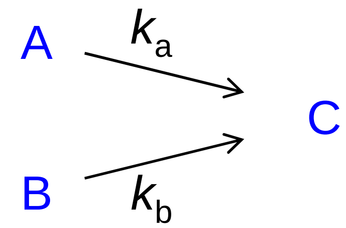
Parallel Reactions – Competing Routes to Product

Consider competitive routes to the same product:

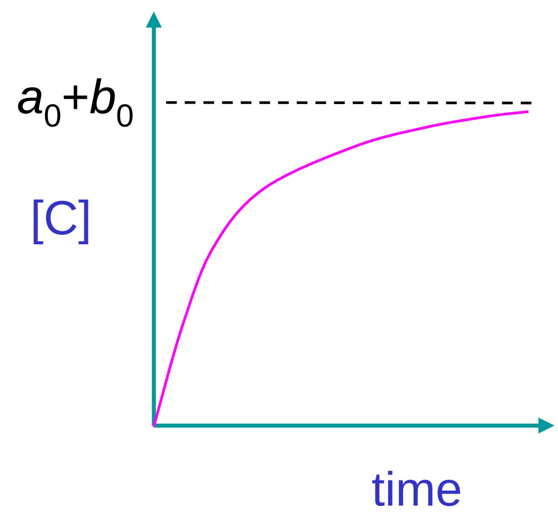


Define a = [A], b = [B], c =[C].

$$-\frac{da}{dt} = k_a a \qquad -\frac{db}{dt} = k_b b \qquad \frac{dc}{dt} = k_a a + k_b b$$

$$\frac{dc}{dt} = k_a a_0 e^{-k_a t} + k_b b_0 e^{-k_b t}$$

$$\Rightarrow c = a_0\left(1 - e^{-k_a t}\right) + b_0\left(1 - e^{-k_b t}\right)$$



Free Radical Clocks

DAVID GRILLER and KEITH U. INGOLD, *Acc. Chem. Res.* 1980, *13,* 317-323
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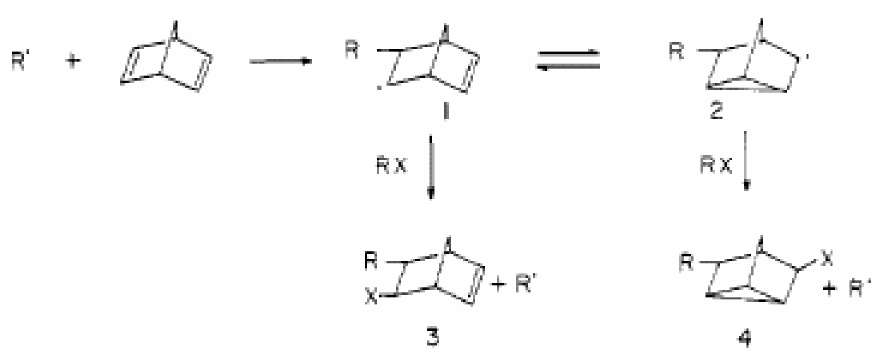
Scheme I



The [3]/[4] product ratio depends on whether the equilibrium between **1** and **2** has been established or not.

$$Me_3CO\cdot \xrightarrow{k_1} Me + Me_2CO$$

$$Me_3CO\cdot \xrightarrow[AH]{k_2} A + Me_3OH$$

$$\frac{k_2}{k_1} = \frac{[Me_3OH]}{[AH][Me_2CO]}$$

If k_1 is known the rate constants k_2 for many different H donors can be found.

Even if k_1 is unknown, the relative rates for AH, BH, etc can be found.

Matrix Method for Complex Reactions

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Z \qquad \frac{da}{dt} = -k_1 a + k_{-1} z, \quad \frac{dz}{dt} = k_1 a - k_{-1} z \quad \Rightarrow \quad \begin{pmatrix} da/dt \\ dz/dt \end{pmatrix} = \begin{pmatrix} -k_1 & k_{-1} \\ k_1 & -k_{-1} \end{pmatrix} \begin{pmatrix} a \\ z \end{pmatrix}$$

$$\frac{d\mathbf{X}}{dt} = \mathbf{K}\,\mathbf{X} \quad \Rightarrow \quad \mathbf{X}_t = e^{\mathbf{K}t}\,\mathbf{X}_0$$

It is necessary to diagonalize X in order to evaluate $e^{\mathrm{K}t}$

$$e^{\mathrm{K}t} = \mathbf{P} e^{\Lambda t} \mathbf{P}^{-1} = \mathbf{P} \begin{pmatrix} e^{\lambda_1 t} & 0 \\ 0 & e^{\lambda_2 t} \end{pmatrix} \mathbf{P}^{-1}$$

