Reaction Mechanisms, Pathways, Bioreactions, and Bioreactors 7

The next best thing to knowing something is knowing where to find it.

Samuel Johnson (1709–1784)

Overview. One of the main threads that ties this chapter together is the pseudo-steady-state-hypothesis (PSSH) and the concept of active intermediates. We shall use it to develop rate laws for both chemical and biological reactions. We begin by discussing reactions which do not follow elementary rate laws and are not zero, first, or second order. We then show how reactions of this type involve a number of reaction steps, each of which is elementary. After finding the net rates of reaction for each species, we invoke the PSSH to arrive at a rate law that is consistent with experimental observation. After discussing gas-phase reactions, we apply the PSSH to biological reactions, with a focus on enzymatic reactions. Next, the concepts of enzymatic reactions are extended to organisms. Here organism growth kinetics are used in modeling both batch reactors and CSTRs (chemostats). Finally, a physiological-based-pharmacokinetic approach to modeling of the human body is coupled with the enzymatic reactions to develop concentration-time trajectories for the injection of both toxic and nontoxic substances.

7.1 Active Intermediates and Nonelementary Rate Laws

In Chapter 3 a number of simple power law models, that is,

$$-r_A = kC_A^n$$

were presented where n was an integer of 0, 1, or 2 corresponding to a zero-, first-, and second-order reaction. However, a large number of reactions, the orders are either noninteger such as the decomposition of acetaldehyde at 500°C

$$CH_3CHO \rightarrow CH_4 + CO$$

where the rate law is

$$-r_{CH_3CHO} = kC_{CH_3CHO}^{3/2}$$

or of a form where there are concentration terms in both the numerator and denominator such as the formation of HBr from hydrogen and bromine

$$H_2 + Br_2 \rightarrow 2HBr$$

with

$$r_{HBr} = \frac{k_1 C_{H_2} C_{Br_2}^{3/2}}{C_{HBr} + k_2 C_{Br}}$$

Rate laws of this form usually involve a number of elementary reactions and at least one active intermediate. An *active intermediate* is a high-energy molecule that reacts virtually as fast as it is formed. As a result, it is present in very small concentrations. Active intermediates (e.g., A^*) can be formed by collision or interaction with other molecules.

$$A + M \rightarrow A^* + M$$

Properties of an active intermediate A*

Here the activation occurs when translational kinetic energy is transferred into energy stored in internal degrees of freedom, particularly vibrational degrees of freedom.[1] An unstable molecule (i.e., active intermediate) is not formed solely as a consequence of the molecule moving at a high velocity (high translational kinetic energy). The energy must be absorbed into the chemical bonds where high-amplitude oscillations will lead to bond ruptures, molecular rearrangement, and decomposition. In the absence of photochemical effects or similar phenomena, the transfer of translational energy to vibrational energy to produce an active intermediate can occur only as a consequence of molecular collision or interaction. Collision theory is discussed in the *Professional Reference Shelf* in Chapter 3. Other types of active intermediates that can be formed are *free radicals* (one or more unpaired electrons, e.g., $CH_3\bullet$), ionic intermediates (e.g., carbonium ion), and enzyme-substrate complexes, to mention a few.

The idea of an active intermediate was first postulated in 1922 by F. A. Lindermann[2] who used it to explain changes in reaction order with changes in reactant concentrations. Because the active intermediates were so short lived

[1] W. J. Moore, *Physical Chemistry*, (Reading, Mass.: Longman Publishing Group, 1998).

[2] F. A. Lindermann, *Trans. Faraday. Soc.*, *17*, 598 (1922).

and present in such low concentrations, their existence was not really definitively seen until the work of Ahmed Zewail who received the Nobel Prize in 1999 for femtosecond spectroscopy.[3] His work on cyclobutane showed the reaction to form two ethylene molecules did not proceed directly, as shown in Figure 7-1(a), but formed the active intermediate shown in the small trough at the top of the energy reaction coordinate diagram in Figure 7-1(b). As discussed in Chapter 3, an estimation of the barrier height, E, can be obtained using computational software packages such as Spartan, Cerius[2], or Gaussian as discussed in the *Molecular Modeling Web Module* in Chapter 3.

Web Modules

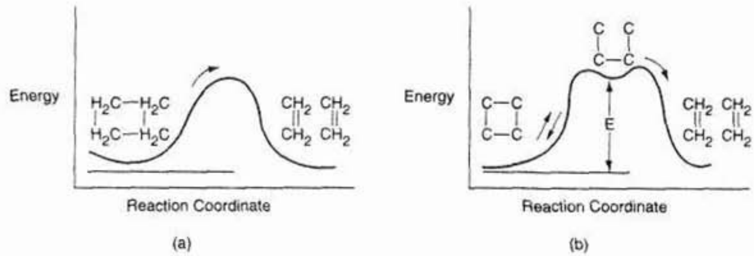


Figure 7-1 Reaction coordinate. Courtesy *Science News*, *156*, 247 (1999).

