

## Kinetics of Two-step Irreversible Consecutive First Order Reactions

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Analytical expressions for the concentrations and the rates of formation of intermediate and product are known for consecutive reactions. These expressions break down when the rate constants for the first and the second steps are equal. Using the approximate method and the l'Hospital rule, equations have been derived for the concentrations and the rates of formation of the intermediate and the product and also the time when the rate of product formation is a maximum, when the rate constants of the two steps are equal.

A two-step irreversible consecutive reaction<sup>1</sup> can be represented as



If the initial concentration of A is  $[A]_0$  and its concentration at time  $t$  is  $[A]$ , then the rate equation for the disappearance of A is

$$-d[A]/dt = k_1 [A] \quad (2)$$

Integration of this simple first order equation, subject to the condition that  $[A] = [A]_0$  when  $t = 0$ , gives

$$[A] = [A]_0 \exp(-k_1 t) \quad (3)$$

The net rate of formation of X is

$$d[X]/dt = k_1[A] - k_2[X] \quad (4)$$

Inserting equation (3) in equation (4) gives

$$d[X]/dt = k_1[A]_0 \exp(-k_1 t) - k_2[X] \quad (5)$$

Integrating the above expression gives

$$[X] = [A]_0 \frac{k_1}{(k_2 - k_1)} \{ \exp(-k_1 t) - \exp(-k_2 t) \} \quad (6)$$

The concentration of  $[X]$  goes through a maximum. The maximum can be mathematically represented as

$$d[X]/dt = 0 \quad (7)$$

Combining equations (6) and (7), we get

$$t_{\max} = \frac{\ln(k_1/k_2)}{(k_1 - k_2)} \quad (8)$$

where,  $t_{\max}$  corresponds to the time when the concentration of X, the intermediate, is a maximum, which is also the moment at which the rate of formation of the final product Z is maximum. If the intermediate X and the final product Z are initially absent, at any time  $t$ , by stoichiometric balance,

$$[A] + [X] + [Z] = [A]_0 \quad (9)$$

so that

$$[Z] = [A]_0 - [A] - [X] \quad (10)$$

Inserting equations (3) and (6) in equation (10) leads to

$$[Z] = \frac{[A]_0}{(k_2 - k_1)} [k_2 \{ 1 - \exp(-k_1 t) \} - k_1 \{ 1 - \exp(-k_2 t) \}] \quad (11)$$

These equations apply to radioactivity<sup>2</sup> where two successive disintegrations are involved and also to chemical reactions. An example for irreversible first order consecutive reaction is the thermal isomerisation<sup>3</sup> of 1,1-dicyclopropylethylene to produce 1-cyclopropylcyclopentene, which further isomerises to give bicyclo[3.3.0]pent-1-ene.

### Results and Discussion

Equations (6), (8) and (11) contain terms such as  $(k_2 - k_1)$  and/or  $\ln(k_1/k_2)$ . When  $k_1 = k_2$ , these equations give rise to indeterminate forms<sup>4</sup> of the type 0/0. To treat this special case, when  $k_1 = k_2$ , expressions for  $t_{\max}$ ,  $[X]$ ,  $[Z]$ ,  $d[X]/dt$  and  $d[Z]/dt$  have been derived using the approximate method<sup>5</sup> and the de l'Hospital rule<sup>6</sup>.

**Derivation for  $t_{\max}$ :** The expression for  $t_{\max}$  when  $k_1 = k_2$  is an indeterminate quantity of the form 0/0. Using the approximate method an expression for  $t_{\max}$  is derived when  $k_1 \approx k_2$  i.e. the difference  $(k_1 - k_2)$  is taken as very small.

The value of  $\ln(1+x)$  can be found by summing the series<sup>7</sup>,

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} \dots \dots \quad (12)$$

when  $x^2 < 1$ . When  $x$  is very small, the terms containing higher powers may be neglected and the series truncated as

$$\ln(1+x) \approx x \quad (13)$$

The term  $\ln(k_1/k_2)$  in equation (8) can be written as

$$\ln \left\{ 1 + \frac{(k_1 - k_2)}{k_2} \right\}$$

and approximated as

$$\ln \left\{ 1 + \frac{(k_1 - k_2)}{k_2} \right\} \approx \frac{(k_1 - k_2)}{k_2} \quad (14)$$

The approximation is valid as  $(k_1 - k_2)$  is very small. Therefore,

$$t_{\max} = \frac{\ln(k_1/k_2)}{(k_1 - k_2)}$$

$$\approx \frac{1}{k_2} \frac{(k_1 - k_2)}{(k_1 - k_2)} \approx \frac{1}{k_2} \quad (15)$$

In the limit  $k_2 \rightarrow k_1$ , one can write

$$t_{\max} = \frac{1}{k_1} = \frac{1}{k_2} \quad (16)$$

This can be verified by numerical examples, by choosing  $k_1$  and  $k_2$  with very small range and calculating  $t_{\max}$  using equation (8).

