REB, The Course
Class 6 Learning Activity Solution

The hydrogenation of the alpha-olefin $RCHCH_2$, reaction (1), is homogeneously catalyzed by Ni. The mechanism is given by reactions (2) through (4). Let $[Ni]_0$ represent the total amount of Ni initially added to the system, expressed as a concentration. Generate an expression for the apparent rate of production of RCH_2CH_3 via reaction (1) that does not contain concentrations of reactive intermediates. Reactions (2) and (4) are reversible, while reaction (3) is effectively irreversible.

$$RCHCH_2 + H_2 \rightleftarrows RCH_2CH_3 \qquad (1)$$

$$RCHCH_2 + Ni \rightleftarrows RCHCH_2 - Ni \qquad (2)$$

$$RCHCH_2 - Ni + H_2 \rightarrow RCH_2CH_3 - Ni \qquad \text{(irrev.) (3)}$$

$$RCH_2CH_3 - Ni \rightleftarrows RCH_2CH_3 + Ni \qquad (4)$$

Assignment Summary

(To simplify the notation, let A represent $RCHCH_2$ and Z represent RCH_2CH_3.)

<u>Apparent Reaction</u>:

$$A + H_2 \rightleftarrows Z \qquad (1)$$

<u>Mechanism</u>:

$$A + Ni \rightleftarrows A{-}Ni \qquad (2)$$

$$A{-}Ni + H_2 \rightarrow Z{-}Ni \qquad \text{(irrev.) (3)}$$

$$Z{-}Ni \rightleftarrows Z + Ni \qquad (4)$$

<u>Quantifiable Reagents</u>: A, H_2, Z, and $(Ni)_0$.

<u>Reactive Intermediates</u>: Ni, A–Ni, and Z–Ni.

<u>Deliverable</u>: mechanistic rate expression for reaction (1), $r_{Z,1}$.

Equations for Generating the Mechanistic Rate Expression

Rates of the Mechanistic Steps

$$r_2 = k_{2,f}[A][Ni] - k_{2,r}[A-Ni] \tag{5}$$

$$r_3 = k_{3,f}[A-Ni][H_2] \tag{6}$$

$$r_4 = k_{4,f}[Z-Ni] - k_{4,r}[Ni][Z] \tag{7}$$

Apparent Rate of the Non-Elementary Reaction

$$r_{Z,1} = r_4 = k_{4,f}[Z-Ni] - k_{4,r}[Ni][Z] \tag{8}$$

Bodenstein Steady-State Approximations[1]

$$\begin{aligned} 0 &= -r_2 + r_4 \\ &= -k_{2,f}[A][Ni] + k_{2,r}[A-Ni] + k_{4,f}[Z-Ni] - k_{4,r}[Ni][Z] \end{aligned} \tag{9}$$

$$0 = r_2 - r_3 = k_{2,f}[A][Ni] - k_{2,r}[A-Ni] - k_{3,f}[A-Ni][H_2] \tag{10}$$

$$0 = r_3 - r_4 = k_{3,f}[A-Ni][H_2] - k_{4,f}[Z-Ni] + k_{4,r}[Ni][Z] \tag{11}$$

Catalyst Conservation Equation

$$[Ni]_0 = [Ni] + [A-Ni] + [Z-Ni] \tag{12}$$

Calculations

The algebraic details for the calculations in this section are presented in the file, Activity 6 Calculations.pdf. The calculations proceed as follows:

1. Substitute the rate expressions for the mechanistic steps into equations (9) through (12).
2. Solve equation (12) together with two of the Bodenstein steady-state approximations, equations (9) through (12), to get expressions for the reactive intermediates.

