REB, The Course
Class 4 Learning Activity Solution

In the mechanism for synthesis of HBr given below, assume step (4) is effectively irreversible and step (5) is kinetically insignificant. Use the Bodenstein steady-state approximation to derive a mechanistic rate expression for the apparent rate of generation of HBr via non-elementary reaction (1). Simplify the mechanism so that it contains only partial pressures of stable species and not those of reactive intermediates. Group and rename combinations of true rate coefficients to minimize the number of apparent rate coefficients in the rate expression.

Apparent (non-elementary) Reaction

$$H_2 + Br_2 \rightleftarrows 2\ HBr \tag{1}$$

Mechanism

$$Br_2 \rightleftarrows 2\ Br\cdot \tag{2}$$

$$Br\cdot + H_2 \rightleftarrows HBr + H\cdot \tag{3}$$

$$H\cdot + Br_2 \rightarrow HBr + Br\cdot \tag{4}$$

$$2\ H\cdot \rightleftarrows H_2 \tag{5}$$

Assignment Summary

Apparent Reaction:

$$H_2 + Br_2 \rightleftarrows 2\ HBr \tag{1}$$

Mechanistic Steps:

$$Br_2 \rightleftarrows 2\ Br\cdot \tag{2}$$

$$Br\cdot + H_2 \rightleftarrows HBr + H\cdot \tag{3}$$

$$H\cdot + Br_2 \rightarrow HBr + Br\cdot \qquad \text{(irrev.)} \tag{4}$$

2 H· ⇄ H_2 (insig.) (5)

Quantifiable Reagents: H_2, Br_2, and 2 HBr

Reactive Intermediates: Br· and H·

Deliverable: simplified expression for $r_{HBr,1}$

Equations for Generating the Mechanistic Rate Expression

Rates of the Mechanistic Steps

$$r_2 = k_{2,f}[Br_2] - k_{2,r}[Br\cdot]^2 \tag{6}$$

$$r_3 = k_{3,f}[Br\cdot][H_2] - k_{3,r}[HBr][H\cdot] \tag{7}$$

$$r_4 = k_{4,f}[H\cdot][Br_2] \tag{8}$$

$$r_5 = 0 \tag{9}$$

Apparent Rate of the Non-Elementary Reaction

$$r_{HBr,1} = r_3 + r_4 \tag{10}$$

Bodenstein Steady-State Approximations

$$0 = 2\, r_2 - r_3 + r_4 \tag{11}$$

$$0 = r_3 - r_4 - 2r_5 \tag{12}$$

Calculations

The algebraic details for the calculations in this section are presented in the file, Activity 4 Calculations.pdf. The calculations proceed as follows:

1. Substitute the rate expressions for the mechanistic steps, equations (6) through (9), in equations (10), (11), and (12).
2. Solve the versions of equations (11) and (12) resulting from step 1 for the concentrations of the reactive intermediates.

$$[Br\cdot] = \sqrt{\frac{k_{2,f}}{k_{2,r}}}\sqrt{[Br_2]} \tag{13}$$

$$[H\cdot] = \frac{k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\sqrt{[Br_2]}[H_2]}{k_{3,r}[HBr] + k_{4,f}[Br_2]} \tag{14}$$

3. Substitute the expressions for the reactive intermediates, equations (13) and (14) into the version of equation (1) resulting from step 1 to get the requested apparent rate expression

$$r_{HBr,1} = 2\frac{k_{3,f}k_{4,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}[Br_2]^{3/2}[H_2]}{k_{3,r}[HBr] + k_{4,f}[Br_2]} \tag{15}$$

Simplification and Discussion

The rate expression has three terms, a numerator and a two term denominator. In this case, the rate expression can be rearranged so that one of the terms does not contain a rate coefficient. It is preferable for that term to be in the denominator. One way of accomplishing that is to divide both the numerator and denominator by $k_{4,f}$ giving equation (17).

$$r_{HBr,1} = 2\frac{k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}[Br_2]^{3/2}[H_2]}{\frac{k_{3,r}}{k_{4,f}}[HBr] + [Br_2]} \tag{17}$$

Combining the rate coefficients as shown in equations (18) and (19) yields the rate expression in terms of two apparent rate coefficients, equation (20).

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

$$k' = \frac{k_{3,r}}{k_{4,f}} \tag{19}$$

$$r_{HBr,1} = \frac{k[Br_2]^{3/2}[H_2]}{k'[HBr] + [Br_2]} \tag{20}$$

Both apparent rate coefficients will display Arrhenius temperature dependence because each is a product of true rate coefficients raised to constant powers. There are two limiting forms of the rate expression. If the concentration of Br_2 is much much greater than $k'[HBr]$, equation (20) reduces to equation (21). If the concentration of Br_2 is much much less than $k'[HBr]$, equation (20) reduces to equation (22). In that case, the two apparent rate coefficients can be combine into a single apparent rate coefficient.

$$r_{HBr,1} = k[Br_2]^{1/2}[H_2] \tag{21}$$

$$r_{HBr,1} = \frac{k}{k'}\frac{[Br_2]^{3/2}[H_2]}{[HBr]} = k''\frac{[Br_2]^{3/2}[H_2]}{[HBr]} \tag{22}$$

If the reaction begins with only the reactants present, equation (21) will initially describe the rate. As the concentration of HBr increases, the rate will be described by equation (20). If Br_2 is not present in excess the rate will finally approach the behavior shown in equation (22).

Deliverables

The apparent rate of generation of HBr according to reaction (1) will be described by the following rate expression if the mechanism is as described. Experimental studies will need to be performed to determine whether it captures the composition and temperature dependence of the rate with sufficient accuracy.

$$r_{HBr,1} = \frac{k[Br_2]^{3/2}[H_2]}{k'[HBr] + [Br_2]}$$