7.1.1 Pseudo-Steady-State Hypothesis (PSSH)

In the theory of active intermediates, decomposition of the intermediate does not occur instantaneously after internal activation of the molecule; rather, there is a time lag, although infinitesimally small, during which the species remains activated. Zewail's work was the first definitive proof of a gas-phase active intermediate that exists for an infinitesimally short time. Because a reactive intermediate reacts virtually as fast as it is formed, the net rate of formation of an active intermediate (e.g., A*) is zero, i.e.,

PSSH

$$r_{A^*} \equiv 0 \tag{7-1}$$

This condition is also referred to as the Pseudo-Steady-State Hypothesis (PSSH). If the active intermediate appears in n reactions, then

$$\boxed{r_{A^*} = \sum_{i=1}^{n} r_{iA^*} = 0} \tag{7-2}$$

To illustrate how rate laws of this type are formed, we shall first consider the gas-phase decomposition of azomethane, AZO, to give ethane and nitrogen:

$$(CH_3)_2N_2 \longrightarrow C_2H_6 + N_2$$

[3] J. Peterson, *Science News*, *156*, 247 (1999).

Experimental observations[4] show that the rate of formation of etha first order with respect to AZO at pressures greater than 1 atm (relatively concentrations)

$$r_{C_2H_6} \propto C_{AZO}$$

and second order at pressures below 50 mmHg (low concentrations):

$$r_{C_2H_6} \propto C_{AZO}^2$$

To explain this first and second order depending on the concentratic AZO we shall propose the following mechanism consisting of three ele tary reactions.

$$\text{Mechanism}\begin{cases}\text{Reaction 1:} & (CH_3)_2N_2 + (CH_3)_2N_2 \xrightarrow{k_{1AZO^*}} (CH_3)_2N_2 + [(CH_3)_2N \\ \text{Reaction 2:} & [(CH_3)_2N_2]^* + (CH_3)_2N_2 \xrightarrow{k_{2AZO^*}} (CH_3)_2N_2 + (CH_3)_2N \\ \text{Reaction 3:} & [(CH_3)_2N_2]^* \xrightarrow{k_{3AZO^*}} C_2H_6 + N_2\end{cases}$$

In *reaction 1*, two AZO molecules collide and the kinetic energy of one molecule is transferred to internal rotational and vibrational energies o other AZO molecule, and it becomes activated and highly reactive AZO*). In *reaction 2*, the activated molecule (AZO*) is deactivated thr collision with another AZO by transferring its internal energy to increas kinetic energy of the molecules with which AZO* collides. In *reaction 3*, high activated AZO* molecule, which is wildly vibrating, spontanec decomposes into ethane and nitrogen. Because each of the reaction ste elementary, the corresponding rate laws for the active intermediate AZC reactions (1), (2), and (3) are

Note: The specific reaction rates, k, are all defined wrt the active intermediate AZO*.

(1) $$r_{1AZO^*} = k_{1AZO^*} C_{AZO}^2$$

(2) $$r_{2AZO^*} = -k_{2AZO^*} C_{AZO^*} C_{AZO}$$

(3) $$r_{3AZO^*} = -k_{3AZO^*} C_{AZO^*}$$

These rate laws [Equations (7-3) through (7-5)] are pretty much us in the design of any reaction system because the concentration of the a intermediate AZO* is not readily measurable. Consequently, we will use Pseudo-Steady-State-Hypothesis (PSSH) to obtain a rate law in terms of surable concentrations.

We first write the rate of formation of product (with $k_3 \equiv k_{3AZO^*}$)

$$\boxed{r_{C_2H_6} = k_3 C_{AZO^*}}$$

[4] H. C. Ramsperger, *J. Am. Chem. Soc.*, *49*, 912 (1927).

To find the concentration of the active intermediate AZO*, we set the net rate of AZO* equal to zero,[5] $r_{\text{AZO}^*} \equiv 0$.

$$r_{\text{AZO}^*} = r_{1\text{AZO}^*} + r_{2\text{AZO}^*} + r_{3\text{AZO}^*} = 0$$

$$= k_1 C_{\text{AZO}}^2 - k_2 C_{\text{AZO}^*} C_{\text{AZO}} - k_3 C_{\text{AZO}^*} = 0 \tag{7-7}$$

Solving for C_{AZO^*}

$$C_{\text{AZO}^*} = \frac{k_1 C_{\text{AZO}}^2}{k_2 C_{\text{AZO}} + k_3} \tag{7-8}$$

Substituting Equation (7-8) into Equation (7-6)

$$\boxed{r_{\text{C}_2\text{H}_6} = \frac{k_1 k_3 C_{\text{AZO}}^2}{k_2 C_{\text{AZO}} + k_3}} \tag{7-9}$$

At low AZO concentrations,

$$k_2 C_{\text{AZO}} \ll k_3$$

for which case we obtain the following second-order rate law:

$$r_{\text{C}_2\text{H}_6} = k_1 C_{\text{AZO}}^2$$

At high concentrations

$$k_2 C_{\text{AZO}} \gg k_3$$

in which case the rate expression follows first-order kinetics,

$$r_{\text{C}_2\text{H}_6} = \frac{k_1 k_3}{k_2} C_{\text{AZO}} = k C_{\text{AZO}}$$

In describing reaction orders for this equation, one would say the reaction is *apparent first order* at high azomethane concentrations and *apparent second order* at low azomethane concentrations.