[1] Only two of the three Bodenstein steady-state approximations are mathematically independent.

$$[Ni] = \frac{[Ni]_0}{1 + \frac{k_{2,f}[A]}{k_{2,r} + k_{3,f}[H_2]} + \frac{k_{2,f}k_{3,f}[A][H_2]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]} \tag{13}$$

$$[A-Ni] = \frac{k_{2,f}[A][Ni]_0}{k_{2,r} + k_{3,f}[H_2]} \times \frac{1}{1 + \frac{k_{2,f}[A]}{k_{2,r} + k_{3,f}[H_2]} + \frac{k_{2,f}k_{3,f}[A][H_2]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]} \tag{14}$$

$$[Z-Ni] = \left(\frac{k_{2,f}k_{3,f}[A][H_2]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]\right) \times \frac{1}{1 + \frac{k_{2,f}[A]}{k_{2,r} + k_{3,f}[H_2]} + \frac{k_{2,f}k_{3,f}[A][H_2]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]} \tag{15}$$

3. Substitute equations (13) and (15) into equation (8).

$$r_{Z,1} = \frac{k_{2,f}k_{3,f}k_{4,f}[Ni]_0[A][H_2]}{\left(\begin{array}{c} k_{2,r}k_{4,f} + k_{2,f}k_{4,f}[A] + k_{3,f}k_{4,f}[H_2] \\ + k_{2,f}k_{3,f}[A][H_2] + k_{3,f}k_{4,r}[H_2][Z] + k_{2,r}k_{4,r}[Z] \end{array}\right)} \tag{16}$$

Simplification and Discussion

Dividing the numerator and denominator of equation (16) by $k_{2,r}k_{4,f}$ will convert the first term in the denominator to a one, equation (17). The combinations of rate coefficients in the other terms can then be used to define effective rate coefficients as shown in equations (18) through (23).

$$r_{Z,1} = \frac{\frac{k_{2,f}k_{3,f}\cancel{k_{4,f}}}{k_{2,r}\cancel{k_{4,f}}}[Ni]_0[A]\,[H_2]}{\left(\begin{array}{c} 1 + \frac{k_{2,f}\cancel{k_{4,f}}[A]}{k_{2,r}\cancel{k_{4,f}}} + \frac{k_{3,f}\cancel{k_{4,f}}}{k_{2,r}\cancel{k_{4,f}}}[H_2] \\ + \frac{k_{2,f}k_{3,f}}{k_{2,r}k_{4,f}}[A]\,[H_2] + \frac{k_{3,f}k_{4,r}}{k_{2,r}k_{4,f}}[H_2]\,[Z] + \frac{\cancel{k_{2,r}}k_{4,r}}{\cancel{k_{2,r}}k_{4,f}}[Z] \end{array}\right)} \tag{17}$$

$$k = \frac{k_{2,f}k_{3,f}}{k_{2,r}} \tag{18}$$

$$k' = \frac{k_{2,f}}{k_{2,r}} \tag{19}$$

$$k'' = \frac{k_{3,f}}{k_{2,r}} \tag{20}$$

$$k''' = \frac{k_{2,f}k_{3,f}}{k_{2,r}k_{4,f}} \tag{21}$$

$$k'''' = \frac{k_{3,f}k_{4,r}}{k_{2,r}k_{4,f}} \tag{22}$$

$$k''''' = \frac{k_{4,r}}{k_{4,f}} \tag{23}$$

Deliverables

Substitution of equations (18) through (23) into equation (17) yields the simplified mechanistic rate expression shown in equation (24). All five of the apparent rate coefficients will display Arrhenius temperature dependence. A number of limiting cases of equation (24) are possible if one to five of the terms in the denominator are much much smaller that the other term or terms. Experimental studies will need to be performed to determine whether this rate expressions or any of its limiting forms captures the composition and temperature dependence of the rate with sufficient accuracy.

$$r_{Z,1} = \frac{k[Ni]_0 [A] [H_2]}{\begin{pmatrix} 1 + k' [A] + k'' [H_2] + k''' [A] [H_2] \\ + k'''' [H_2] [Z] + k''''' [Z] \end{pmatrix}} \qquad (24)$$