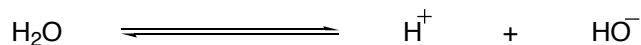
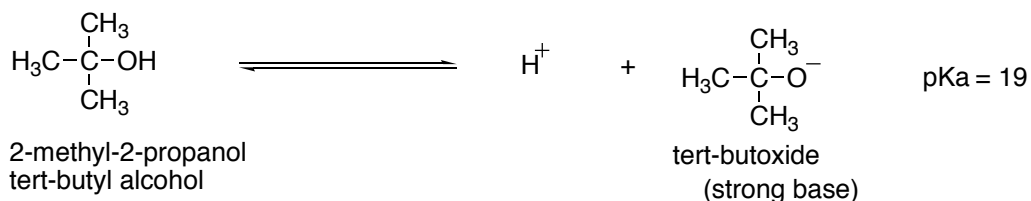
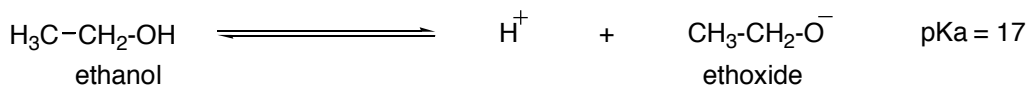
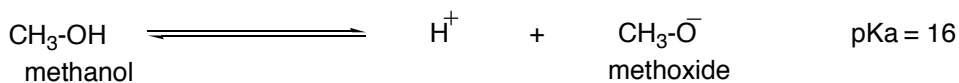


Acidity:

$$K_a = \frac{[\text{H}^+][\text{HO}^-]}{[\text{H}_2\text{O}]} = [\text{H}^+][\text{HO}^-] = 10^{-15.7}$$

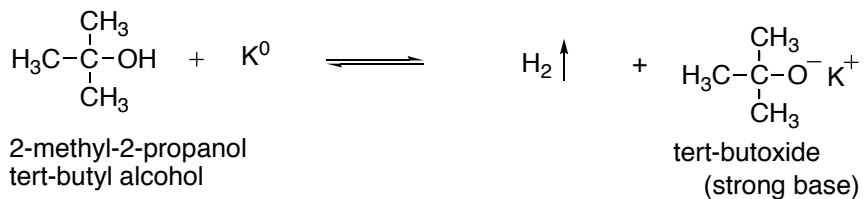
$$\text{p}K_a = -\log(K_a) \quad , \text{ for H}_2\text{O} , \text{p}K_a = 15.7$$

i) Acidity of simple alcohols:

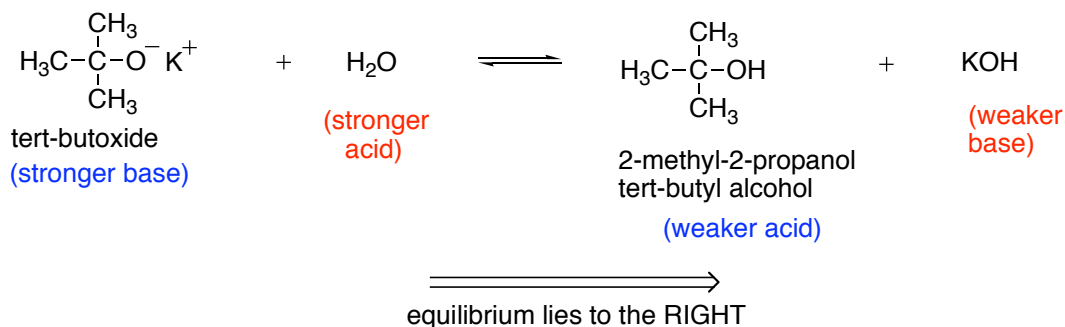


Due to inductive donating effect of alkyl groups that make anion less stable (corresponding alcohol less acidic)

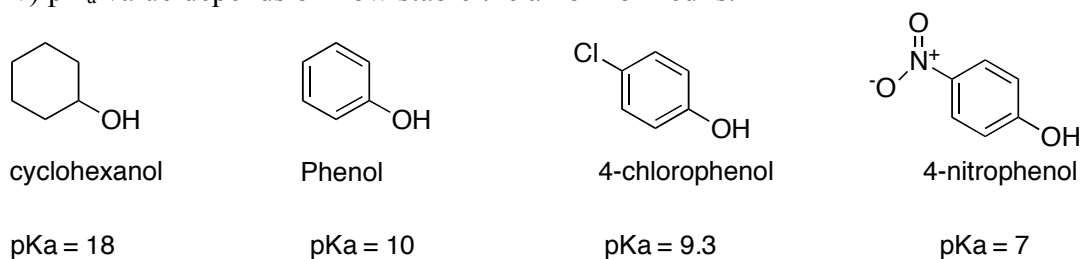
ii) Preparation of potassium tert-butoxide (equation not balanced):



iii) Acid-Base equilibrium:

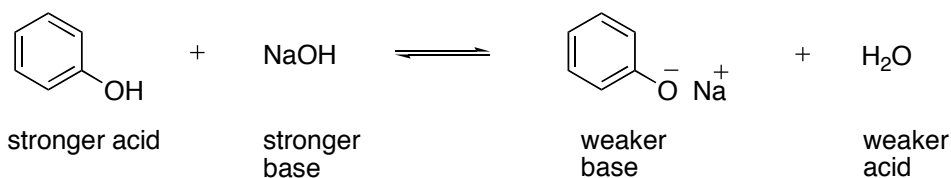


iv) pK_a value depends on how stable the anion formed is:

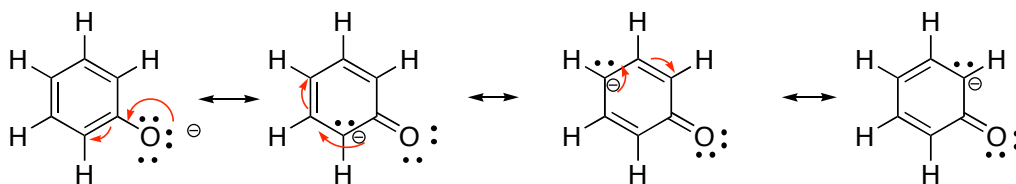


- Why phenol is more acidic?

- the anion formed (phenoxide) can be stabilized by conjugation onto benzene ring – resonance forms can be obtained
- the negative charge on the oxygen is delocalized

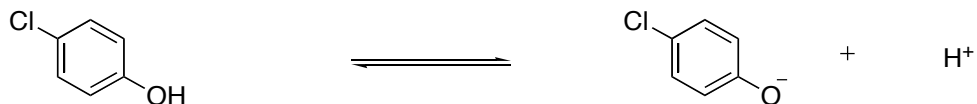


- resonance forms of phenoxide anion:



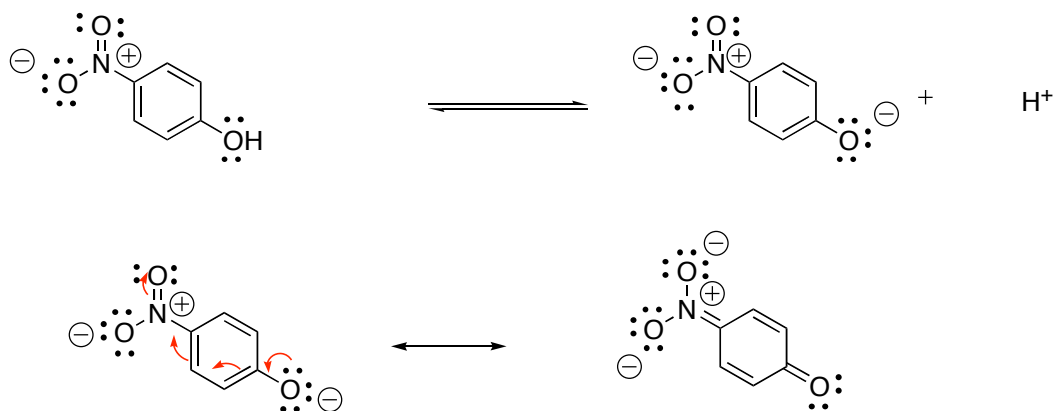
More examples:

1.



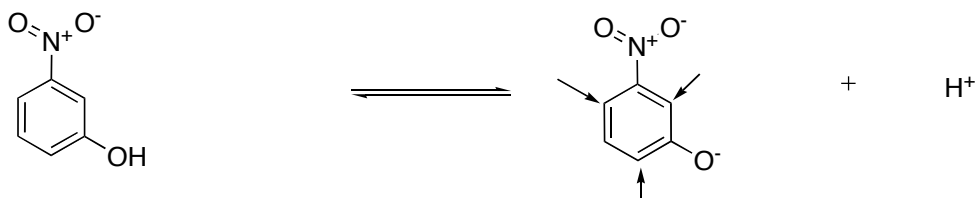
- Cl is electron withdrawing, so anion is stabilized, giving a lower pK_a value than phenol

2.



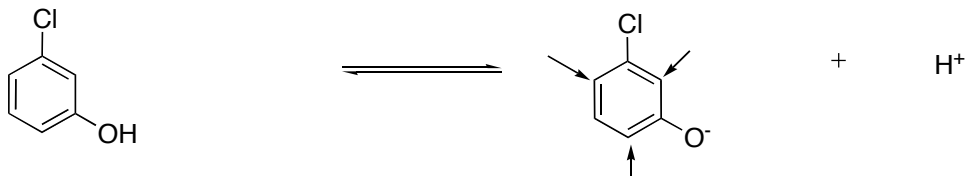
- an additional resonance form can be obtained with 4-nitrophenol (in comparison to phenoxide) which gives more stability to the anion formed

3.