Find the eigenvalues by solving the characteristic equation

$$\begin{vmatrix} -k_1 - \lambda & k_{-1} \\ k_1 & -k_{-1} - \lambda \end{vmatrix} = 0 \quad \Rightarrow \quad \lambda = \begin{cases} 0 \\ -(k_1 + k_{-1}) \end{cases}$$

Construct the eigenvectors $\begin{pmatrix} k_{-1} \\ k_1 \end{pmatrix}, \quad \begin{pmatrix} 1 \\ -1 \end{pmatrix}$ and thence $\mathbf{P} = \begin{pmatrix} k_{-1} & 1 \\ k_1 & -1 \end{pmatrix}, \quad \mathbf{P}^{-1} = \frac{1}{k_1 + k_{-1}} \begin{pmatrix} 1 & 1 \\ k_1 & -k_{-1} \end{pmatrix}$

$$\mathbf{X}_t = e^{\mathrm{K}t}\mathbf{X}_0 = \mathbf{P} \begin{pmatrix} 1 & 0 \\ 0 & e^{-(k_1 + k_{-1})t} \end{pmatrix} \mathbf{P}^{-1} \begin{pmatrix} a_0 \\ z_0 \end{pmatrix} \quad \Rightarrow \quad \begin{pmatrix} a \\ z \end{pmatrix} = \frac{a_0}{(k_1 + k_{-1})} \begin{pmatrix} k_{-1} + k_1 e^{-(k_1 + k_{-1})t} \\ k_1 - k_1 e^{-(k_1 + k_{-1})t} \end{pmatrix}$$

$z_0 = 0$

To show $\mathrm{e}^{\mathbf{K}t} = \mathbf{P}\mathrm{e}^{\Lambda t}\mathbf{P}^{-1}$ where $\mathbf{K} = \mathbf{P}\Lambda\mathbf{P}^{-1}$

$$
\begin{aligned}
\mathrm{e}^{\mathbf{K}t} &= 1 + \mathbf{K}t + \tfrac{1}{2}(\mathbf{K}t)^2 + \ldots \\
&= \mathrm{PP}^{-1} + \mathrm{P}\Lambda\mathrm{P}^{-1}t + \tfrac{1}{2}\left(\mathrm{P}\Lambda\mathrm{P}^{-1}\right)\left(\mathrm{P}\Lambda\mathrm{P}^{-1}\right)t^2 + \ldots \\
&= \mathrm{PP}^{-1} + \mathrm{P}\Lambda\mathrm{P}^{-1}t + \tfrac{1}{2}\left(\mathrm{P}\Lambda^2\mathrm{P}^{-1}\right)t^2 + \ldots \\
&= \mathrm{P}\left(1 + \Lambda t + \tfrac{1}{2}\Lambda^2 t^2 + \ldots\right)\mathrm{P}^{-1} \\
&= \mathrm{P}\mathrm{e}^{\Lambda t}\mathrm{P}^{-1}
\end{aligned}
$$

Similarly

$$
\begin{aligned}
\mathrm{e}^{\Lambda} &= 1 + \Lambda + \tfrac{1}{2}\Lambda^2 + \ldots \\
&= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} \lambda_1^2 & 0 & 0 \\ 0 & \lambda_2^2 & 0 \\ 0 & 0 & \lambda_3^2 \end{pmatrix} + \ldots \\
&= \begin{pmatrix} 1 + \lambda_1 + \frac{1}{2}\lambda_1^2 + \ldots & 0 & 0 \\ 0 & 1 + \lambda_2 + \frac{1}{2}\lambda_2^2 + \ldots & 0 \\ 0 & 0 & 1 + \lambda_3 + \frac{1}{2}\lambda_3^2 + \ldots \end{pmatrix} = \begin{pmatrix} \mathrm{e}^{\lambda_1} & 0 & 0 \\ 0 & \mathrm{e}^{\lambda_2} & 0 \\ 0 & 0 & \mathrm{e}^{\lambda_3} \end{pmatrix}
\end{aligned}
$$

To find eigenvalues of $\begin{pmatrix} -k_1 & k_{-1} \\ k_1 & -k_{-1} \end{pmatrix}$ solve the characteristic equation

$$(\mathbf{K}-\lambda\mathbf{1})\mathbf{X}=0$$

$$\begin{vmatrix} -k_1-\lambda & k_{-1} \\ k_1 & -k_{-1}-\lambda \end{vmatrix}=0$$