The PSSH can also explain why one observes so many first-order reactions such as

$$(\text{CH}_3)_2\text{O} \rightarrow \text{CH}_4 + \text{H}_2 + \text{CO}$$

[5] For further elaboration on this section, see R. Aris, *Am. Sci.*, *58*, 419 (1970).

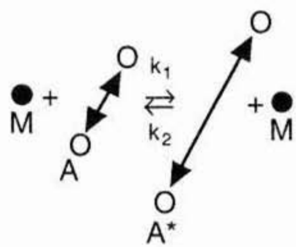
Symbolically this reaction will be represented as A going to product P, that is,

$$A \rightarrow P$$

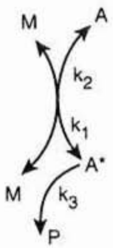
with

$$-r_A = kC_A$$

The reaction is first order but the reaction is not elementary. The reaction proceeds by first forming an active intermediate, A*, from the collision of the reactant molecule and an inert molecule of M. Either this wildly oscillating active intermediate is deactivated by collision with inert M, or it decomposes to form product.



Reaction pathways



The mechanism consists of the three elementary reactions:

Activation (1) $A + M \xrightarrow{k_1} A^* + M$

Deactivation (2) $A^* + M \xrightarrow{k_2} A + M$

Decomposition (3) $A^* \xrightarrow{k_3} P$

Writing the rate of formation of product

$$r_P = k_3 C_{A^*}$$

and using the PSSH to find the concentrations of A* in a manner similar to the azomethane decomposition described earlier, the rate law can be shown to be

$$r_P = -r_A = \frac{k_3 k_1 C_A C_M}{k_2 C_M + k_3} \tag{7-10}$$

Because the concentration of the inert M is constant, we let

$$k = \frac{k_1 k_3 C_M}{k_2 C_M + k_3} \tag{7-11}$$

to obtain the first-order rate law

$$-r_A = kC_A$$

First-order rate law for a nonelementary reaction

Consequently, we see the reaction

$$A \rightarrow P$$

follows an elementary rate law but is not an elementary reaction.

7.1.2 Searching for a Mechanism

In many instances the rate data are correlated before a mechanism is found. It is a normal procedure to reduce the additive constant in the denominator to 1. We therefore divide the numerator and denominator of Equation (7-9) by k_3 to obtain

$$\boxed{r_{C_2H_6} = \frac{k_1 C_{AZO}^2}{1 + k' C_{AZO}}} \tag{7-12}$$

General Considerations. The rules of thumb listed in Table 7-1 may be of some help in the development of a mechanism that is consistent with the experimental rate law. Upon application of Table 7-1 to the azomethane example just discussed, we see the following from rate equation (7-12):

1. The active intermediate, AZO*, collides with azomethane, AZO [Reaction 2], resulting in the concentration of AZO in the denominator.
2. AZO* decomposes spontaneously [Reaction 3], resulting in a constant in the denominator of the rate expression.
3. The appearance of AZO in the numerator suggests that the active intermediate AZO* is formed from AZO. Referring to Reaction 1, we see that this case is indeed true.

TABLE 7-1. RULES OF THUMB FOR DEVELOPMENT OF A MECHANISM

1. Species having the concentration(s) appearing in the *denominator* of the rate law probably collide with the active intermediate, for example,

$$A + A^* \longrightarrow \text{[Collision products]}$$

2. If a constant appears in the *denominator*, one of the reaction steps is probably the spontaneous decomposition of the active intermediate, for example,

$$A^* \longrightarrow \text{[Decomposition products]}$$

3. Species having the concentration(s) appearing in the *numerator* of the rate law probably produce the active intermediate in one of the reaction steps, for example,

$$\text{[reactant]} \longrightarrow A^* + \text{[Other products]}$$

Finding the Reaction Mechanism. Now that a rate law has been synthesized from the experimental data, we shall try to propose a mechanism that is consistent with this rate law. The method of attack will be as given in Table 7-2.

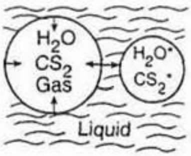
Once the rate law is found, the search for the mechanism begins.

TABLE 7-2. STEPS TO DEDUCE A RATE LAW

1. Assume an active intermediate(s).
2. Postulate a mechanism, utilizing the rate law obtained from experime data, if possible.
3. Model each reaction in the mechanism sequence as an elementary reacti
4. After writing rate laws for the rate of formation of desired product, w the rate laws for each of the active intermediates.
5. Use the PSSH.
6. Eliminate the concentration of the intermediate species in the rate laws solving the simultaneous equations developed in Steps 4 and 5.
7. If the derived rate law does not agree with experimental observat assume a new mechanism and/or intermediates and go to Step 3. A str background in organic and inorganic chemistry is helpful in predicting activated intermediates for the reaction under consideration.