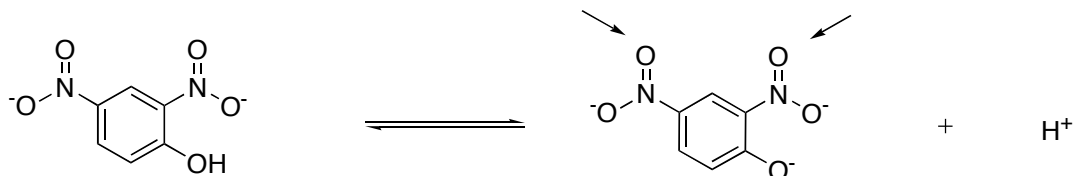
- the negative charge can only be placed on the positions shown by arrow, so that it is not possible to delocalize the negative charge onto the nitro group, thus $pK_a = 9.3$ instead of $pK_a = 7$ as for the 4-nitrophenol

4.

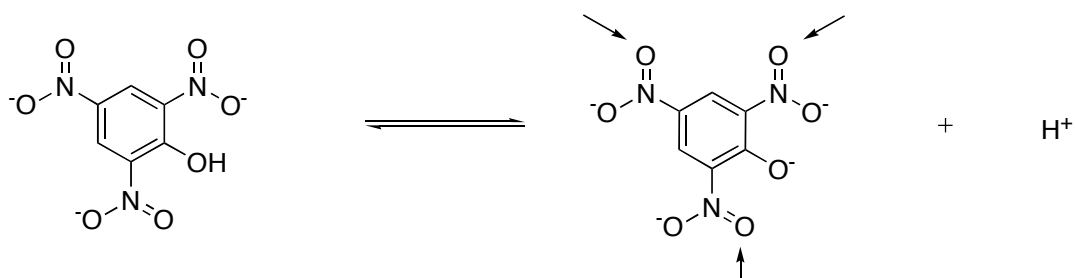


- negative charge cannot be stabilized by additional resonance into Cl, $pK_a = 9.3$

5.



2,4-dinitrophenol – negative charge can be placed on two additional conjugated oxygens (indicated by straight arrows) as in the 4-nitrophenol



2,4,6-trinitrophenol
(picric acid – explosive – match head)

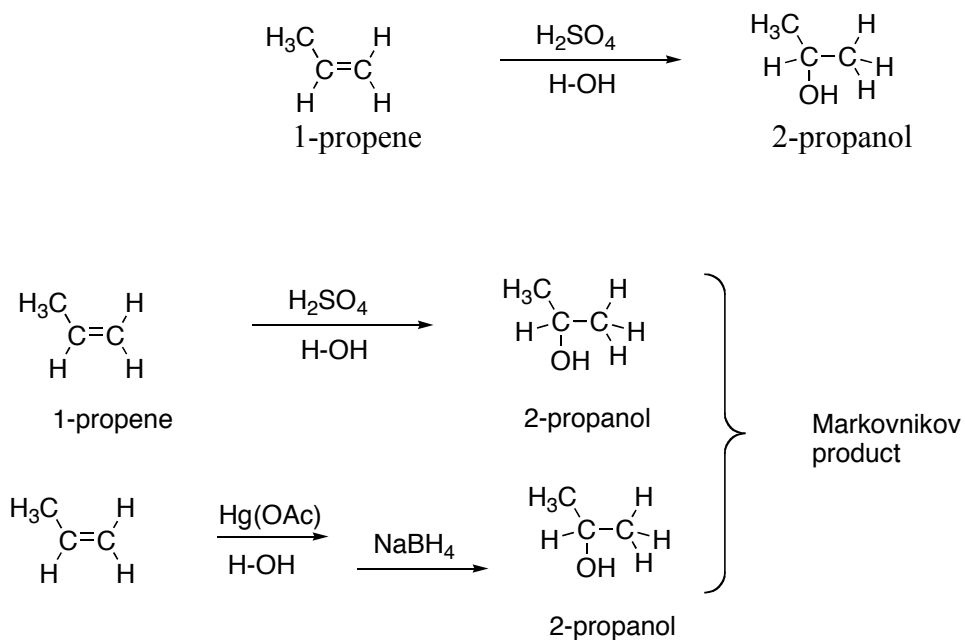
- in the above two cases, the negative charge can be delocalized onto the doubly bonded oxygen of the nitro groups.

- in the case of dinitrophenol – $pK_a = 4.5$ (approx.)

- in the case of trinitrophenol – $pK_a = 0.5$ (approx.)

Synthesis (Preparation) of Alcohols: (Review of reactions seen earlier)

i) From alkenes: Addition of water



Formal Anti-Markovnikov water addition – different reagents – seen earlier as Hydroboration of Alkenes followed by Oxidation

