OC2

Synthesis
–
Properties of Amines

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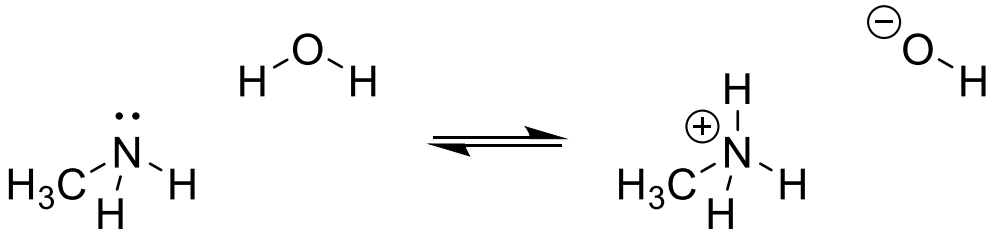
Basicity of Amines

All amines are **weak bases**

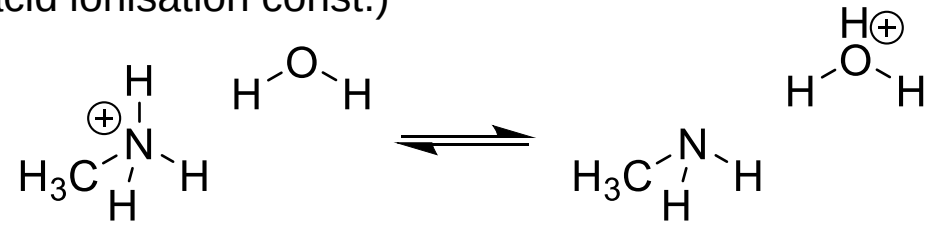
NH_3	$R-NH_2$	$R-\underset{R}{NH}$	$R-\underset{R}{\overset{R}{N}}$
ammonia	primary	secondary	tertiary
pK_a 33	pK_a 10.7	pK_a 11.0	pK_a 10.3

i.e. aqueous solutions of amines are basic



Tertiary amines are weakest bases because steric hindrance of 3 substituents hinders hydrogen bonding between nitrogen and water

It is common to discuss the basicity of amines by reference to the pK_a values of their **conjugate acid** (i.e. acid ionisation const.)



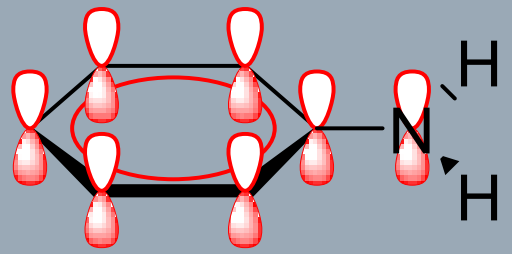
NOTE:
If the pK_a value of the conjugate acid is **low**, then the corresponding amine is a **poor base**.

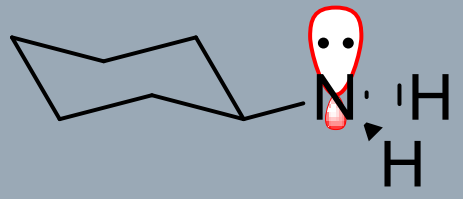
If the pK_a value of the conjugate acid is **high**, then the corresponding amine is a **good base**.