Example 7–1 The Stern–Volmer Equation

Collapsing cavitation microbubble



Light is given off when a high-intensity ultrasonic wave is applied to water.[6] light results from microsize gas bubbles (0.1 mm) being formed by the ultra wave and then being compressed by it. During the compression stage of the the contents of the bubble (e.g., water and whatever else is dissolved in the e.g., CS_2, O_2, N_2) are compressed adiabatically.

This compression gives rise to high temperatures and kinetic energies gas molecules, which through molecular collisions generate active intermediate cause chemical reactions to occur in the bubble.

$$M + H_2O \longrightarrow H_2\dot{O} + M$$

The intensity of the light given off, I, is proportional to the rate of deactivati an activated water molecule that has been formed in the microbubble.

$$H_2O^* \xrightarrow{k} H_2O + h\nu$$

$$\text{Light intensity (I)} \propto (-r_{H_2O^*}) = kC_{H_2O^*}$$

An order-of-magnitude increase in the intensity of sonoluminesce observed when either carbon disulfide or carbon tetrachloride is added to the The intensity of luminescence, I, for the reaction

$$CS_2^* \xrightarrow{k_4} CS_2 + h\nu$$

is

$$I \propto (-r_{CS_2^*}) = k_4 C_{CS_2^*}$$

A similar result exists for CCl_4.

[6] P. K. Chendke and H. S. Fogler, *J. Phys. Chem.*, *87*, 1362 (1983).

However, when an aliphatic alcohol, X, is added to the solution, the intensity decreases with increasing concentration of alcohol. The data are usually reported in terms of a Stern–Volmer plot in which relative intensity is given as a function of alcohol concentration, C_X. (See Figure E7-1.1, where I_0 is the sonoluminescence intensity in the absence of alcohol and I is the sonoluminescence intensity in the presence of alcohol.) Suggest a mechanism consistent with experimental observation.

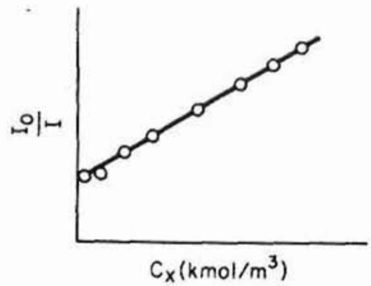


Figure E7-1.1 Ratio of luminescence intensities as a function of Scavenger concentration.

Stern–Volmer plot

Solution

From the linear plot we know that

$$\frac{I_0}{I} = A + BC_X \equiv A + B(X) \qquad \text{(E7-1.1)}$$

where $C_X \equiv (X)$. Inverting yields

$$\frac{I}{I_0} = \frac{1}{A + B(X)} \qquad \text{(E7-1.2)}$$

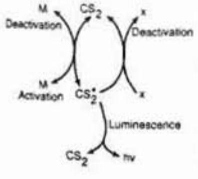
From rule 1 of Table 7-1, the denominator suggests that alcohol (X) collides with the active intermediate:

$$X + \text{Intermediate} \longrightarrow \text{Deactivation products} \qquad \text{(E7-1.3)}$$

Reaction Pathways

The alcohol acts as what is called a scavenger to deactivate the active intermediate. The fact that the addition of CCl_4 or CS_2 increases the intensity of the luminescence,

$$I \propto (CS_2) \qquad \text{(E7-1.4)}$$



leads us to postulate (rule 3 of Table 7-1) that the active intermediate was probably formed from CS_2:

$$M + CS_2 \longrightarrow CS_2^* + M \qquad \text{(E7-1.5)}$$

where M is a third body (CS_2, H_2O, N_2, etc.).

We also know that deactivation can occur by the reverse of Reaction (E7-1.5). Combining this information, we have as our mechanism:

The mechanism

$$\text{Activation:} \quad M + CS_2 \xrightarrow{k_1} CS_2^* + M \tag{E7-1.5}$$

$$\text{Deactivation:} \quad M + CS_2^* \xrightarrow{k_2} CS_2 + M \tag{E7-1.6}$$

$$\text{Deactivation:} \quad X + CS_2^* \xrightarrow{k_3} CS_2 + X \tag{E7-1.3}$$

$$\text{Luminescence:} \quad CS_2^* \xrightarrow{k_4} CS_2 + h\nu \tag{E7-1.7}$$

$$I = k_4(CS_2^*) \tag{E7-1.8}$$

Using the PSSH on CS_2^* yields

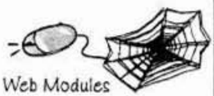
$$r_{CS_2^*} = 0 = k_1(CS_2)(M) - k_2(CS_2^*)(M) - k_3(X)(CS_2^*) - k_4(CS_2^*)$$

Solving for CS_2^* and substituting into Equation (E7-1.8) gives us

$$I = \frac{k_4 k_1 (CS_2)(M)}{k_2(M) + k_3(X) + k_4} \tag{E7-1.9}$$

In the absence of alcohol,

$$I_0 = \frac{k_4 k_1 (CS_2)(M)}{k_2(M) + k_4} \tag{E7-1.10}$$



For constant concentrations of CS_2 and the third body, M, we take a ratio of Equation (E7-1.10) to (E7-1.9):

$$\frac{I_0}{I} = 1 + \frac{k_3}{k_2(M) + k_4}(X) = 1 + k'(X) \tag{E7-1.11}$$

Glow sticks

which is of the same form as that suggested by Figure E7-1.1. Equation (E7-1.11) and similar equations involving scavengers are called *Stern–Volmer equations.*

A discussion of luminescence is continued on the **CD-ROM Web Module, Glow Sticks.** Here, the PSSH is applied to glow sticks. First, a mechanism for the reactions and luminescence is developed. Next, mole balance equations are written on each species and coupled with rate law obtained using the PSSH and the resulting equations are solved and compared with experimental data.

