Kinetics of Reversible Consecutive Reactions

Tae Jun Park

Department of Chemistry, Dongguk University, Seoul 100-715, Korea. E-mail: tjpark@dgu.edu
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Rate equations are exactly solved for the reversible consecutive reaction of the first-order and the time-dependence of concentrations is analytically determined for species in the reaction. With the assumption of pseudo first-order reaction, the calculation applies and determines the concentration of product accurately and explicitly as a function of time in the unimolecular decomposition of Lindemann and in the enzyme catalysis of Michaelis-Menten whose rate laws have been approximated in terms of reactant concentrations by the steady-state approximation.

Key Words : Consecutive reaction, Unimolecular, Lindemann mechanism, Enzyme catalysis

Introduction

Mechanisms and rate laws of most chemical reactions can be described based on reversible, consecutive or parallel processes whose reaction rates are determined in detail as functions of time provided that they consist of the first-order or pseudo first-order steps. Concentrations in terms of time for species involved in these simple processes are easily obtained mathematically and the exact results are found in usual chemical kinetics texts. However many realistic reactions in fact contain the variety of combinations of the three rudimentary processes aforementioned and this complicates solving rate equations analytically and makes it difficult determining time-dependence of rates accurately. Approximate methods thus have been developed and introduced to handle these reactions. A typical example is the steady-state approximation (SSA) which is often used to describe reactions in which reversible processes are combined with consecutive steps. It has been developed from the first-order reversible consecutive reaction which is represented by $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \overset{k_2}{\rightarrow} C$. If the rate of consumption of B is much greater than its rate of formation ($k_2 \gg k_1$) in the reaction scheme, the concentration of B may be presumed to change little with time and can be estimated in terms of reactant concentration from the assumption. The overall rate of reaction is then evaluated using the approximate concentration without detailed integration of rate equations. This simple but efficient technique is widely applied in reactions consisting with many steps to determine rates approximately. Examples are the unimolecular decomposition known for Lindemann mechanism and the enzyme catalysis of Michaelis-Menten.[1]

The rate of reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \overset{k_2}{\rightarrow} C$, if it is obtained fully as a function of time, can be extended under the pseudo first-order reaction condition to precisely determine the time-dependent behavior of reactions obeying mechanism of Lindemann or of Michaelis-Menten. Analytical solution to the rate equations of these reactions, however, has not been reported and the detailed time-dependence of concentrations is not known yet within the author's knowledge.

In this work, rate equations of the first-order reversible consecutive reaction are exactly solved and two sample calculations are performed with different set of rate constants to show how concentrations depend on time in detail. The derivations are applied to reactions of the named mechanisms to calculate concentrations of products analytically and are used to check the approximate rate laws by SSA for validity and limitations. Then a brief summary concludes the article.

Theoretical Development

Rate of Reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \overset{k_2}{\rightarrow} C$**.** Rate equations of species involved in the reversible consecutive reaction are given

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

$$\frac{d[B]}{dt} = k_1[A] - (k_{-1} + k_2)[B]$$

$$\frac{d[C]}{dt} = k_2[B], \tag{1}$$

where $[A]_0 = [A] + [B] + [C]$. To solve Eq. (1), $y(t)$ is defined as the ratio of concentrations of B over A

$$y(t) \equiv \frac{[B](t)}{[A](t)}, \tag{2}$$

which satisfies the differential equation

$$\frac{dy}{dt} = -k_{-1}y^2 + (k_1 - k_{-1} - k_2)y + k_1. \tag{3}$$

With a few algebraic manipulations and using $\Delta_F = -(k_1 - k_{-1} - k_2)^2 - 4k_1k_{-1}$, Eq. (3) can be integrated to yield[2]

$$y(t) = \frac{2k_1 \tanh\frac{\sqrt{-\Delta_F}}{2}t}{\sqrt{-\Delta_F} - (k_1 - k_2 - k_{-1})\tanh\frac{\sqrt{-\Delta_F}}{2}t} \,. \qquad (4)$$

Since we assume that the initial concentration of A is $[A]_0$ and that $[B]_0 = [C]_0 = 0$, $y(0)$ is identified to be equal to 0. The rate equation of A is changed by substituting Eqs. (2) and (4) into the first differential equation of Eq. (1)

$$\frac{1}{[A]}\frac{d[A]}{dt} = k_1 \left(\frac{(k_1 - k_2 + k_{-1})\tanh\frac{\sqrt{-\Delta_F}}{2}t - \sqrt{-\Delta_F}}{\sqrt{-\Delta_F} - (k_1 - k_2 - k_{-1})\tanh\frac{\sqrt{-\Delta_F}}{2}t} \right) \qquad (5)$$

