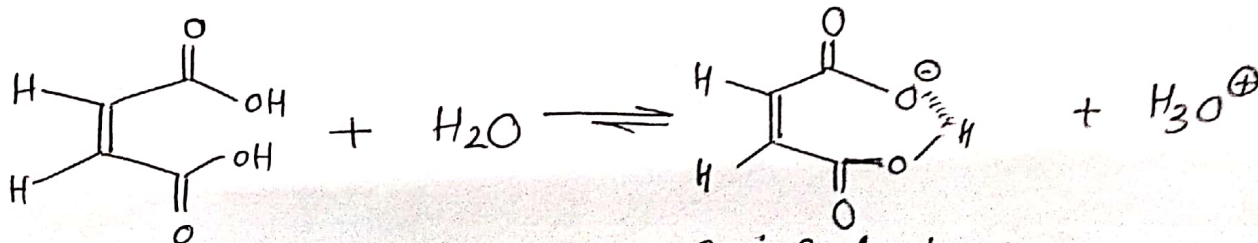
So, higher the pK_a value less is the acidity, lower the pK_a value higher is the acidity.

Acidity of dicarboxylic acid



The pK_{a1} or pK_1 value of this acid is lower than pK_{a2} or pK_2 value.

Consider the dissociation in H_2O .

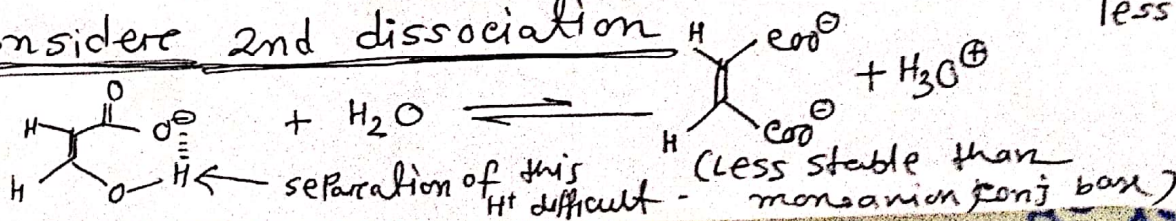


Conjugate base highly stabilised by intramolecular H-bond.

So, 1st dissociation of H^+ is much

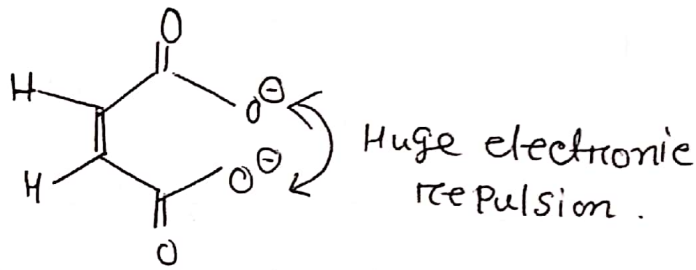
easy $\rightarrow K_1$ more (acidity more) $\rightarrow pK_1$ less.