7.1.3 Chain Reactions

Now, let us proceed to some slightly more complex examples involving chain reactions. A chain reaction consists of the following sequence:

Steps in a chain reaction

1. *Initiation:* formation of an active intermediate.
2. *Propagation or chain transfer:* interaction of an active intermediate with the reactant or product to produce another active intermediate.
3. *Termination:* deactivation of the active intermediate to form products.

Example 7–2 PSSH Applied to Thermal Cracking of Ethane

The thermal decomposition of ethane to ethylene, methane, butane, and hydrogen is believed to proceed in the following sequence:

Initiation:

(1) $$C_2H_6 \xrightarrow{k_{C_2H_6}} 2CH_3\bullet \qquad r_{1C_2H_6} = -k_{1C_2H_6}[C_2H_6]$$

Let $k_1 = k_{1C_2H_6}$

Propagation:

(2) $$CH_3\bullet + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5\bullet \qquad r_{2C_2H_6} = -k_2[CH_3\bullet][C_2H_6]$$

(3) $$C_2H_5\bullet \xrightarrow{k_3} C_2H_4 + H\bullet \qquad r_{3C_2H_4} = k_3[C_2H_5\bullet]$$

(4) $$H\bullet + C_2H_6 \xrightarrow{k_4} C_2H_5\bullet + H_2 \qquad r_{4C_2H_6} = -k_4[H\bullet][C_2H_6]$$

Termination:

(5) $$2C_2H_5\bullet \xrightarrow{k_5} C_4H_{10} \qquad r_{5C_2H_5\bullet} = -k_{5C_2H_5}[C_2H_5\bullet]^2$$

Let $k_5 \equiv k_{5C_2H_5\bullet}$

(a) Use the PSSH to derive a rate law for the rate of formation of ethylene.

(b) Compare the PSSH solution in Part **(a)** to that obtained by solving the complete set of ODE mole balances.

Solution

Part (a) ***Developing the Rate Law***

The rate of formation of ethylene (Reaction 3) is

$$\boxed{r_{3C_2H_4} = k_3[C_2H_5\bullet]} \qquad \text{(E7-2.1)}$$

Given the following reaction sequence:

For the active intermediates: $CH_3\bullet$, $C_2H_5\bullet$, $H\bullet$ the net rates of reaction are

$$[\mathbf{C_2H_5\bullet}]: \quad r_{C_2H_5\cdot} = r_{2C_2H_5\cdot} + r_{3C_2H_5\cdot} + r_{4C_2H_5\cdot} + r_{5C_2H_5\cdot} = 0$$

From reaction stoichiometry we have

$$r_{2C_2H_5\cdot} = -r_{2C_2H_6}, \; r_{3C_2H_5\cdot} = -r_{3C_2H_4} \text{ and } r_{4C_2H_5\cdot} = -r_{4C_2H_6}$$

then

$$r_{C_2H_5\cdot} = -r_{2C_2H_6} - r_{3C_2H_4} - r_{4C_2H_6} + r_{5C_2H_5\cdot} = 0 \qquad \text{(E7-2.2)}$$

$$[\mathbf{H\bullet}]: \quad r_{H\cdot} = r_{3H\cdot} + r_{4H\cdot} = r_{3C_2H_4} + r_{4C_2H_6} = 0 \qquad \text{(E7-2.3)}$$

$$[\mathbf{CH_3\bullet}]: \quad r_{CH_3\cdot} = r_{1CH_3\cdot} + r_{2CH_3\cdot} = -2r_{1C_2H_6} + r_{2C_2H_6} = 0 \qquad \text{(E7-2.4)}$$

Substituting the concentrations into the elementary Equation (E7-2.4) gives

$$2k_1[C_2H_6] - k_2[CH_3\bullet][C_2H_6] = 0 \qquad \text{(E7-}$$

Solving for the concentration of the free radical $[CH_3\bullet]$,

$$[CH_3\bullet] = \frac{2k_1}{k_2} \qquad \text{(E7-}$$

Adding Equations (E7-2.2) and (E7-2.3) yields

$$-r_{2C_2H_6} + r_{5C_2H_5\bullet} = 0$$

Substituting for concentrations in the rate laws

$$k_2[CH_3\bullet][C_2H_6] - k_5[C_2H_5\bullet]^2 = 0 \qquad \text{(E7-}$$

PSSH solution

Solving for $[C_2H_5\bullet]$ gives us

$$[C_2H_5\bullet] = \left\{\frac{k_2}{k_5}[CH_3\bullet][C_2H_6]\right\}^{1/2} = \left\{\frac{2k_1k_2}{k_2k_5}[C_2H_6]\right\}^{1/2} = \left\{\frac{2k_1}{k_5}[C_2H_6]\right\}^{1/2} \qquad \text{(E7-}$$

