REB, The Course
Class 7 Learning Activity Solution

Suppose that the chlorination of toluene, reaction (1) proceeds according to mechanistic steps (2) through (6). Assume step (4) is rate-determining and effectively irreversible, $AlCl_3$ is the most abundant intermediate, and the amount of Al_2Cl_6 initially added to the system is known. Derive a mechanistic expression for the rate of reaction (1) that includes the minimum number of apparent rate coefficients and only concentrations of easily quantifiable reagents.

$$Cl_2 + C_7H_8 \rightarrow C_7H_7Cl + HCl \tag{1}$$

$$Al_2Cl_6 \rightarrow AlCl_3 + AlCl_5 \tag{2}$$

$$AlCl_3 + Cl_2 \rightleftarrows AlCl_5 \tag{3}$$

$$AlCl_5 + C_7H_8 \rightarrow C_7H_8\text{-}AlCl_5 \tag{4}$$

$$C_7H_8\text{-}AlCl_5 \rightleftarrows C_7H_8\text{-}Cl_2 + AlCl_3 \tag{5}$$

$$C_7H_8\text{-}Cl_2 \rightleftarrows C_7H_7Cl + HCl \tag{6}$$

Assignment Summary

Apparent Reaction:

$$Cl_2 + C_7H_8 \rightarrow C_7H_7Cl + HCl \tag{1}$$

Mechanism:

$$Al_2Cl_6 + Cl_2 \rightarrow AlCl_3 + AlCl_5 \tag{2}$$

$$AlCl_3 + Cl_2 \rightleftarrows AlCl_5 \tag{3}$$

$$AlCl_5 + C_7H_8 \rightarrow C_7H_8\text{-}AlCl_5 \qquad \text{(rate det., irrev.)} \tag{4}$$

$$C_7H_8\text{-}AlCl_5 \rightleftarrows C_7H_8\text{-}Cl_2 + AlCl_3 \tag{5}$$

$$C_7H_8\text{-}Cl_2 \rightleftarrows C_7H_7Cl + HCl \tag{6}$$

Quantifiable Reagents: Cl_2, C_7H_8, C_7H_7Cl, HCl, and $(Al_2Cl_6)_0$.

Reactive Intermediates: Al_2Cl_6, $AlCl_3$ (most abundant), $AlCl_5$, $C_7H_8\text{-}AlCl_5$, and $C_7H_8\text{-}Cl_2$.

Deliverable: mechanistic rate expression for reaction (1), r_1

Equations for Generating the Mechanistic Rate Expression

Apparent Rate of the Non-Elementary Reaction

$$r_1 = k_{4,f}\left[AlCl_5\right]\left[C_7H_8\right] \tag{7}$$

Quasi-Equilibrium Expressions

$$K_2 = \frac{\left[AlCl_3\right]\left[AlCl_5\right]}{\left[Al_2Cl_6\right]\left[Cl_2\right]} \tag{8}$$

$$K_3 = \frac{\left[AlCl_5\right]}{\left[AlCl_3\right]\left[Cl_2\right]} \tag{9}$$

$$K_5 = \frac{\left[C_7H_8\text{-}Cl_2\right]\left[AlCl_3\right]}{\left[C_7H_8\text{-}AlCl_5\right]} \tag{10}$$

$$K_6 = \frac{\left[C_7H_7Cl\right]\left[HCl\right]}{\left[C_7H_8\text{-}Cl_2\right]} \tag{11}$$

Catalyst Conservation Equation

$$2\left[Al_2Cl_6\right]_0 = 2\left[Al_2Cl_6\right] + \left[AlCl_3\right] + \left[AlCl_5\right] + \left[C_7H_8-AlCl_5\right] \tag{12}$$

Calculations

To generate the mechanistic rate expression, equations (8) through (12) must be solved to get expressions for the concentrations of the reactive intermediates. Then the resulting expression of $[AlCl_5]$ can be substituted into equation (7). Attempting to do so, however, is not straightforward, because one of the equations to be solved is a quadratic equation. As seen in the following, solving the quadratic is not necessary for this analysis because $AlCl_3$ is the most abundant intermediate.

Rearrange equations (8) and (9) to get expressions for the concentrations of Al_2Cl_6 and $AlCl_5$.

$$\left[Al_2Cl_6\right] = \frac{1}{K_2}\frac{\left[AlCl_3\right]\left[AlCl_5\right]}{\left[Cl_2\right]} \tag{13}$$

$$\left[AlCl_5\right] = K_3\left[AlCl_3\right]\left[Cl_2\right] \tag{14}$$

Then substitute equation (14) in equation (13).

$$\left[Al_2Cl_6\right] = \frac{K_3}{K_2}\frac{\left[AlCl_3\right]^2}{\left[Cl_2\right]} \tag{15}$$

Rearrange equations (10) and (11) to get expressions for the concentrations of C_7H_8-$AlCl_5$, and C_7H_8-Cl_2.

$$\left[C_7H_8{-}AlCl_5\right] = \frac{1}{K_5}\left[C_7H_8{-}Cl_2\right]\left[AlCl_3\right] \tag{16}$$

$$\left[C_7H_8{-}Cl_2\right] = \frac{1}{K_6}\left[C_7H_7Cl\right]\left[HCl\right] \tag{17}$$

Then substitute equation (17) in equation (16).

$$\left[C_7H_8{-}AlCl_5\right] = \frac{1}{K_5K_6}\left[C_7H_7Cl\right]\left[HCl\right]\left[AlCl_3\right] \tag{18}$$

