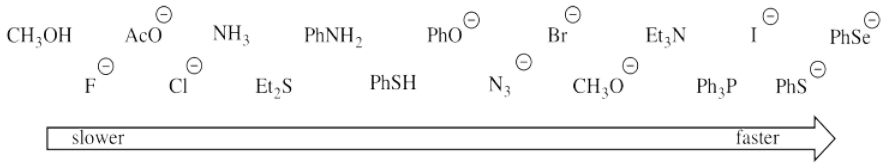
4.8: Nucleophilicity

The nucleophile can sometimes play a pronounced role in nucleophilic substitutions. The following relative rates have been observed when these nucleophiles reacted with methyl bromide in methanol:



note: Ph = phenyl, C_6H_5; Ac = acetyl, $CH_3C{=}O$; Et = ethyl, CH_3CH_2.

Presumably, some of the species react much more quickly with methyl bromide because they are better nucleophiles than others.

Exercise 4.8.1

Sometimes we can draw general conclusions about kinetic factors by looking at sub-groups among the data. Determine how the following factors influence nucleophilicity (the ability of a species to act as a nucleophile). Support your ideas with groups of examples from the data (preferably more than just a pair of entries).

a. charge on the nuclophile
b. size of the atom bearing the charge
c. electronegativity of the atom bearing the charge
d. delocalization of charge

Exercise 4.8.2

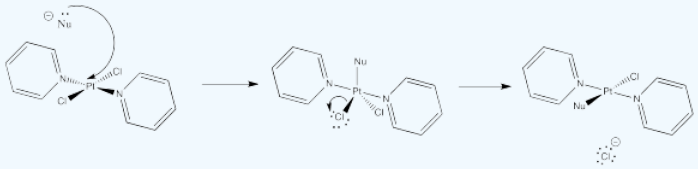
Nucleophilicity plays a strong role in the rate of one type of substitution mechanism, but not the other.

a. In which mechanism is it important? Support your idea.
b. Is the reaction of methyl bromide likely to proceed via this mechanism? Why or why not?

Exercise 4.8.3

A trend very similar to the data above is found in substitution reactions of py_2PtCl_2 (py = pyridine) in methanol. Draw a mechanism for this substitution and explain why nucleophilicity plays an important role.

Answer



Exercise 4.8.4

Very fast nucleophiles are sometimes more likely to undergo S_N2 reactions than S_N1 reactions. Explain why.