Substituting for $C_2H_5\bullet$ in Equation (E7-2.1) yields the rate of formation of ethy

$$\boxed{r_{C_2H_4} = k_3[C_2H_5\bullet] = k_3\left(\frac{2k_1}{k_5}\right)^{1/2}[C_2H_6]^{1/2}} \qquad \text{(E7-}$$

Next we write the net rate of $H\bullet$ formation in Equation (E7-2.3) in terms of centration

$$k_3[C_2H_5\bullet] - k_4[H\bullet][C_2H_6] = 0$$

Using Equation (E7-2.8) to substitute for $(C_2H_5\bullet)$ gives the concentration o hydrogen radical

$$[H\bullet] = \frac{k_3}{k_4}\left(\frac{2k_1}{k_5}\right)^{1/2}[C_2H_6]^{-1/2} \qquad \text{(E7-2}$$

The rate of disappearance of ethane is

$$r_{C_2H_6} = -k_1[C_2H_6] - k_2[CH_3\bullet][C_2H_6] - k_4[H\bullet][C_2H_6] \qquad \text{(E7-2}$$

Substituting for the concentration of free radicals, the rate law of disappearan ethane is

$$\boxed{-r_{C_2H_6} = (k_1 + 2k_1)(C_2H_6) + k_3\left(\frac{2k_1}{k_5}\right)^{1/2} C_2H_6^{1/2}} \qquad \text{(E7-2}$$

For a constant-volume batch reactor, the combined mole balances and rate laws for disappearance of ethane ($P1$) and the formation of ethylene ($P5$) are

$$\frac{dC_{P1}}{dt} = -\left[(3k_1C_{P1}) + k_3\left(\frac{2k_1}{k_5}\right)^{1/2} C_{P1}^{1/2}\right] \tag{E7-2.13}$$

Combined mole balance and rate law using the PSSH

$$\frac{dC_{P5}}{dt} = k_3\left(\frac{2k_1}{k_5}\right)^{1/2} C_{P1}^{1/2} \tag{E7-2.14}$$

The P in $P1$ (i.e., C_{P1}) and $P5$ (i.e., C_{P5}) is to remind us that we have used the PSSH in arriving at these balances.

At 1000 K the specific reaction rates are $k_1 = 1.5 \times 10^{-3}\ \text{s}^{-1}$, $k_2 = 2.3 \times 10^6\ \text{dm}^3/\text{mol}\cdot\text{s}$, $k_3 = 5.71 \times 10^4\ \text{s}^{-1}$, $k_4 = 9.53 \times 10^8\ \text{dm}^3/\text{mol}\cdot\text{s}$, and $k_5 = 3.98 \times 10^9\ \text{dm}^3/\text{mol}\cdot\text{s}$.

For an entering ethane concentration of 0.1 mol/dm^3 and a temperature of 1000 K, Equations (E7-2.13) and (E7-2.14) were solved and the concentrations of ethane, C_{P1}, and ethylene, C_{P5}, are shown as a function of time in Figures E7-2.2 and E7-2.3.

In developing this concentration–time relationship, we used PSSH. However, we can now utilize the techniques described in Chapter 6 to solve the full set of equations for ethane cracking and then compare these results with the much simpler PSSH solutions.

Part (b) *Testing the PSSH for Ethane Cracking*

The thermal cracking of ethane is believed to occur by the reaction sequence given in Part (a). The specific reaction rates are given as a function of temperature:

$k_1 = 10e^{(87{,}500/R)(1/1250 - 1/T)}\text{s}^{-1}$ $\quad k_2 = 8.45 \times 10^6 e^{(13{,}000/R)(1/1250 - 1/T)}\text{dm}^3/\text{mol}\cdot\text{s}$

$k_3 = 3.2 \times 10^6 e^{(40{,}000/R)(1/1250 - 1/T)}\text{s}^{-1}$ $\quad k_4 = 2.53 \times 10^9 e^{(9700/R)(1/1250 - 1/T)}\text{dm}^3/\text{mol}\cdot\text{s}$

$k_5 = 3.98 \times 10^9\ \text{dm}^3/\text{mol}\cdot\text{s}$ $\quad E = 0$

Part (b): Carry out mole balance on every species, solve, and then plot the concentrations of ethane and ethylene as a function of time and compare with the PSSH concentration–time measurements. The initial concentration of ethane is 0.1 mol/dm^3 and the temperature is 1000 K.

