L18 Steady-State Problems

① In this problem, we will use steady-state approximation to derive the rate law for the formation of CH_4 from the thermal decomposition of CH_3CHO (acetaldehyde):

$$CH_3CHO \rightarrow CH_4 + CO$$

This reaction is known to proceed through a radical chain mechanism.

Step 1: Initiation Step to generate free radical species

$$CH_3CHO \xrightarrow{k_i} \bullet CH_3 + \bullet CHO$$

Step 2a/2b: Propagation Steps to generate product and additional free radicals

$$CH_3CHO + \bullet CH_3 \xrightarrow{k_p} CH_4 + CH_3CO\bullet$$

$$CH_3CO\bullet \xrightarrow{k_{p'}} \bullet CH_3 + CO$$

Step 3: Termination Step to end chain reaction

$$\bullet CH_3 + \bullet CH_3 \xrightarrow{k_t} CH_3CH_3$$

(a) Write an expression for the rate of formation of CH_4 in terms of any of the rate constants or chemical species.

(b) Write a steady-state equation for both $\bullet CH_3$ and $CH_3CO\bullet$ (one for each) (You may neglect the $\bullet CHO$ radical that appears to go nowhere. This mechanism presented is part of a larger mechanism in which $\bullet CHO$ is completely accounted for.)

(c) Use steady-state equations in part (b) to eliminate any intermediates in rate law of part (a). (Hint: begin by adding the two steady-state equations together.) What is the order of acetaldehyde in the final rate law?

(2) The presence of inert gases such as He can affect the rate of gas-phase isomerization. To explain this phenomenon, Frederick Lindemann proposed the Lindemann mechanism:

Isomerization Overall Reaction: $A \rightarrow B$

Step 1: $A + He \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + He$

Step 2: $A^* \xrightarrow{k_2} B$

He collides with A to form a highly-energetic excited state A^*. A^* then rearranges to form B.

(a) Derive an expression for the rate of formation of B in terms of [A], [HE], and any of the rate constants. Assume intermediates are in steady state. (He is not an intermediate. It is a catalyst, and can therefore appear in the final rate law.)

(b) What is the rate law when [He] is small? When [He] is large?

CHALLENGE

(c) Interestingly, in the absence of He, scientists observe that the isomerization reaction is second order at low concentrations of A, but first order at high concentrations of A.

Modify the Lindemann mechanism to account for these observations. Justify your answer.