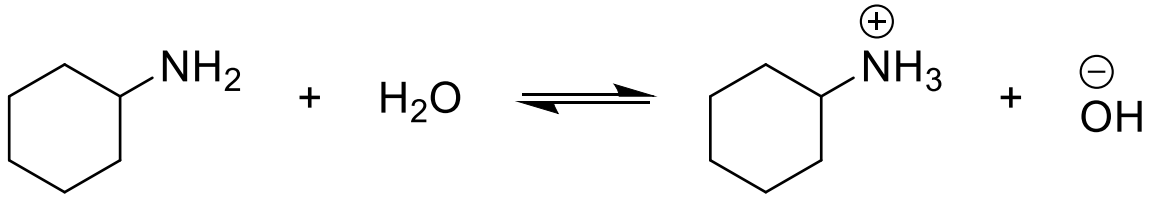
Basicity of Amines

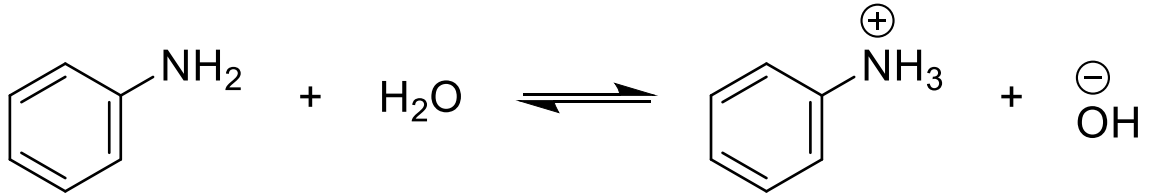
NOTE:
Aromatic amines are weaker bases than aliphatic amines

→ Breaking resonance stabilisation (by protonation) is energetically unfavourable!

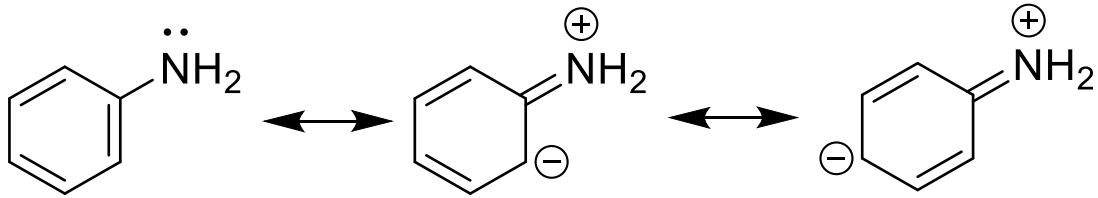








Consider delocalisation of the nitrogen lone pair:



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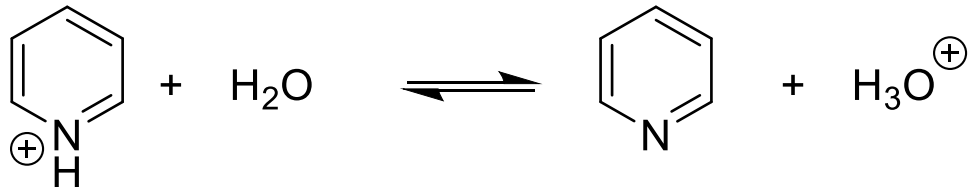
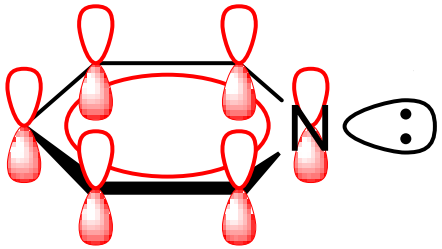
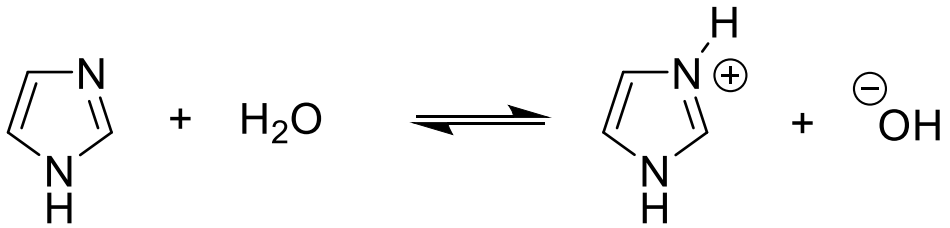


