Ex 41A - Nucleophiles/Leaving groups

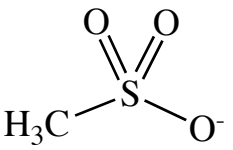
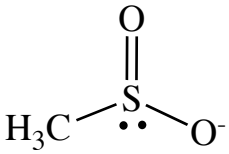
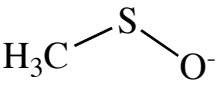
Principles to remember: Basicity correlates directly with basicity for atoms in the same row of the periodic table with the same charge. In the same column, bigger is more nucleophilic. Good leaving groups make poor nucleophiles, and vice versa, except for Br^- and I^- which are good at both.

Question One

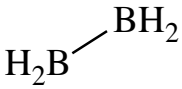
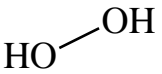
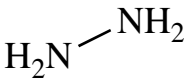
Rank the following in order of increasing nucleophilicity.

PH_3 $\ominus PH_2$ Anion always more basic than its conjugate acid.

Ph_2NH Ph_2PH Ph_2AsH By size, and size matters here.

The negative charge is shared by 3, 2 and 1 O atom respectively, so we would expect them to be ranked in this order by increasing basicity.

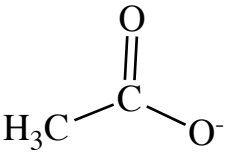
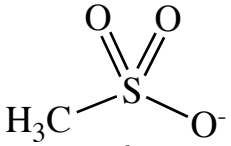
B has no lone pair, indeed is an electrophile, not a nucleophile. Hydrazine is more nucleophilic than hydrogen peroxide because N is less electronegative, more basic.

H_2O NH_3 PH_3

P more nucleophilic than N by size; N more nucleophilic than O due to its lower electronegativity and therefore greater basicity.

Question Two

Rank the following in order of increasing leaving groupness. I.e. worst to best leaving groups.

	HO^-		H_2O	
By basicity				
pKa of conj.:	15.6	5	-2	-6

Rank the following in order of increasing leaving groupness. I.e. worst to best leaving groups.

	$:CH_3^-$	$:H^-$	HO^-	Cl^-
By basicity				
pKa of conj.:	50	35	15.6	-6