REB, The Course
Class 4 Practice Assignment Solution

The formation of phosgene appears macroscopically to take place according to reaction (1) below. It has been suggested that this reaction is non-elementary, and that the actual events taking place are given by reactions (2), (3) and (4). Supposing that reactions (2) and (3) are reversible, but reaction (4) is irreversible, derive an expression for the apparent rate of reaction (1). 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.

$$CO + Cl_2 \rightleftarrows COCl_2 \tag{1}$$

$$Cl_2 \rightleftarrows 2\,Cl \tag{2}$$

$$Cl + Cl_2 \rightleftarrows Cl_3 \tag{3}$$

$$CO + Cl_3 \rightleftarrows COCl_2 + Cl \tag{4}$$

Assignment Summary

Apparent Reaction:

$$CO + Cl_2 \rightleftarrows COCl_2 \tag{1}$$

Mechanistic Steps:

$$Cl_2 \rightleftarrows 2\,Cl \tag{2}$$

$$Cl + Cl_2 \rightleftarrows Cl_3 \tag{3}$$

$$CO + Cl_3 \rightleftarrows COCl_2 + Cl \qquad \text{(irrev.) (4)}$$

Quantifiable Reagents: CO, Cl_2, and $COCl_2$

Reactive Intermediates: Cl and Cl_3

Deliverable: simplified expression for r_1

Equations for Generating the Mechanistic Rate Expression

Rates of the Mechanistic Steps

$$r_2 = k_{2,f}\left[\mathrm{Cl_2}\right] - k_{2,r}\left[\mathrm{Cl}\right]^2 \tag{5}$$

$$r_3 = k_{3,f}\left[\mathrm{Cl}\right]\left[\mathrm{Cl_2}\right] - k_{3,r}\left[\mathrm{Cl_3}\right] \tag{6}$$

$$r_4 = k_{4,f}\left[\mathrm{CO}\right]\left[\mathrm{Cl_3}\right] \tag{7}$$

Apparent Rate of the Non-Elementary Reaction

$$r_1 = r_4 \tag{8}$$

Bodenstein Steady-State Approximations

$$0 = 2\,r_2 - r_3 + r_4 \tag{9}$$

$$0 = r_3 - r_4 \tag{10}$$

Calculations

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

1. Substitute the rate expressions for the mechanistic steps, equations (5) through (7) into equations (8) through (10).
2. Solve the versions of equations (9) and (10) resulting from step 1 to obtain expressions for the concentrations of the reactive intermediates.

$$\left[\mathrm{Cl}\right] = \sqrt{\frac{k_{2,f}\left[\mathrm{Cl_2}\right]}{k_{2,r}}} \tag{11}$$

$$\left[\mathrm{Cl_3}\right] = \frac{k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\left[\mathrm{Cl_2}\right]^{\frac{3}{2}}}{k_{3,r} + k_{4,f}\left[\mathrm{CO}\right]} \tag{12}$$

3. Substitute the expressions for the reactive intermediates, equations (11) and (12), into the version of equation (8) resulting from step 1 to get the mechanistic rate expression.

$$r_1 = \frac{k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\,[\mathrm{CO}]\left[\mathrm{Cl_2}\right]^{\frac{3}{2}}}{\frac{k_{3,r}}{k_{4,f}} + [\mathrm{CO}]} \tag{13}$$

Simplification and Discussion

Combining the rate coefficients as shown in equations (14) and (15) yields the rate expression in terms of two apparent rate coefficients, equation (16).

$$k = k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}} \tag{14}$$

$$k' = \frac{k_{3,r}}{k_{4,f}} \tag{15}$$

$$r_1 = \frac{k\left[\mathrm{Cl_2}\right]^{\frac{3}{2}}[\mathrm{CO}]}{k' + [\mathrm{CO}]} \tag{16}$$

The effective rate coefficients, k and k', will display Arrhenius temperature dependence (because they are products of true rate coefficients raised to constant powers). There are two limiting forms of the rate expression. If the concentration of CO is much, much greater than k', the rate only depends on the concentration of Cl_2, equation (17). However, if k' is much, much greater than the concentration of CO, the rate depends on the concentrations of both Cl_2 and CO as shown equation (18). In this case, the two apparent rate coefficients can be combined, as shown.

$$r_1 = k\left[\mathrm{Cl_2}\right]^{\frac{3}{2}} \tag{17}$$

$$r_1 = \frac{k}{k'} \left[\mathrm{Cl_2}\right]^{\frac{3}{2}} [\mathrm{CO}] = k'' \left[\mathrm{Cl_2}\right]^{\frac{3}{2}} [\mathrm{CO}] \tag{18}$$

Deliverables

If the proposed mechanism is correct, the mechanistic rate expression will have the form shown in equation (16). Two limiting forms are possible for this rate expression as shown in equations (17) and (18).Experimental studies will need to be performed to determine whether any of these rate expressions capture the composition and temperature dependence of the rate with sufficient accuracy.

$$r_1 = \frac{k \left[\mathrm{Cl_2}\right]^{\frac{3}{2}} [\mathrm{CO}]}{k' + [\mathrm{CO}]} \tag{16}$$

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