Substitution of equations (14), (15), and (18) in equation (12) yields an equation that can be solved to get an expression for the concentration of $AlCl_3$.

$$2\left[Al_2Cl_6\right]_0 = 2\frac{K_3}{K_2}\frac{\left[AlCl_3\right]^2}{\left[Cl_2\right]} + \left[AlCl_3\right] + K_3\left[AlCl_3\right]\left[Cl_2\right] + \frac{1}{K_5K_6}\left[C_7H_7Cl\right]\left[HCl\right]\left[AlCl_3\right]$$

$$0 = \left(2\frac{K_3}{K_2\left[Cl_2\right]}\right)\left[AlCl_3\right]^2 + \left(1 + K_3\left[Cl_2\right] + \frac{1}{K_5K_6}\left[C_7H_7Cl\right]\left[HCl\right]\right)\left[AlCl_3\right] - 2\left[Al_2Cl_6\right]_0 \tag{19}$$

Equation (19) is a quadratic equation that could be solved for the concentration of $AlCl_3$. However, doing so would yield an unwieldy expression. Instead, equation (19) first can be simplified by noting that $AlCl_3$ is the most abundant intermediate. The concentration of $AlCl_3$ is much greater than each of the other intermediates. In the case of Al_2Cl_6, using equation (15) leads to equation (20).

$$\left[AlCl_3\right] \gg \left[Al_2Cl_6\right]$$

$$\left[AlCl_3\right] \gg \frac{K_3}{K_2}\frac{\left[AlCl_3\right]^2}{\left[Cl_2\right]} \tag{20}$$

In the case of $AlCl_5$, using equation (14) leads to equation (21).

$$\left[AlCl_3\right] \gg \left[AlCl_5\right]$$

$$\left[AlCl_3\right] \gg K_3\left[AlCl_3\right]\left[Cl_2\right]$$

$$1 \gg K_3\left[Cl_2\right] \tag{21}$$

In the case of C_7H_8-$AlCl_5$, using equation (18) leads to equation (22).

$$\left[AlCl_3\right] \gg \left[C_7H_8{-}AlCl_5\right]$$

$$\left[AlCl_3\right] \gg \frac{1}{K_5K_6}\left[C_7H_7Cl\right]\left[HCl\right]\left[AlCl_3\right]$$

$$1 \gg \frac{1}{K_5K_6}\left[C_7H_7Cl\right]\left[HCl\right] \tag{22}$$

Equations (21) and (22) allow simplification of the second term on the right side of equation (19), leading to equation (23).

$$\begin{aligned} 0 = &\left(2\frac{K_3}{K_2\left[Cl_2\right]}\right)\left[AlCl_3\right]^2 \\ &+\left(1 + \cancel{K_3\left[Cl_2\right]} + \cancel{\frac{1}{K_5K_6}\left[C_7H_7Cl\right]\left[HCl\right]}\right)\left[AlCl_3\right] \\ &-2\left[Al_2Cl_6\right]_0 \end{aligned}$$

$$0 = \left(2\frac{K_3}{K_2\left[Cl_2\right]}\right)\left[AlCl_3\right]^2 + \left[AlCl_3\right] - 2\left[Al_2Cl_6\right]_0 \tag{23}$$

Equation (20) indicates that the first term is negligible compared to the second which allows equation (23) to be solved for the concentration of AlCl3, equation (24).

$$0 = \cancel{\left(2\frac{K_3}{K_2\left[Cl_2\right]}\right)\left[AlCl_3\right]^2} + \left[AlCl_3\right] - 2\left[Al_2Cl_6\right]_0$$

$$\left[AlCl_3\right] = 2\left[Al_2Cl_6\right]_0 \tag{24}$$

Substitution of equation (14) in equation (7) followed by substitution of equation (24) in the result yields the requested rate expression, equation (25).

$$r_1 = k_{4,f}\left[AlCl_5\right]\left[C_7H_8\right] = k_{4,f}K_3\left[AlCl_3\right]\left[Cl_2\right]\left[C_7H_8\right]$$

$$r_1 = 2k_{4,f}K_3 \left[Al_2Cl_6\right]_0 \left[Cl_2\right] \left[C_7H_8\right] \tag{25}$$

Simplification and Discussion

An apparent rate coefficient can be defined as shown in equation (26), leading to the simplified rate expression, equation (27). As long as the equilibrium constant, K_4, displays Arrhenius temperature dependence, the apparent rate coefficient will, as well.

$$k = 2k_{4,f}K_3 \tag{26}$$

$$r_1 = k \left[Al_2Cl_6\right]_0 \left[Cl_2\right] \left[C_7H_8\right] \tag{27}$$

In deriving the rate expression, it was assumed that $AlCl_3$ is the most abundant intermediate, leading to equation (24), reproduced below. This makes sense because if $AlCl_3$ is the most abundant intermediate, then essentially all of the added Al_2Cl_6 will be present in the form of $AlCl_3$, with each original mole of Al_2Cl_6 yielding two moles of $AlCl_3$.

$$\left[AlCl_3\right] = 2 \left[Al_2Cl_6\right]_0 \tag{24}$$

Deliverables

If step (4) is rate-determining and effectively irreversible and AlCl is the most abundant intermediate, the apparent rate of reaction (1) will be described by the rate expression shown below. Experimental studies will need to be performed to determine whether it captures the composition and temperature dependence of the rate with sufficient accuracy.

$$r_1 = k \left[Al_2Cl_6\right]_0 \left[Cl_2\right] \left[C_7H_8\right]$$