consider 2nd dissociation



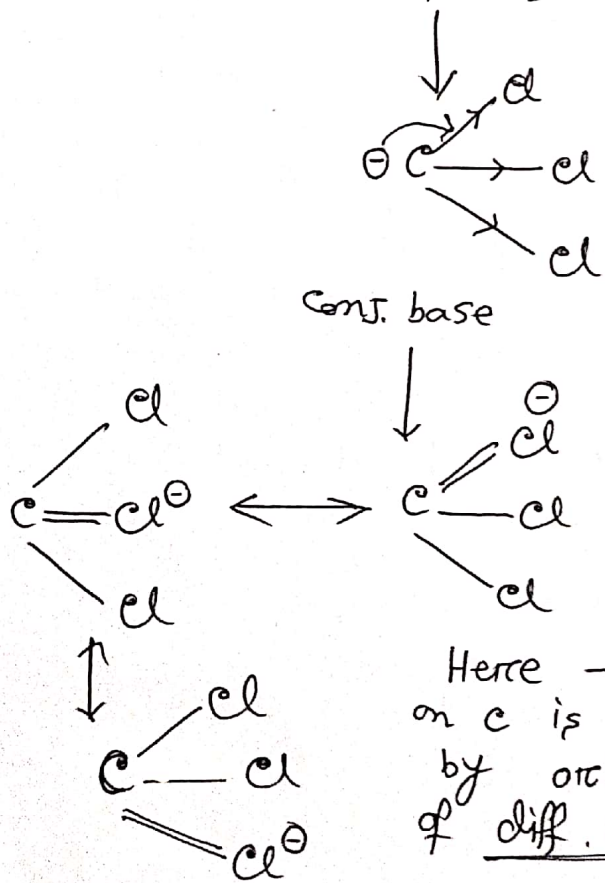
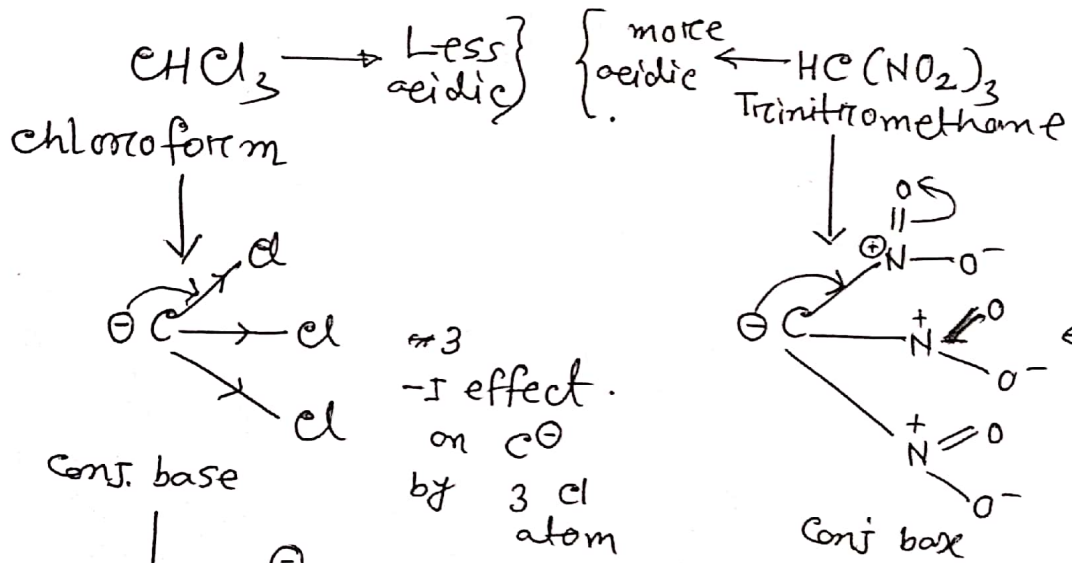
(Less stable than monoanion conj base)

So, 2nd H^+ can't be easily removed and the corresponding conjugate base will not be stabilised by H-bond rather it will be destabilised by the repulsion between two CO_2^- gr. (electronic repulsion) from the cis position.

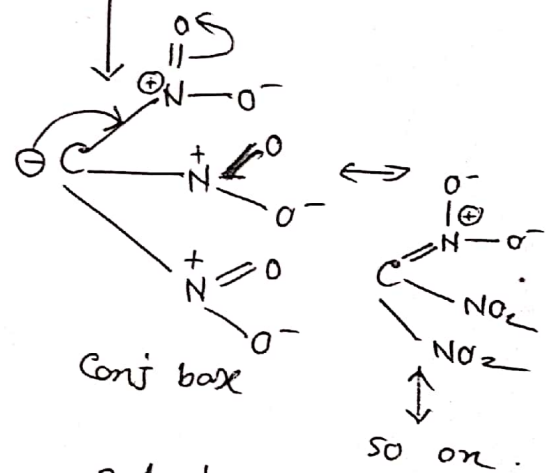


So, 2nd dissociation of H^+ will be less, K_2 will be less, pK_2 will be more (acidity will be less).

* Compare the acidity between $CHCl_3$ and $CH(NO_2)_3$.



Here $-ve$ charge on C is also stabilised by orbital overlap of diff. size ($2p-3d$).



But here conj base is stabilised both by $-I$, $-R$ effect of NO_2 gr.
 ↳ But here ($2p-2p$) same size/same type orbital overlap make it more stable