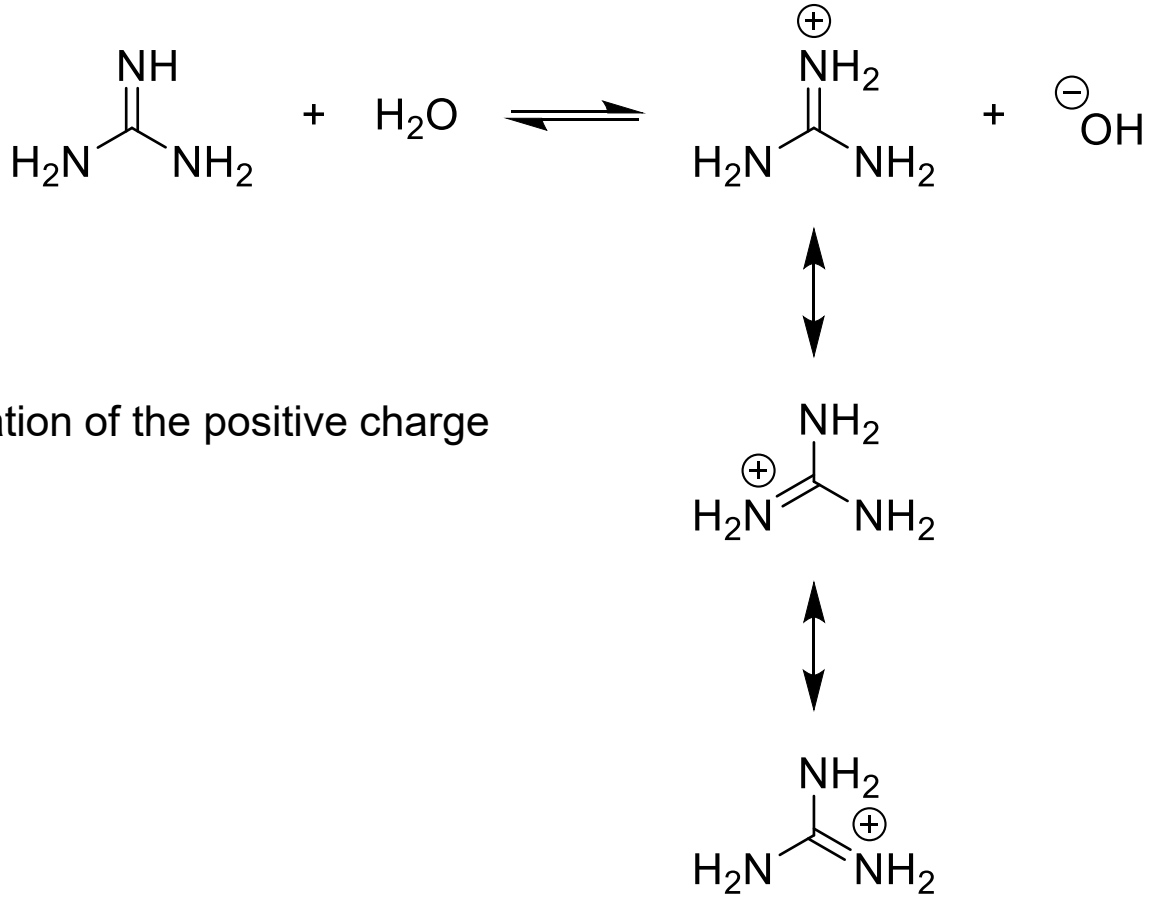


Which lone pair gets protonated in imidazole? → The one which is <u>not</u> part of the aromatic system!