The solution to this equation gives the concentration of A as a function of time

$$[A](t) = [A]_0 e^{-\frac{k_F}{2}t}\left(\cosh\frac{\sqrt{-\Delta_F}}{2}t - \frac{(k_1 - k_{-1} - k_2)}{\sqrt{-\Delta_F}}\sinh\frac{\sqrt{-\Delta_F}}{2}t \right). \qquad (6)$$

with $k_F = k_1 + k_{-1} + k_2$. Concentration of B is derived from Eqs. (2), (4) and (6)

$$[B](t) = \frac{2k_1}{\sqrt{-\Delta_F}}[A]_0 e^{-\frac{k_F}{2}t}\sinh\frac{\sqrt{-\Delta_F}}{2}t \qquad (7)$$

and by mass balance, $[C](t)$ is

$$[C](t) = [A]_0\left[1 - e^{-\frac{k_F}{2}t}\left(\cosh\frac{\sqrt{-\Delta_F}}{2}t + \frac{k_F}{\sqrt{-\Delta_F}}\sinh\frac{\sqrt{-\Delta_F}}{2}t \right) \right] \qquad (8)$$

This development thus analytically determines the concentrations and reproduces corresponding results of the consecutive reaction without the reverse step by setting $k_{-1} = 0$. When $k_2 \gg k_1$, Eq. (7) reduces to

$$[B] \approx \frac{k_1}{k_{-1} + k_2}[A](1 - e^{-(k_{-1} + k_2)t}) \approx \frac{k_1}{k_{-1} + k_2}[A], \qquad (9)$$

which yields $\frac{d[B]}{dt} \approx 0$, the steady-state condition for intermediate B.

Based on the derivations, two sample calculations are done with different set of rate constants and results are shown in Figure 1 and Figure 2. Exact solution for $k_1 > k_{-1} \gg k_2$ is shown in Figure 1 where the intermediate B rapidly reaches a concentration close to $[A]_0$ and then slowly decreases. SSA is not available and is invalid since [B] is held substantial for a long time. Eqs. (6)-(8) can only provide with exact concentrations as functions of time.

Figure 2 shows concentrations for $k_2 \gg k_1$ in which both the rate of formation and the concentration of B are close to 0 during the reaction. This meets the condition under which SSA may be considered appropriate. But the concentration
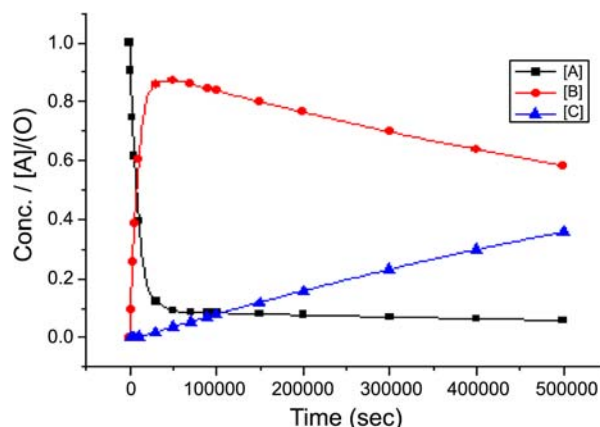

Figure 1. Concentration of A, B and C calculated by Eqs. (6)-(8) with $k_1 = 1.0 \times 10^{-4}$, $k_{-1} = 1.0 \times 10^{-5}$, and $k_2 = 1.0 \times 10^{-6}$.
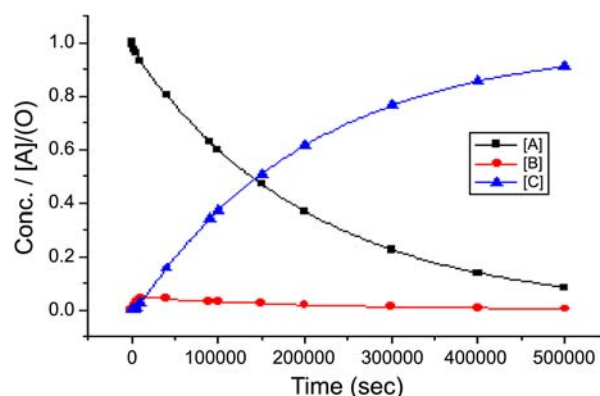

Figure 2. Concentration of A, B and C calculated by Eqs. (6)-(8) with $k_1 = 1.0 \times 10^{-5}$, $k_{-1} = 1.0 \times 10^{-4}$, and $k_2 = 1.0 \times 10^{-4}$.

of B cannot be determined accurately because the initial rise of [B] is not adequately produced by the approximation.

Time-Dependent Behavior of Simple Catalytic Reactions. Typical examples of the use of SSA are the unimolecular decomposition of Lindemann and the enzyme catalysis of Michaelis-Menten. And these reactions contain substances which are neither produced nor consumed in the process, namely, catalysts. Since the concentrations of catalysts may change little during the reaction, accurate rate behavior can be described by the previous derivations under the pseudo first-order condition.

