Outline of the solution to Problem 5: A race to racemize

10 marks

5 September, 2020

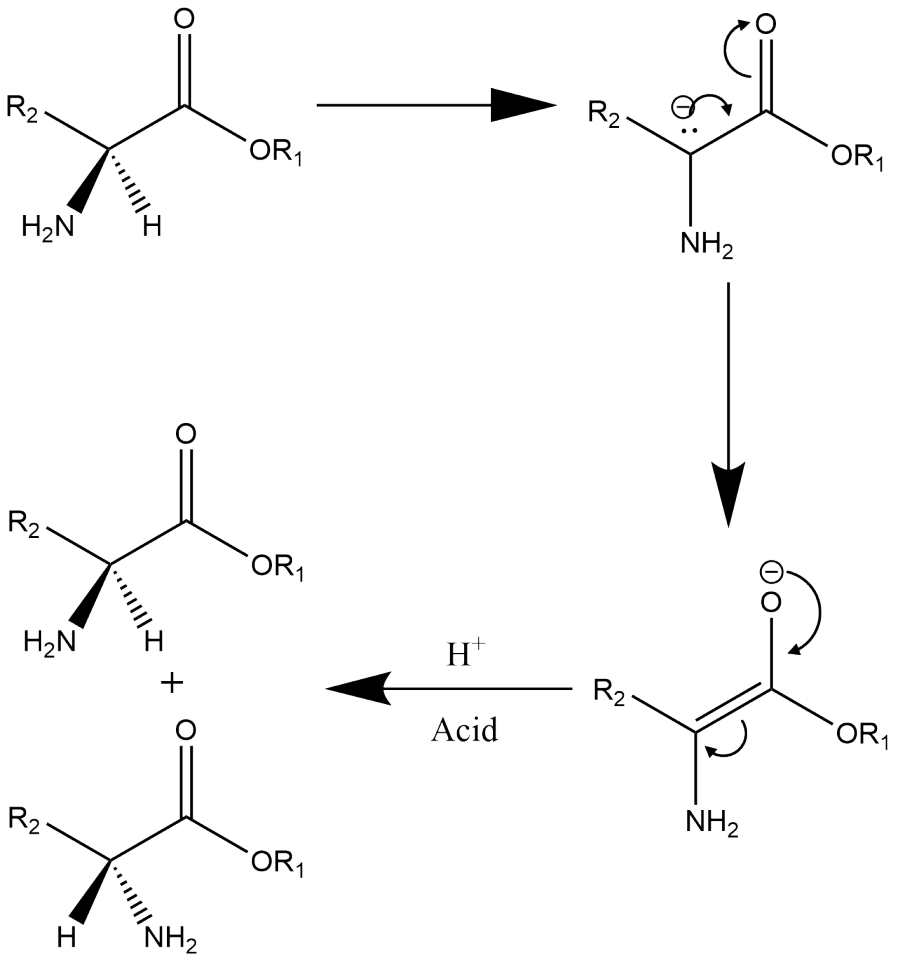

Figure 1: Mechanism for racemization reaction

1. i Serine has electron withdrawing -OH group which stabilizes the carbanion transition state

   ii When unsubstituted, the -COOH moiety loses the proton and has more cross conjugation. The substitution of the carboxylate moiety decreases cross conjugation and thus the carbanion transition state is stabilized.

2. L $\rightleftharpoons$ D

   Rate constant for forward reaction $k_1 = 5.1 \times 10^3$

   Rate constant for forward reaction k_2

   $\frac{D}{L} = \gamma_0$ before boiling, γ_b after boiling, γ_{hK} after hydrolyzing the king, γ_{hQ} after hydrolyzing the queen. Then,

$$\begin{aligned} ln(\frac{1+\gamma_{hK}}{1-\gamma_{hK}}) &= ln(\frac{1+\gamma_{hQ}}{1-\gamma_{hQ}}) + 2k_1 t_{boil} \\ &= ln(\frac{1+\gamma_{hQ}}{1-\gamma_{hQ}}) + ln(\frac{1+\gamma_b}{1-\gamma_b}) \end{aligned}$$

$$\therefore ln(\frac{1+\gamma_b}{1-\gamma_b}) = 2 \times 5.1 \times 10^3 \times t_{boil} \tag{1}$$

3. L $\rightleftharpoons$ D

   $k_{conv} = 1.38$

   Rate constant for forward reaction $k_1 = 9.02 \times 10^{-5}$

   $\therefore$ Rate constant for forward reaction $k_2 = 6.536 \times 10^{-5}$

   $x_0 = [L]_0 - [L]_{eq} = 1 - [L]_{eq}$

   After boiling, $x_t = [L]_t - [L]_{eq} = x_0 e^{-(k_1+k_2)t}$

   At equillibrium, $\frac{[D]_{eq}}{[L]_{eq}} = \frac{[L]_0 - [L]_{eq}}{[L]_{eq}} = k_{conv} = 1.38$

   $\Rightarrow L_{eq} = 0.42$

   $x = x_0 e^{-(k_1+k_2)t} = 0.429$

   $d_e = 69.8\%$

4. $\frac{L_0}{L_t} = k_1 t; [L]_t = [L]_0 + [D]_t$

   d_e before boiling $= 100\%$

   d_e after boiling $= 67.8\%$