Example question: Nucleophilic reactions

Following concentrations for anionic constituents are determined for a water sample with a pH value of 7.0 at 25℃.

Constituents	Ionic weight	Concentration (mg/L)
NO_3^-	62.0	27.2
SO_4^{2-}	96.1	76.5
Cl^-	35.5	204.7
OH^-	17.0	can be derived from pH

The $n_{Nu,\,CH_3Br}$ values for the anions are shown below:

Anionic nucleophiles	$n_{Nu,\,CH_3Br}$
NO_3^-	1.0
SO_4^{2-}	2.5
Cl^-	3.0
OH^-	4.2

i) Determine the $[Nu]_{50\%}$ values for the anionic nucleophiles assuming s=1. Considering the $[Nu]_{50\%}$ values and the nucleophile concentrations, list nucleophiles that are significant for reaction with CH_3Br in the water. If the reaction rate for a nucleophile is more than 5% of the hydrolysis rate, determine the nucleophile as significant.

Answer)

Firstly, calculate the molar concentration of the nucleophiles:

Nucleophile	*Ionic weight*	*Concentration (mg/L)*	*Concentration (M)*
NO_3^-	*62.0*	27.2	4.39×10^{-4}
SO_4^{2-}	*96.1*	76.5	7.96×10^{-4}
Cl^-	*35.5*	204.7	5.77×10^{-3}
OH^-			10^{-6}

$$[Nu]_{50\%} = 55.3 \times 10^{-n_{Nu,\,CH_3Br}}$$

Nucleophile	n_{Nu,CH_3Br}	$[Nu]_{50\%}$ (M)	[Nu] (M)	$[Nu]/[Nu]_{50\%}$
NO_3^-	1.0	5.53	4.39×10^{-4}	7.94×10^{-5}
SO_4^{2-}	2.5	0.175	7.96×10^{-4}	4.55×10^{-3}
Cl^-	3.0	0.0553	5.77×10^{-3}	0.104
OH^-	4.2	3.49×10^{-3}	10^{-6}	2.87×10^{-4}

Concentration of all anions are smaller than $[Nu]_{50\%}$. Therefore, water is the most significant nucleophile.

As $k_{Nu}[Nu]_{50\%} = k_{H_2O}[H_2O]$

and

$k_{obs,Nu} = k_{Nu}[Nu]$ *($k_{obs,Nu}$: pseudo-first order rate constant for Nu; Nu concentrations are all way higher than $[CH_3Br]$ provided)*

$$\frac{k_{obs,Nu}}{k_{obs,H_2O}} = \frac{k_{Nu}[Nu]}{k_{Nu}[Nu]_{50\%}} = \frac{[Nu]}{[Nu]_{50\%}}$$

Therefore, H_2O and those with $[Nu]/[Nu]_{50\%}>0.05$ are significant nucleophiles.

Significant: H_2O and Cl^-

Insignificant: NO_3^-, SO_4^{2-}, OH^-

ii) If 10^{-5} M of CH_3Br is added to the water sample, what will be the concentration of the products of nucleophilic substitution (including hydrolysis) after all the reactions occur completely? Consider only significant nucleophiles.

Answer)

This is "reactions in parallel" problem.

CH_3Cl production by Cl^- nucleophilic attack and CH_3OH production by hydrolysis are significant reactions.

Because for parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$ (k_1, k_2 = 1st order rate constants)

$$\frac{d[A]}{dt} = -(k_1 + k_2)[A]$$

and

$$\frac{d[B]}{dt} = k_1[A], \quad \frac{d[C]}{dt} = k_2[A]$$

The product [B] and [C] after termination of the reaction will have the concentration ratio of k_1/k_2.

So:

$$[CH_3OH]_{final} = [CH_3Br]_{initial} \times \frac{k_{obs,H_2O}}{k_{obs,H_2O} + k_{obs,Cl^-}} = [CH_3Br]_{initial} \times \frac{1}{1 + [Nu]/[Nu]_{50\%}}$$

$$= 10^{-5}\,M \times \frac{1}{1 + 0.104} = 9.06 \times 10^{-6}\,M$$

and

$$[CH_3Cl]_{final} = [CH_3Br]_{initial} \times \frac{k_{obs,Cl^-}}{k_{obs,H_2O} + k_{obs,Cl^-}} = [CH_3Br]_{initial} \times \frac{[Nu]/[Nu]_{50\%}}{1 + [Nu]/[Nu]_{50\%}}$$

$$= 10^{-5}\,M \times \frac{0.104}{1 + 0.104} = 9.4 \times 10^{-7}\,M$$