The role of temperature dependence of ion-ion reactions in determining the mechanism

Reaction: $A + B \rightleftharpoons AB^{\ddagger} \rightarrow$ products

Based on the relations $\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P$ and $\Delta G_{e.s.} = \frac{N z_A z_B e^2}{4\pi\varepsilon_o\varepsilon_r r_{\ddagger}}$, we have

$$\Delta S^{\ddagger}_{\text{e.s.}} = \frac{N z_A z_B e^2}{4\pi\varepsilon_o\varepsilon_r^2 r_{\ddagger}}\left(\frac{\partial\varepsilon_r}{\partial T}\right)_P = \frac{N z_A z_B e^2}{4\pi\varepsilon_o\varepsilon_r r_{\ddagger}}\left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_P$$

With $N = 6.022 \times 10^{-23}$ mol^{-1}, $e = 1.602 \times 10^{-19}$ C and $\varepsilon_o = 8.854 \times 10^{-12}$ F/m (or C/(Vm)), using typical data in a solvent of water: $\varepsilon_o \approx 80$, $r_{\ddagger} = 200$ pm and $\left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_P \approx -0.0046\ \text{K}^{-1}$, we get

$$\Delta S^{\ddagger}_{\text{e.s.}} \approx -40 z_A z_B \frac{\text{J}}{\text{mol K}}$$

As the pre-exponential factor in the Arrhenius equation is $A = \frac{k_B T}{h} e^{\frac{\Delta S^{\ddagger}}{R}}$, we get

$$\Delta S^{\ddagger}_{\text{e.s.}} \approx -4.8\ z_A z_B$$

Thus

$$e^{-4.8\, z_A z_B} = 10^{-\frac{4.8}{\ln 10} z_A z_B} \approx 10^{-2\, z_A z_B}$$

It means that 1 unit increase in the product $z_A z_B$ is equivalent to a 100-fold decrease in A.

Let us suppose $\Delta S^{\ddagger}_{\text{neutral}} = 0$, and $A_{\text{neutral}} = 10^{13}$ dm^3/(mol s), then we have the following data:

(Left: calculated, right: experimental.)

z_A	z_B	A dm^3/(mol s)	$\Delta S^{\ddagger}$ J / (mol K)	$A_{\text{experimental}}$ dm^3/(mol s)	$\Delta S^{\ddagger}_{\text{experimental}}$ dm^3/(mol s)	Reaction
+3	–1	10^{19}	120	~10^{19}	~120	$Cr(H_2O)_6^{3+} + CNS^-$
+2	–1	10^{17}	80	5×10^{19}	92	$Co(NH_3)_5Br^{2+} + OH^-$
0	–2	10^{13}	0	1×10^{14}	25	$Cr(H_2O)_6^{3+} + CNS^-$
–1	–1	10^{11}	–40	6×10^{10}	–45	$CH_2BrCOOCH_3 + S_2O_3^{2-}$
–1	–1	10^{11}	–40	9×10^{8}	–71	$ClO^- + ClO^{2-}$
–1	–2	10^{9}	–80	1×10^{9}	–80	$CH_2BrCOO^- + S_2O_3^{2-}$
+2	+2	10^{5}	–160	1×10^{8}	–100	$Co(NH_3)_5Br^{2+} + Hg^{2+}$
–2	–2	10^{5}	–160	2×10^{4}	–170	$S_2O_4^{2-} + S_2O_4^{2-}$
–2	–2	10^{5}	–160	2×10^{6}	–130	$S_2O_3^{2-} + S_2O_3^{2-}$

As it can be seen, experimental determination of the pre-exponential factor can be used to check the reaction mechanism.