REB, The Course
Class 5 Practice Assignment Solution

N_2O_5 can decompose into N_2O_4 and O_2, as indicated in reaction (1), but that reaction is not elementary. One possible mechanism for it is given in reactions (2) through (5). Derive an expression for the apparent rate of reaction (1) assuming step (3) to be rate-determining. Eliminate concentrations of reactive intermediates from the rate expression, and group and re-name products of powers of the true rate coefficients to minimize the number of apparent rate coefficients in the rate expression.

$$2\,N_2O_5 \rightleftarrows 2\,N_2O_4 + O_2 \qquad (1)$$

$$N_2O_5 \rightleftarrows NO_2 + NO_3 \qquad (2)$$

$$NO_2 + NO_3 \rightleftarrows NO_2 + O_2 + NO \qquad (3)$$

$$NO + N_2O_5 \rightleftarrows NO_2 + N_2O_4 \qquad (4)$$

$$2\,NO_2 \rightleftarrows N_2O_4 \qquad (5)$$

Assignment Summary

<u>Apparent Reaction</u>:

$$2\,N_2O_5 \rightleftarrows 2\,N_2O_4 + O_2 \qquad (1)$$

<u>Mechanistic Steps</u>:

$$N_2O_5 \rightleftarrows NO_2 + NO_3 \qquad (2)$$

$$NO_2 + NO_3 \rightleftarrows NO_2 + O_2 + NO \qquad \text{(rate det.) } (3)$$

$$NO + N_2O_5 \rightleftarrows NO_2 + N_2O_4 \qquad (4)$$

$$2\,NO_2 \rightleftarrows N_2O_4 \qquad (5)$$

<u>Quantifiable Reagents</u>: N_2O_5, N_2O_4, and O_2

Reactive Intermediates: NO_2, NO_3, and NO

Deliverables: simplified expression for r_1.

Equations for Generating the Mechanistic Rate Expression

Apparent Rate of the Non-Elementary Reaction

$$r_1 = k_{3,f}\left[NO_2\right]\left[NO_3\right] - k_{3,r}\left[NO_2\right]\left[O_2\right]\left[NO\right] \tag{6}$$

Quasi-Equilibrium Expressions

$$K_2 = \frac{\left[NO_2\right]\left[NO_3\right]}{\left[N_2O_5\right]} \tag{7}$$

$$K_4 = \frac{\left[NO_2\right]\left[N_2O_4\right]}{\left[NO\right]\left[N_2O_5\right]} \tag{8}$$

$$K_5 = \frac{\left[N_2O_4\right]}{\left[NO_2\right]^2} \tag{9}$$

Calculations

The algebraic details for the calculations in this section are presented in the file, Practice Assignment 5 Calculations.pdf. The calculations proceed as follows:

1. Solve the quasi-equilibrium expressions, equations (7) through (9), to get expressions for the concentrations of the reactive intermediates.

$$\left[NO_2\right] = \sqrt{\frac{\left[N_2O_4\right]}{K_5}} \tag{10}$$

$$\left[NO\right] = \frac{\left[N_2O_4\right]^{\frac{3}{2}}}{K_4\sqrt{K_5}\left[N_2O_5\right]} \tag{11}$$

$$\left[NO_3\right] = \frac{K_2\sqrt{K_5}\left[N_2O_5\right]}{\sqrt{\left[N_2O_4\right]}} \tag{12}$$

2. Substitute the expressions for the concentrations of the reactive intermediates, equations (10) through (12) into equation (6) to get the mechanistic rate expression.

$$r_1 = k_{3,f}K_2\left[N_2O_5\right] - \frac{k_{3,r}}{K_4K_5}\frac{\left[N_2O_4\right]^2\left[O_2\right]}{\left[N_2O_5\right]} \tag{13}$$

Simplification and Discussion

The rate coefficients and equilibrium constants can be grouped as shown in equations (14) and (15). Substitution into equation (13) yields the rate expression in terms of apparent rate coefficients, equation (16). As long as the equilibrium constants for steps (2) through (4) display Arrhenius-like temperature dependence, the effective rate coefficients, k_f and k_r, will also display Arrhenius temperature dependence.

$$k_f = k_{3,f}K_2 \tag{14}$$

$$k_r = \frac{k_{3,r}}{K_4K_5} \tag{15}$$

$$r_1 = k_f\left[N_2O_5\right] - k_r\frac{\left[N_2O_4\right]^2\left[O_2\right]}{\left[N_2O_5\right]} \tag{16}$$

Deliverables

If the proposed mechanism is correct, the apparent rate of reaction (1) will be given by equation (16). Experimental studies will need to be performed to determine whether it captures the composition and temperature dependence of the rate with sufficient accuracy.

$$r_1 = k_f \left[N_2O_5\right] - k_r \frac{\left[N_2O_4\right]^2 \left[O_2\right]}{\left[N_2O_5\right]} \tag{16}$$