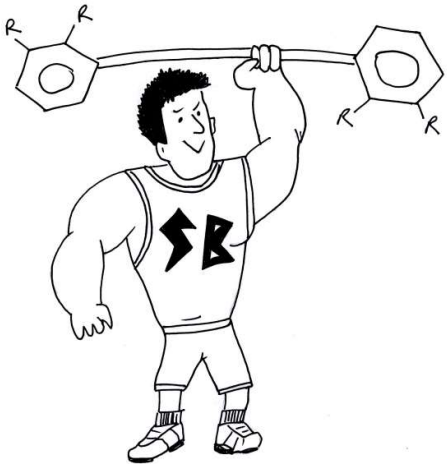
5. This question is about Superbases

The hydroxide ion is the strongest possible base in aqueous solution, but in organic solvents it is possible to have stronger bases.

For many years the strongest known base was the methyl anion, but in 2008 a team of scientists synthesised the lithium monoxide anion which was found to be an even stronger base.

2016 has seen the records rewritten again as Australian researchers announced the formation of an organic gas-phase dianion (DEB^{2-}) which has the highest proton affinity ever reported, i.e. is the strongest base.



How strong a base is may be defined by its proton affinity. The proton affinity of species X^-, $PA(X^-)$, is given by the standard enthalpy change of the reaction:

$$HX \longrightarrow H^+ + X^-.$$

(a) Using the data in the table below, calculate the proton affinity of the methyl anion, $PA(CH_3^-)$, in kJ mol^{-1}.

Reaction 1	$CH_4 \longrightarrow H^\bullet + CH_3^\bullet$	439 kJ mol^{-1}
Reaction 2	$H^\bullet \longrightarrow H^+ + e^-$	2.18×10^{-18} J
Reaction 3	$CH_3^\bullet + e^- \longrightarrow CH_3^-$	–7.52 kJ mol^{-1}

With a proton affinity of 1778 kJ mol^{-1}, the lithium monoxide anion was found to be a stronger base than the methyl anion. The lithium monoxide anion is formed in a mass spectrometer when a lithium oxalate anion, $LiC_2O_4^-$, firstly loses a neutral molecule **P** of mass 44 and subsequently another neutral molecule **Q** of mass 28.

(b) Draw the structure of the oxalate anion ($C_2O_4^{2-}$) and give the formulae for **P** and **Q**.

The organic gas-phase dianion (DEB^{2-}) has the highest proton affinity ever reported of 1843 kJ mol^{-1}. This dianion is produced from compound **A** which belongs to a family of disubstituted benzenes, $C_6H_4R_2$, where both substituents R are the same. Compound **A** has the molecular formula $C_{12}H_6O_4$ and effervesces on addition of sodium hydrogen carbonate.

(c) Suggest the functional group present in R responsible for the effervescence, and hence deduce a structure for R.

(d) Draw all of the possible disubstituted benzenes, $C_6H_4R_2$, and state the number of signals you would expect in the ^{13}C NMR for each.

DEB^{2-} was observed in the negative-ion mass spectrum of Compound **A**. It is formed via species $\mathbf{B^{2-}}$ and $\mathbf{C^{2-}}$. Compound **A** is found to have 6 signals in its ^{13}C NMR spectrum.

Compound **A**		$\mathbf{B^{2-}}$		$\mathbf{C^{2-}}$		$\mathbf{DEB^{2-}}$
$C_{12}H_6O_4$		$m/z = 106$		$m/z = 84$		$m/z = 62$

(e) Determine the structures of intermediates $\mathbf{B^{2-}}$ and $\mathbf{C^{2-}}$, and DEB^{2-}.