Solution Part (b)

Let $1 = C_2H_6$, $2 = CH_3\bullet$, $3 = CH_4$, $4 = C_2H_5\bullet$, $5 = C_2H_4$, $6 = H\bullet$, $7 = H_2$, and $8 = C_4H_{10}$. The combined mole balances and rate laws become

$$(\mathbf{C_2H_6}):\quad \frac{dC_1}{dt} = -k_1C_1 - k_2C_1C_2 - k_4C_1C_6 \tag{E7-2.15}$$

Full numerical solution

$$(\mathbf{CH_3\bullet}):\quad \frac{dC_2}{dt} = 2k_1C_1 - k_2C_2C_1 \tag{E7-2.16}$$

$$(\mathbf{CH_4}):\quad \frac{dC_3}{dt} = k_2 C_1 C_2 \tag{E7-2.17}$$

$$(\mathbf{C_2H_5\bullet}):\quad \frac{dC_4}{dt} = k_2 C_1 C_2 - k_3 C_4 + k_4 C_1 C_6 - k_5 C_4^2 \tag{E7-2.18}$$

$$(\mathbf{C_2H_4}):\quad \frac{dC_5}{dt} = k_3 C_4 \tag{E7-2.19}$$

$$(\mathbf{H\bullet}):\quad \frac{dC_6}{dt} = k_3 C_4 - k_4 C_1 C_6 \tag{E7-2.20}$$

$$(\mathbf{H_2}):\quad \frac{dC_7}{dt} = k_4 C_1 C_6 \tag{E7-2.21}$$

$$(\mathbf{C_4H_{10}}):\quad \frac{dC_8}{dt} = \frac{1}{2} k_5 C_4^2 \tag{E7-2.22}$$

The Polymath program is given in Table E7-2.1.

TABLE E7-2.1. POLYMATH PROGRAM

POLYMATH Results
Example 7-2 PSSH Applied to Thermal Cracking of Ethane 08-18-2004, Rev5.1.232
ODE Report (STIFF)

```
Differential equations as entered by the user
 [1]  d(C1)/d(t) = -k1*C1-k2*C1*C2-k4*C1*C6
 [2]  d(C2)/d(t) = 2*k1*C1-k2*C1*C2
 [3]  d(C6)/d(t) = k3*C4-k4*C6*C1
 [4]  d(C4)/d(t) = k2*C1*C2-k3*C4+k4*C6*C1-k5*C4^2
 [5]  d(C7)/d(t) = k4*C1*C6
 [6]  d(C3)/d(t) = k2*C1*C2
 [7]  d(C5)/d(t) = k3*C4
 [8]  d(C8)/d(t) = 0.5*k5*C4^2
 [9]  d(CP5)/d(t) = k3*(2*k1/k5)^0.5*CP1^0.5
 [10] d(CP1)/d(t) = -k1*CP1-2*k1*CP1-(k3*(2*k1/k5)^0.5)*(CP1^0.5)

Explicit equations as entered by the user
 [1]  k5 = 3980000000
 [2]  T = 1000
 [3]  k1 = 10*exp((87500/1.987)*(1/1250-1/T))
 [4]  k2 = 8450000*exp((13000/1.987)*(1/1250-1/T))
 [5]  k4 = 2530000000*exp((9700/1.987)*(1/1250-1/T))
 [6]  k3 = 3200000*exp((40000/1.987)*(1/1250-1/T))
```

Living Example Problem

Figure E7-2.1 shows the concentration time trajectory for $CH_3\bullet$ (i.e., C_2). One notes a flat plateau where the PSSH is valid. Figure E7-2.2 shows a comparison of the concentration–time trajectory for ethane calculated from the PSSH (C_{P1}) with the ethane trajectory (C_1) calculated from solving the mole balance Equations (E7-2.13) through (E7-2.22). Figure E7-2.3 shows a similar comparison for ethylene (C_{P5}) and (C_5). One notes that the curves are identical, indicating the validity of the PSSH under these conditions. Figure E7-2.4 shows a comparison of the concentration–time trajectories for methane (C_3) and butane (C_8). Problem P7-2(a) explores the temperature for which the PSSH is valid for the cracking of ethane.

Note: Curves for C_1 and C_{P1} are virtually identical.

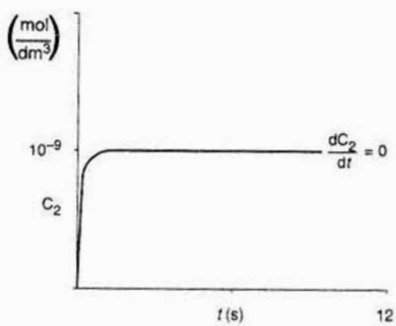


Figure E7-2.1 Concentration of active intermediate $CH_3\bullet$ as a function of time.

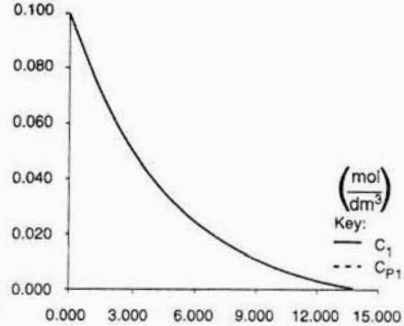


Figure E7-2.2 Comparison of concentration–time trajectories for ethane.

Note: Curves for C_5 and C_{P5} are virtually identical.

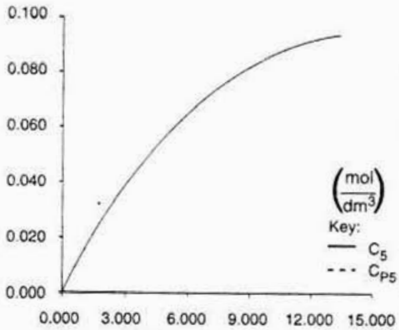


Figure E7-2.3 Comparison of concentration–time trajectory for ethylene.

