REB, The Course
Class 4 Learning Activity Calculations

Equation numbers correspond to Activity 4 Solution

Rate expressions for the mechanistic steps:

$$r_j = k_{j,f} \prod_{i_r} [i_r]^{-\nu_{i_r,j}} - k_{j,r} \prod_{i_p} [i_p]^{\nu_{i_p,j}}$$

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

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

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

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

Expression for $r_{HBr,1}$ in terms of the rates of the mechanistic steps:

$$r_{i,j_{non}} = \sum_{j'} \nu_{i,j'} r_{j'}$$

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

Bodenstein steady-state approximations for Br· and H·:

$$0 = \sum_{j_{step}} \nu_{i_{RI},j_{step}} r_{j_{step}}$$

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

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

To solve equations (11) and (12) for Br· and H· start by adding them together to get equation (A). Then substitute equations (6) and (9) and solve for the concentration of Br·, equation (14).

$$0 = 2r_2 - 2r_5 \tag{A}$$

$$0 = 2\left(k_{2,f}[Br_2] - k_{2,r}[Br\cdot]^2\right)$$

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

Substitute equations (7) through (9) into equation (12) and solve for the concentration of H·. Finally substitute equation (13) to get equation (14).

$$0 = k_{3,f}[Br\cdot][H_2] - k_{3,r}[HBr][H\cdot] - k_{4,f}[H\cdot][Br_2]$$

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

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

To generate the rate expression, substitute equations (7) and (8) into equation (10), then substitute equations (13) and (14) to get equation (15).

$$r_{HBr,1} = k_{3,f}[Br\cdot][H_2] - k_{3,r}[HBr][H\cdot] + k_{4,f}[H\cdot][Br_2]$$

$$r_{HBr,1} = k_{3,f}[Br\cdot][H_2] - \left(k_{3,r}[HBr] - k_{4,f}[Br_2]\right)[H\cdot]$$

$$r_{HBr,1} = k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\sqrt{[Br_2]}[H_2] - \left(k_{3,r}[HBr] - k_{4,f}[Br_2]\right)\frac{k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\sqrt{[Br_2]}[H_2]}{k_{3,r}[HBr] + k_{4,f}[Br_2]}$$

$$r_{HBr,1} = k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\sqrt{[Br_2]}[H_2] - \left(\frac{k_{3,r}[HBr] - k_{4,f}[Br_2]}{k_{3,r}[HBr] + k_{4,f}[Br_2]}\right)k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\sqrt{[Br_2]}[H_2]$$

$$r_{HBr,1} = k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\sqrt{[Br_2]}[H_2]\left(1 - \frac{k_{3,r}[HBr] - k_{4,f}[Br_2]}{k_{3,r}[HBr] + k_{4,f}[Br_2]}\right)$$

$$r_{HBr,1} = k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\sqrt{[Br_2]}[H_2]\left(\frac{2k_{4,f}[Br_2]}{k_{3,r}[HBr] + k_{4,f}[Br_2]}\right)$$

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