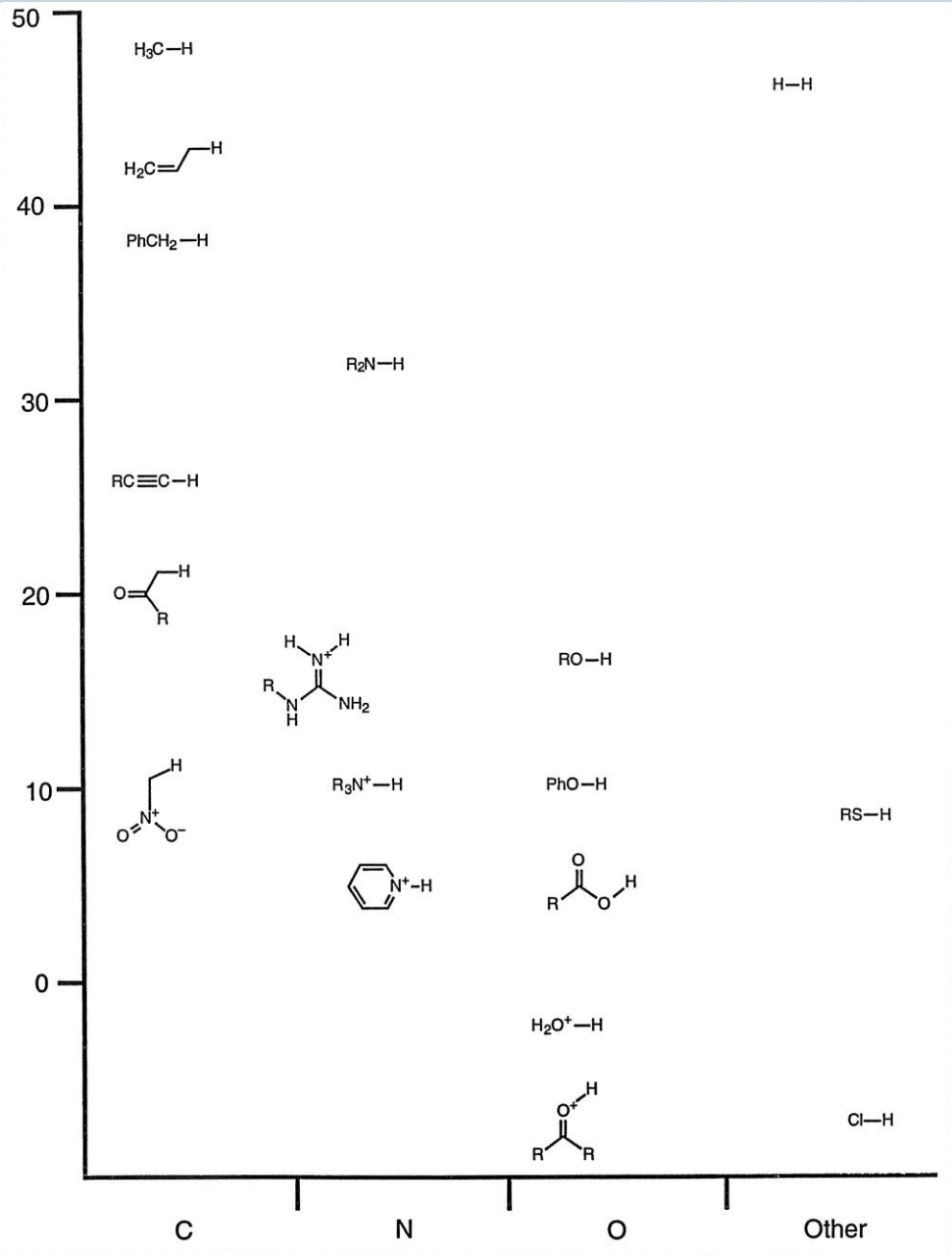
Basicity of Amines

Guanidine is the strongest base among neutral organic compounds…

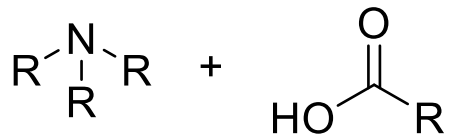


… chiefly because of the delocalisation of the positive charge (stable cation).

Summary of pKa Values in Solution



Can predict a good base for deprotonation:



What’s next?

Amine Synthesis

Academic Insights #4

When you try to arrange a meeting with your advisor