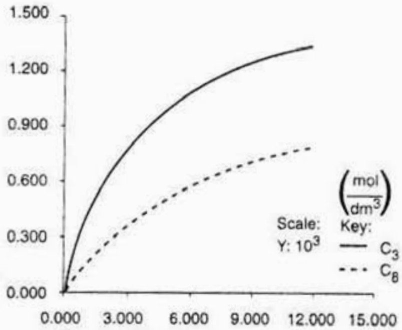


Figure E7-2.4 Comparison of concentration–time trajectories for methane (C_3) and butane (C_8).

7.1.4 Reaction Pathways

Reaction pathways help see the connection of all interacting species for multiple reactions. We have already seen two relatively simple reaction pathways, one to explain the first-order rate law, $-r_A = kC_A$, ($M + A \rightarrow A^* + M$) and one for the sonoluminescence of CS_2 in Example 7-1. We now will develop reaction pathways for ethane cracking and for smog generation.

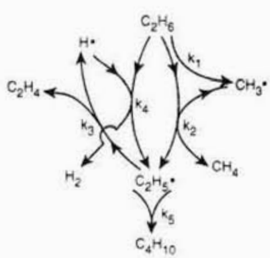


Figure 7-2 Pathway of ethane cracking.

Ethane Cracking. With the increase in computing power, more and m analyses involving free-radical reactions as intermediates are carried out us the coupled sets of differential equations (cf. Example 7-2). The key in such analyses is to identify which intermediate reactions are important in overall sequence in predicting the end products. Once the key reactions identified, one can sketch the pathways in a manner similar to that shown the ethane cracking in Example 7-2 where Reactions 1 through 5 are show Figure 7-2.

Web Modules

Smog Formation. In Chapter 1, Problem P1-14, in the **CD-ROM Sr Web Module**, we discussed a very simple model for smog removal in the L basin by a Santa Ana wind. We will now look a little deeper into the chemi of smog formation. Nitrogen and oxygen react to form nitric oxide in the inder of automobile engines. The NO from automobile exhaust is oxidize NO_2 in the presence of peroxide radicals.

$$RO\dot{O} + NO \xrightarrow{k_1} \dot{R}O + NO_2$$

Nitrogen dioxide is then decomposed photochemically to give nascent oxy

$$NO_2 + h\nu \xrightarrow{k_2} NO + O$$

which reacts to form ozone

$$O + O_2 \xrightarrow{k_3} O_3$$

The ozone then becomes involved in a whole series of reactions with hy carbons in the atmosphere to form aldehydes, various free radicals, and o intermediates, which react further to produce undesirable products in pollution:

$$\text{Ozone} + \text{Olefin} \longrightarrow \text{Aldehydes} + \text{Free radicals}$$

$$O_3 + RCH{=}CHR \xrightarrow{k_4} RCHO + \dot{R}O + H\dot{C}O$$

$$\xrightarrow[h\nu]{k_5} \dot{R} + H\dot{C}O$$

One specific example is the reaction of ozone with 1,3-butadiene to f acrolein and formaldehyde, which are *severe eye irritants*.

Eye irritants

$$\frac{2}{3}O_3 + CH_2{=}CHCH{=}CH_2 \xrightarrow[h\nu]{k_6} CH_2{=}CHCHO + HCHO$$

By regenerating NO_2, more ozone can be formed and the cycle continued. regeneration may be accomplished through the reaction of NO with the radicals in the atmosphere Reaction (R1). For example, the free radical formed in Reaction (R4) can react with O_2 to give the peroxy free radical,

$$\dot{R} + O_2 \xrightarrow{k_7} RO\dot{O} \tag{R7}$$

The coupling of the preceding reactions is shown schematically in Figure 7-3.

We see that the cycle has been completed and that with a relatively small amount of nitrogen oxides, a large amount of pollutants can be produced. Of course, many other reactions are taking place, so do not be misled by the brevity of the preceding discussion; it does, however, serve to present, in rough outline, the role of nitrogen oxides in air pollution.

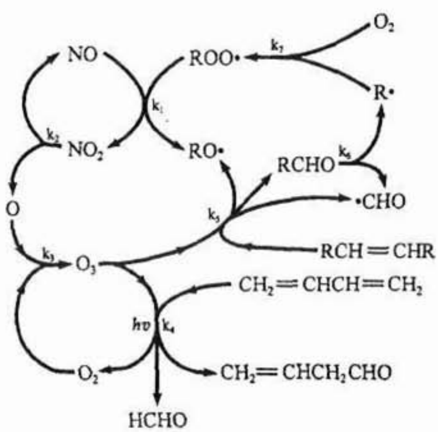


Figure 7-3 Reaction pathways in smog formation.

Metabolic Pathways. Reaction pathways find their greatest use in metabolic pathways where the various steps are catalyzed by enzymes. The metabolism of alcohol is catalyzed by a different enzyme in each step.