REB, The Course
Class 5 Learning Activity Solution

At high temperatures nitric oxide can be reduced by molecular hydrogen. Macroscopically, the reaction appears to occur as written in reaction (1), but it is actually non-elementary. Suppose that the mechanism presented in reactions (2) through (4) is being evaluated to determine whether it is consistent with experimental kinetics. Compare the rate expression for the apparent rate of reaction (1) assuming step (3) to be rate-determining to the rate expression assuming step (3) to be effectively irreversible, but not rate-determining. In both cases, eliminate concentrations of reactive intermediates from the rate expression, and group true rate and equilibrium constants into the minimum number of apparent rate coefficients.

$$2\,NO + 2\,H_2 \rightleftarrows N_2 + 2\,H_2O \qquad (1)$$

$$2\,NO \rightleftarrows N_2O_2 \qquad (2)$$

$$H_2 + N_2O_2 \rightleftarrows N_2 + H_2O_2 \qquad (3)$$

$$H_2 + H_2O_2 \rightleftarrows 2\,H_2O \qquad (4)$$

Assignment Summary

Apparent Reaction:

$$2\,NO + 2\,H_2 \rightleftarrows N_2 + 2\,H_2O \qquad (1)$$

Mechanistic Steps:

$$2\,NO \rightleftarrows N_2O_2 \qquad (2)$$

$$H_2 + N_2O_2 \rightleftarrows N_2 + H_2O_2 \qquad \text{(rate det. or irrev.)} \quad (3)$$

$$H_2 + H_2O_2 \rightleftarrows 2\,H_2O \qquad (4)$$

Quantifiable Reagents: NO, H_2, N_2, and H_2O

Reactive Intermediates: N_2O_2 and H_2O_2

Deliverables: simplified expressions for r_1 (a) if step (3) is rate-determining, and (b) if step (3) is effectively irreversible, but not rate-determining.

Equations for Generating the Mechanistic Rate Expression

Rates of the Mechanistic Steps for cases (a) and (b)

$$r_2 = k_{2,f}[NO]^2 - k_{2,r}[N_2O_2] \tag{5}$$

$$r_3 = k_{3,f}[H_2][N_2O_2] - k_{3,r}[N_2][H_2O_2] \tag{6a}$$

$$r_3 = k_{3,f}[H_2][N_2O_2] \tag{6b}$$

$$r_4 = k_{4,f}[H_2][H_2O_2] - k_{4,r}[H_2O]^2 \tag{7}$$

Apparent Rate of the Non-Elementary Reaction in both cases

$$r_1 = r_3 \tag{8}$$

Quasi-Equilibrium Expressions for case (a)

$$K_2 = \frac{\left[N_2O_2\right]}{\left[NO\right]^2} \tag{9}$$

$$K_4 = \frac{\left[H_2O\right]^2}{\left[H_2\right]\left[H_2O_2\right]} \tag{10}$$

Bodenstein Steady-State Approximations for case (b)

$$0 = r_2 - r_3 \tag{11}$$

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

Calculations

The algebraic details for the calculations in this section are presented in the file, Activity 5 Calculations.pdf. The calculations for case (a) proceed as follows:

1. Substitute equation (6a) in equation (8).

2. Solve the quasi-equilibrium expressions, equations (9) and (10), to get expressions for the concentrations of the reactive intermediates.

$$\left[N_2O_2\right] = K_2 \left[NO\right]^2 \tag{13}$$

$$\left[H_2O_2\right] = \frac{\left[H_2O\right]^2}{\left[H_2\right] K_4} \tag{14}$$

3. Substitute equations (13) and (14) into the version of equation (8) resulting from step 1 to get the apparent rate expression for case (a).

$$r_1 = k_{3,f} \left[H_2\right] K_2 \left[NO\right]^2 - k_{3,r} \left[N_2\right] \frac{\left[H_2O\right]^2}{\left[H_2\right] K_4} \tag{15}$$

The calculations for case (b) proceed as follows:

1. Substitute equations (5), (6b), and (7) in equations (8), (11), and (12).
2. Solve the version of the Bodenstein steady-state approximation, equation (11), resulting from step 1, to get an expression for the concentration of N_2O_2. (The other Bodenstein steady-state approximation, equation (12), could be used to calculate the concentration of H_2O_2, but it doesn't appear in the rate expression, so it isn't needed.)

$$[N_2O_2] = \frac{k_{2,f}[NO]^2}{k_{2,r} + k_{3,f}[H_2]} \tag{16}$$

3. Substitute equation (16) into the version of equation (8) resulting from step 1 to get the apparent rate expression for case (b).

$$r_1 = \frac{k_{2,f} k_{3,f} [H_2][NO]^2}{k_{2,r} + k_{3,f}[H_2]} \tag{17}$$

Simplification and Discussion

There are two terms in the rate expression for case (a), and each term contains true rate coefficients and equilibrium constants. There is no way to eliminate the constants from either term, so two apparent rate coefficients, k_f and k_r, can be defined as shown in equations (18) and (19), giving the mechanistic rate expression shown in equation (20) for case (a) where mechanistic step (3) is rate-determining.

$$k_f = k_{3,f} K_2 \tag{18}$$

$$k_r = \frac{k_{3,r}}{K_4} \tag{19}$$

$$r_1 = k_f \left[H_2\right] \left[NO\right]^2 - k_r \frac{\left[N_2\right] \left[H_2O\right]^2}{\left[H_2\right]} \tag{20}$$

When step (3) is irreversible, but not rate-determining, the rate expression, equation (17), 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 $k_{2,r}$ giving equation (21).

$$r_1 = \frac{\frac{k_{2,f} k_{3,f}}{k_{2,r}} [H_2][NO]^2}{1 + \frac{k_{3,f}}{k_{2,r}} [H_2]} \tag{21}$$

Combining the rate coefficients as shown in equations (22) and (23) yields the mechanistic rate expression for case (b) in terms of two apparent rate coefficients, equation (24).

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

$$k' = \frac{k_{3,f}}{k_{2,r}} \tag{23}$$

$$r_1 = \frac{k[H_2][NO]^2}{1 + k'[H_2]} \tag{24}$$

All four apparent rate coefficients, k_f, k_r, k, and k', are products of rate coefficients and equilibrium constants raised to constant powers. If the equilibrium constants for mechanistic steps (2) and (4) display Arrhenius temperature dependence, the all of the apparent rate coefficients will do so as well.

The apparent rate expression for case (a) does not have any limiting forms. If $k'[H_2]$ is much, much smaller than 1, the rate expression for case (b) reduces to equation (25), and if it is much, much greater than 1, the rate expression reduces to equation (26).

$$r_1 = k[H_2][NO]^2 \tag{25}$$

$$r_1 = \frac{k}{k'}[NO]^2 = k''[NO]^2 \tag{26}$$

Deliverables

By making two different assumptions about step (3), the four rate expressions below were generated from the proposed mechanism. It can be noted that equation (20) becomes equal to equation (26) if the second term in equation (20) is negligible. Additional rate expressions would likely result if assumptions were made about the other mechanistic steps. Experimental studies would need to be performed to determine whether any of these rate expressions captures the composition and temperature dependence of the rate with sufficient accuracy.

$$r_1 = k_f \left[H_2\right] \left[NO\right]^2 - k_r \frac{\left[N_2\right] \left[H_2O\right]^2}{\left[H_2\right]} \tag{20}$$

$$r_1 = \frac{k[H_2][NO]^2}{1 + k'[H_2]} \tag{24}$$

$$r_1 = k[H_2][NO]^2 \tag{25}$$

$$r_1 = = k''[NO]^2 \tag{26}$$