3.5: Solutions to Selected Problems

KP5. Solutions to Selected Problems

Problem KP1.1.

Two C-C σ bonds and one new π bond are made. Three old π bonds are lost.

ΔH = bonds broken - bonds made

ΔH = (3 x 64) - ((2 x 83) + 64) kcal/mol

ΔH = -38 kcal/mol

Problem KP1.2.

$T_c = \Delta H / (\Delta S + R\log[M])$

$T_c = - 7{,}000 \text{ cal mol}^{-1} (-8.6 \text{ cal K}^{-1} \text{ mol}^{-1} + 1.98 \text{ cal K}^{-1} \text{ mol}^{-1} \log(8.7))$

$T_c = - 7{,}000 (-8.6 + 1.98 (0.939))$ K

$T_c = - 7{,}000 (-6.74)$ K

$T_c = 1038$ K = 765 °C

Problem KP1.3.

For each amide bond, a C-N bond and a H-Cl bond are made. A C-Cl and a N-H bond are lost.

ΔH = bonds broken - bonds made

= (C-Cl + N-H) - (C-N + H-Cl)

ΔH = (81 + 93) - (73 + 102) kcal/mol

ΔH = -1 kcal/mol

Problem KP2.1.

75% conversion means 0.75 in terms of fractions.

DP = 1 / (1 - p)

DP = 1 / (1 - 0.75)

DP = 1 / 0.25

DP = 4

Problem KP2.2.

slope = $2 [M]_0 k = 0.717 \text{ s}^{-1}$

$k = 0.717 \text{ s}^{-1} / (2 \text{ x } 17 \text{ mol L}^{-1})$

$k = 0.021 \text{ L mol}^{-1}\text{s}^{-1}$

Problem KP2.3.

$M_n = M_0 / (1 - p)$

= 120 g/mol / (1 - 0.99)

= 120 g/mol / 0.01

= 12,000 g/mol

$M_w = M_0(1 + p) / (1 - p)$

= 120 g/mol (1 + 0.99) / (1 - 0.99)

= 120 g/mol (1.99) / 0.01

= 23,800 g/mol

$D = 1 + p$

$= 1 + 0.99$

$= 1.99$

Problem KP3.1.

Rate = k' [M][I]$^{1/2}$

slope = k' [I]$^{1/2}$

0.0024136 s = k' (0.00025)$^{1/2}$

k' = 0.015 s^{-1}

Problem KP3.2.

At steady state:

$\text{Rate}_{\text{init}} = \text{Rate}_{\text{term}}$

k_i [M][I] = k_t[M$^+$]

Rearranging:

[M$^+$] = (k_i/k_t) [M][I]

Problem KP3.3.

$\text{Rate}_{\text{prop}}$ = k_p [M$^+$][M]

Substituting the steady state expression for [M$^+$]:

Rate = ($k_i k_p$/k_t) [M]^2[I]

Problem KP3.4.

$\bar{v} = \text{Rate}_{\text{prop}}/\text{Rate}_{\text{init}}$

$\bar{v}$ = k_p [M$^+$][M] / k_i [M][I] = (k_p / k_i)[M$^+$] / [I]

but [M$^+$] is not a known quantity. Alternatively, at steady state, $\text{Rate}_{\text{init}} = \text{Rate}_{\text{term}}$

$\bar{v} = \text{Rate}_{\text{prop}}/\text{Rate}_{\text{term}}$

$\bar{v}$ = k_p [M$^+$][M] / k_t [M$^+$] = (k_p / k_t)[M]

Problem KP3.5.

a) $\bar{v}$ = [M]$_0$/[I]$_0$ = 4.5 / 1.25 x 10^{-3} = 3,400

b) $\bar{v}$ = (k_p/2f k_t k_d)([M]/[I]$^{1/2}$)

$\bar{v}$ = (0.003 / 2(0.5)(0.003)(0.0001))(4.5/(1.25 x 10^{-3})$^{1/2}$) = (1/0.0001)(4.5/0.035) = 128/0.0001 = 1,280,000

c) $\bar{v}$ = (k_p/2f k_t k_d)([M]/[I]$^{1/2}$)

$\bar{v}$ = (0.003 / 2(0.5)(0.03)(0.0001))(4.5/(1.25 x 10^{-3})$^{1/2}$) = (0.01/0.0001)(4.5/0.035) = 128/0.01 = 12,800

d) $\bar{v}$ = (k_p/2f k_t k_d)([M]/[I]$^{1/2}$)

$\bar{v}$ = (0.003 / 2(0.5)(0.003)(0.1))(4.5/(1.25 x 10^{-3})$^{1/2}$) = (1/0.1)(4.5/0.035) = 128/0.1 = 1,280

Problem KP4.1.

The key point is that, when two terms are added together and one is much larger than the other, the sum is approximately the same as the larger of the two terms. You can ignore the smaller one.

$$\text{Rate}_p = \frac{k_p K_{eq}[\text{M}][\text{Cat}]\text{x}^*}{1 + \underbrace{\cancel{K_{eq}[\text{M}]}}_{\sim 0}}$$

$$\text{Rate}_p = \frac{k_p K_{eq}[\text{M}][\text{Cat}]\text{x}^*}{1}$$

$$\text{Rate}_p = k_p K_{eq}[\text{M}][\text{Cat}]\text{x}^*$$

<u>Problem KP4.2.</u>

$$\text{Rate}_p = \frac{k_p K_{eq}[\text{M}][\text{Cat}]\text{x}^*}{\underbrace{\cancel{1}}_{\sim 0} + K_{eq}[\text{M}]}$$

$$\text{Rate}_p = \frac{k_p K_{eq}[\text{M}][\text{Cat}]\text{x}^*}{K_{eq}[\text{M}]}$$

$$\text{Rate}_p = k_p[\text{Cat}]\text{x}^*$$