Consider the unimolecular decomposition reaction of Lindemann by whom the mechanism was simply proposed to be

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \overset{k_2}{\longrightarrow} P, \qquad (10)$$
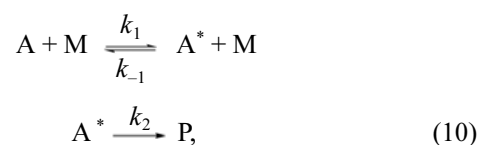
where M represents the collision partner which can act to energize reactant A. M may be regarded as a catalyst and its concentration is assumed to maintain constant. Cole and Wilder[3] presented an approximate solution of the more

general three-step Lindemann model, but the exact solution to rate equations of the above scheme has not been reported yet.

Rate equations for the reaction are solved analytically in this work and the concentration of product P is obtained as follows;

$$[P](t) = [A]_0 \left[1 - e^{-\frac{k_M}{2}t} \left(\cosh\frac{\sqrt{-\Delta_M}}{2}t + \frac{k_M}{\sqrt{-\Delta_M}}\sinh\frac{\sqrt{-\Delta_M}}{2}t \right) \right],$$

(11)

in which $k_M = K_1 + K_{-1} + k_2$ and $\Delta_M = -(K_1 - k_2 - K_{-1})^2 - 4K_1K_{-1}$. Rate constants for the pseudo first-order steps are replaced with $K_1 = k_1[M]$ and $K_{-1} = k_{-1}[M]$ respectively where [M] is included as a constant parameter. The concentration, $[P](t)$ thus obtained, demonstrates accurate time-dependence of the concentration of decomposition product that can not be determined by rate laws of SSA. When $k_2 \gg K_1$ and t is large, the result of SSA would be reproduced as

$$\left. \frac{d[P]}{dt} \right|_{t\to\infty} \approx \frac{k_2k_1[M]}{k_2+k_{-1}[M]}[A].$$

The second reaction of example is the simple enzyme catalysis of Michaelis-Menten

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X$$

$$X \xrightarrow{k_2} P + E,$$

(12)
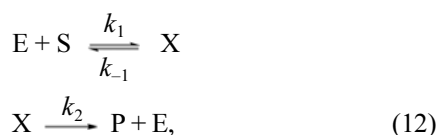
Here E and S represent an enzyme and a substrate respectively. Provided that the concentration of the enzyme is constant, the product concentration $[P](t)$ is again explicitly determined as

$$[P](t) = [S]_0 \left[1 - e^{-\frac{k_E}{2}t} \left(\cosh\frac{\sqrt{-\Delta_E}}{2}t + \frac{k_E}{\sqrt{-\Delta_E}}\sinh\frac{\sqrt{-\Delta_E}}{2}t \right) \right],$$

(13)

where $k_E = K_1 + k_{-1} + k_2$, $\Delta_E = -(K_1 - k_2 - k_{-1})^2 - 4K_1k_{-1}$, and $K_1 = k_1[E]_0$ respectively. Figure 3 shows the time-dependence of concentrations determined by Eq. (13) and by corresponding formulas which is in excellent agreement with exact numerical calculation.[4]
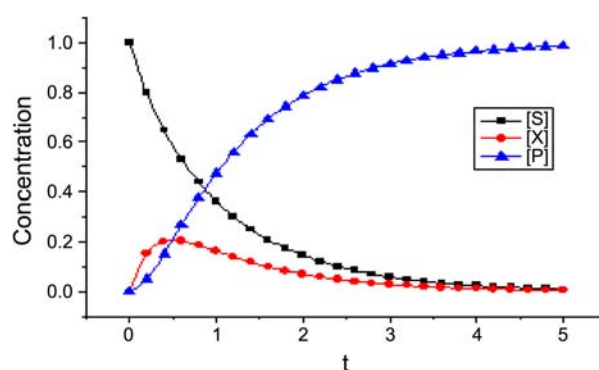

Figure 3. Concentration of S, X, and P that are determined analytically using the same rate constants and initial concentration as those of Ref. 3. Concentration of enzyme is assumed to maintain constant.

Conclusion

In the present work, rate equations are exactly solved for the reversible consecutive reaction of the first-order and the concentrations of species are analytically determined in the reaction. With the assumption of pseudo first-order reaction, the calculation directly applies and determines the concentration of product as a function of time in the unimolecular decomposition and in the enzyme catalysis whose rate laws have been obtained approximately only in terms of reactant concentrations by SSA. The current calculation reproduces the steady-state results for these reactions when t is large and confirms that the approximation is only valid at the time long after reactions started.

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