Equation (16) can also be derived by applying the de l'Hospital rule, which for indeterminates of the type 0/0 is given as follows. If  $f(x)$  and  $g(x)$  are differentiable and  $g(x) \neq 0$  for all  $x$  on some interval  $0 < |x - a| < \delta$ , and if  $\lim_{x \rightarrow a} f(x) = 0$  and  $\lim_{x \rightarrow a} g(x) = 0$ , then

$$\lim_{x \rightarrow a} \frac{f(x)}{g(x)} = \lim_{x \rightarrow a} \frac{d/dx [f(x)]}{d/dx [g(x)]} \quad (17)$$

Equation (17) is the expression of the de l'Hospital rule. Applying it to equation (8), reduces to

$$\lim_{k_2 \rightarrow k_1} t_{\max} = \frac{d/dk_2 [\ln(k_1/k_2)]}{d/dk_2 [k_1 - k_2]} = 1/k_1 \quad (18)$$

**Derivation for  $d[Z]/dt$  :** The rate of formation of product is given by

$$d[Z]/dt = k_2 [X] \quad (19)$$

Inserting the expression for  $[X]$  from equation (6) in equation (19) gives

$$d[Z]/dt = \frac{[A]_0 k_1 k_2}{(k_2 - k_1)} \{ \exp(-k_1 t) - \exp(-k_2 t) \} \quad (20)$$

When  $k_1 = k_2$ , this equation also becomes indeterminate of the type 0/0. Equation (20) can be rewritten as

$$d[Z]/dt = \frac{[A]_0 k_1 k_2}{(k_2 - k_1)} \{ \exp(-k_2 t) \} \{ \exp(k_2 - k_1)t - 1 \} \quad (21)$$

$e^x$  can be expanded according to the series.

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots \quad (22)$$

when  $x$  is very small, higher power terms can be neglected and the series truncated as

$$e^x \approx 1 + x \quad (23)$$

Similarly,  $\exp \{ (k_2 - k_1)t \}$  can be approximated as

$$\exp \{ (k_2 - k_1)t \} \approx 1 + (k_2 - k_1)t \quad (24)$$

as  $(k_2 - k_1)$  is very small. Inserting equation (24) in equation (21) gives

$$d[Z]/dt = [A]_0 k_1 k_2 \exp(-k_2 t) \quad (25)$$

In the limit  $k_2 \rightarrow k_1$ , equation (25) can be rewritten as

$$d[Z]/dt = [A]_0 k_1^2 t \exp(-k_1 t) \quad (26)$$

The concentration of the intermediate,  $[X]$ , and the rate of product formation,  $d[Z]/dt$ , go through a maximum. Hence, the second derivative of  $[Z]$  with respect to time is equal to zero at  $t_{\max}$ , when the rate of product formation is highest. Differentiating equation (26) with respect to time gives

$$d^2[Z]/dt^2 = 0 = [A]_0 k_1^2 \exp(-k_1 t_{\max}) (1 - k_1 t_{\max}) \quad (27)$$

In equation (27), only the term  $(1 - k_1 t_{\max})$  can be zero, which reduces to equation (16).

Equation (26) can also be derived by applying the de l'Hospital rule. Differentiating the numerator and the denominator of equation (20) with respect to  $k_2$  gives

$$\lim_{k_2 \rightarrow k_1} \frac{d[Z]}{dt} = \frac{[A]_0 k_1 d/dk_2 [k_2 \{ \exp(-k_1 t) - \exp(-k_2 t) \}]}{d/dk_2 [k_2 - k_1]}$$

$$= [A]_0 k_1 [k_2 t \exp(-k_2 t) + \{ \exp(-k_1 t) - \exp(-k_2 t) \}]$$

$$= [A]_0 k_1^2 t \exp(-k_1 t) \quad (28)$$

When  $k_1$  and  $k_2$  are equal or almost equal, expressions for  $[X]$ ,  $d[X]/dt$  and  $[Z]$  can be derived using the principles outlined here. Hence,

$$[X] = [A]_0 k_1 t \exp(-k_1 t) \quad (29)$$

$$d[X]/dt = [A]_0 k_1 \exp(-k_1 t) (1 - k_1 t) \quad (30)$$

$$[Z] = [A]_0 \{ 1 - \exp(-k_1 t) (1 + k_1 t) \} \quad (31)$$

**Conclusion :** In two-step, irreversible, consecutive, first order reactions, when the rate constants of the two steps are identical or almost equal, the integrated expressions for concentrations and rates break down due to terms like  $(k_1 - k_2)$  in the denominator giving rise to indeterminate quantities of the type 0/0. Using the approximate method and the de l'Hospital rule the expressions for the concentrations and the rates when  $k_1 \approx k_2$  have been derived.

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