REB, The Book
Example 4.8.1 Solution

Suppose that nitrogen oxidation, equation (1), occurs via the chain reaction mechanism given in equations (2) through (5). Classify each of the mechanistic steps as initiation/termination, propagation, chain branching or chain transfer, and show that there is a linear combination the mechanistic steps that is equal to the apparent, non-elementary reaction. Then generate an expression for the apparent rate of generation of NO by reaction (1), assuming that step (4) is effectively irreversible and step (5) is kinetically insignificant. Group and rename combinations of true rate coefficients to minimize the number of apparent rate coefficients in the rate expression.

$$N_2 + O_2 \rightarrow 2\,NO \tag{1}$$

$$O_2 \rightleftarrows 2\,O\cdot \tag{2}$$

$$O\cdot \;+\; N_2 \;\rightleftarrows\; NO \;+\; N\cdot \tag{3}$$

$$N\cdot \;+\; O_2 \;\rightleftarrows\; NO \;+\; O\cdot \tag{4}$$

$$2\,N\cdot \;\rightleftarrows\; N_2 \tag{5}$$

Assignment Summary

Apparent Reaction:

$$N_2 + O_2 \rightarrow 2\,NO \tag{1}$$

Mechanistic Steps:

$$O_2 \rightleftarrows 2\,O\cdot \tag{2}$$

$$O\cdot \;+\; N_2 \;\rightleftarrows\; NO \;+\; N\cdot \tag{3}$$

$$N\cdot \;+\; O_2 \;\rightleftarrows\; NO \;+\; O\cdot \qquad \text{(irrev.) (4)}$$

$$2\,N\cdot \;\rightleftarrows\; N_2 \qquad \text{(insig.) (5)}$$

Quantifiable Reagents: N_2, O_2, and NO

Reactive Intermediates: O· and N·

Deliverables: classification of the mechanistic steps, the linear combination of the steps that equals the apparent reaction, and a simplified expression for $r_{NO,1}$

Classification of the Mechanistic Steps

Initiation steps have no reactive intermediates as reactants and one or more reactive intermediates as products, while termination steps have one or more reactive intermediates as reactants and no reactive intermediates as products. Thus, as written, reaction (2) is an initiation step and reaction (5) is a termination step.

Propagation steps have one reactive intermediate among the reactants and a different reactive intermediate among the products. In reaction (3) O· is a reactant while N· is a product, and in reaction (4) N· is a reactant while O· is a product. That means reactions (3) and (4) are both propagation steps. There are no chain branching or chain transfer steps in this mechanism.

Apparent Reaction as a Linear Combination of the Mechanistic Steps

There must be a linear combination of the mechanistic steps that equals the apparent, non-elementary reaction. In chain reaction mechanisms, the sum usually includes only the propagation steps, (3) and (4) in the present system. In this instance it is easy to see that adding steps (3) and (4) yields the apparent, non-elementary reaction, reaction (1).

Equations for Generating the Mechanistic Rate Expression

Rates of the Mechanistic Steps

$$r_2 = k_{2,f}\left[O_2\right] - k_{2,r}\left[O\cdot\right]^2 \tag{6}$$

$$r_3 = k_{3,f}[O\cdot][N_2] - k_{3,r}[NO][N\cdot] \tag{7}$$

$$r_4 = k_{4,f}[N\cdot][O_2] \tag{8}$$

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

Apparent Rate of the Non-Elementary Reaction

$$r_{NO,1} = r_3 + r_4 \tag{10}$$

Bodenstein Steady-State Approximations

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

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

Calculations

The algebraic details for the calculations in this section are presented in the file, Example 4.8.1 Calculations.pdf. The calculations proceed as follows:

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

$$\left[O\cdot\right] = \sqrt{\frac{k_{2,f}}{k_{2,r}}\left[O_2\right]} \tag{13}$$

$$[N\cdot] = \frac{k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}\left[O_2\right]}\left[N_2\right]}{\left(k_{3,r}\left[NO\right] + k_{4,f}\left[O_2\right]\right)} \tag{14}$$

3. Substitute equations (13) and (14) into the version of equation (10) from step 1 and rearrange to get the mechanistic rate expression, equation (15).

$$r_{NO,1} = \left(\frac{2k_{3,f}k_{4,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\left[O_2\right]^{\frac{3}{2}}[N_2]}{k_{3,r}[NO] + k_{4,f}[O_2]}\right) \tag{16}$$

Simplification and Discussion

The rate expression has three terms, a numerator and a two term denominator. The minimum number of apparent rate coefficients will result if the equation is rearranged so that one of the three terms does not contain a rate coefficient. One way of doing so is shown in equation (17).

$$r_{NO,1} = \left(\frac{\frac{2k_{3,f}\cancel{k_{4,f}}}{\cancel{k_{4,f}}}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\left[O_2\right]^{\frac{3}{2}}[N_2]}{\frac{k_{3,r}}{k_{4,f}}[NO] + \frac{\cancel{k_{4,f}}}{\cancel{k_{4,f}}}[O_2]} \right)$$

$$r_{NO,1} = \left(\frac{2k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\left[O_2\right]^{\frac{3}{2}}[N_2]}{\frac{k_{3,r}}{k_{4,f}}[NO] + [O_2]} \right) \tag{17}$$

Combining the rate coefficients as shown in equations (18) and (19) yields the rate expression in terms of two apparent rate coefficients, equation (20). The apparent rate coefficients, k and k', will display Arrhenius temperature dependence because each is a product of true rate coefficients raised to constant powers.

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

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

$$r_{NO,1} = \frac{k\left[O_2\right]^{\frac{3}{2}}[N_2]}{[O_2] + k'[NO]} \tag{20}$$

There are two limiting forms of the rate expression. If O_2 is present in sufficient excess and $[O_2] \gg k'[NO]$, the rate expression will take the form shown in equation (21) because the second term in the denominator will be negligible. Alternatively, if N_2 is present in excess, the rate expression will asymptotically approach equation (22) as the concentration of O_2 decreases. Indeed, if NO is present initially and $k'[NO] \gg [O_2]$ at the initial conditions, then the rate expression in equation (22) will apply at all times.

$$r_{NO,1} = k\left[O_2\right]^{\frac{1}{2}}[N_2] \tag{21}$$

$$r_{NO,1} = \frac{k}{k'}\frac{[O_2]^{\frac{3}{2}}[N_2]}{[NO]} = k''\frac{[O_2]^{\frac{3}{2}}[N_2]}{[NO]} \tag{22}$$

Deliverables

If reaction (1) actually occurs as described, its rate will be given by equation (20). Depending upon the initial composition, the rate expression shown in equation (21) or that shown in equation (22) *<u>might</u>* apply. In all cases, the apparent rate coefficients will exhibit Arrhenius temperature dependence. Experimental studies will need to be performed to determine whether any of the rate expressions, (20), (21), or (22), capture the composition and temperature dependence of the rate with sufficient accuracy at compositions and temperatures of interest.

$$r_{NO,1} = \frac{k\left[O_2\right]^{\frac{3}{2}}[N_2]}{[O_2] + k'[NO]} \tag{20}$$

$$r_{NO,1} = k\left[O_2\right]^{\frac{1}{2}}[N_2] \tag{21}$$

$$r_{NO,1} = k''\frac{[O_2]^{\frac{3}{2}}[N_2]}{[NO]} \tag{22}$$