$$(k_1+\lambda)(k_{-1}+\lambda)-k_1k_{-1}=0$$

$$\lambda^2+\lambda(k_1+k_{-1})=0$$

$$\lambda=0,-(k_1+k_{-1})$$

To find eigenvectors substitute λ into characteristic equation

For $\lambda=0$

$$-k_1a+k_{-1}z=0$$

$$k_1a=k_{-1}z$$

For $\lambda=-(k_1+k_{-1})$

$$\left[-k_1+(k_1+k_{-1})\right]a+k_{-1}z=0$$

$$k_{-1}a+k_{-1}z=0$$

$$a=-z$$

Then combine eigenvectors

$$\varphi_1=\begin{pmatrix} k_{-1} \\ k_1 \end{pmatrix} \qquad \varphi_2=\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\mathbf{P}=\begin{pmatrix} k_{-1} & 1 \\ k_1 & -1 \end{pmatrix},\quad \mathbf{P}^{-1}=\frac{1}{k_1+k_{-1}}\begin{pmatrix} 1 & 1 \\ k_1 & -k_{-1} \end{pmatrix}$$

$$a = \frac{a_0 k_{-1}}{\left(k_1 + k_{-1}\right)} + \frac{a_0 k_1}{\left(k_1 + k_{-1}\right)} \mathrm{e}^{-\left(k_1 + k_{-1}\right)t}$$

$$a_\infty = \frac{a_0 k_{-1}}{\left(k_1 + k_{-1}\right)}$$

$$= \frac{a_0 k_{-1}}{\left(k_1 + k_{-1}\right)} + \left(a_0 - \frac{a_0 k_{-1}}{k_1 + k_{-1}}\right) \mathrm{e}^{-\left(k_1 + k_{-1}\right)t}$$

$$= a_\infty + \left(a - a_\infty\right) \mathrm{e}^{-\left(k_1 + k_{-1}\right)t}$$

Laplace Transforms

The Laplace Transform is an integral transform which can be used to convert differentiation into multiplication.

$$F(s) = \mathfrak{L}\left[f(t)\right] = \int_0^\infty e^{-st} f(t)\, dt \qquad f(t) = \mathfrak{L}^{-1}\left[F(s)\right] = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} e^{st} F(s)\, ds$$

The Laplace variable *s* is complex.

time domain, $f(t)$ $\underset{\mathcal{L}^{-1}}{\overset{\mathcal{L}}{\rightleftharpoons}}$	frequency domain $F(s)$
$f'(t)$	$sF(s) - f(0)$
$\int_0^t f(\tau)\, d\tau$	$\frac{1}{s}F(s)$
e^{-at}	$\frac{1}{s+a}$
$\frac{1}{b-a}\left(e^{-at} - e^{-bt}\right)$	$\frac{1}{(s+a)(s+b)}$

Laplace Transform Method for Complex Reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

$$\frac{da}{dt} = -k_1 a \qquad \frac{db}{dt} = k_1 a - k_2 b \qquad \frac{dc}{dt} = k_2 b$$

$$sF(a) - a_0 = -k_1 F(a)$$

$$sF(b) - b_0 = k_1 F(a) - k_2 F(b)$$

$$sF(c) - c_0 = k_2 F(b)$$

or

$$\begin{pmatrix} s+k_1 & 0 & 0 \\ -k_1 & s+k_2 & 0 \\ 0 & -k_2 & s \end{pmatrix} \begin{pmatrix} F(a) \\ F(b) \\ F(c) \end{pmatrix} = \begin{pmatrix} a_0 \\ b_0 \\ c_0 \end{pmatrix}$$

$$F(a) = \frac{a_0}{(s+k_1)}$$

$$F(b) = \frac{a_0 k_1}{(s+k_1)(s+k_2)} + \frac{b_0}{(s+k_2)}$$

$$F(c) = \frac{a_0 k_1 k_2}{s(s+k_1)(s+k_2)} + \frac{b_0 k_2}{s(s+k_2)} + \frac{c_0}{s}$$

$$a = a_0\, \mathrm{e}^{-k_1 t}$$

$$b = a_0 \frac{k_1}{k_2 - k_1}\left[\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}\right] + b_0\, \mathrm{e}^{-k_2 t}$$

$$c = a_0 \left[1 - \frac{k_2}{k_2 - k_1}\mathrm{e}^{-k_1 t} + \frac{k_1}{k_2 - k_1}\mathrm{e}^{-k_2 t}\right]$$

$$+ b_0 \frac{k_2}{k_1}\left(1 - \mathrm{e}^{-k_2 t}\right) + c_0$$

To Solve Simultaneous Equations by Cramer's Rule

$$\begin{pmatrix} s+k_1 & 0 & 0 \\ -k_1 & s+k_2 & 0 \\ 0 & -k_2 & s \end{pmatrix}\begin{pmatrix} F(a) \\ F(b) \\ F(c) \end{pmatrix} = \begin{pmatrix} a_0 \\ b_0 \\ c_0 \end{pmatrix}$$

$$\Delta = \begin{vmatrix} s+k_1 & 0 & 0 \\ -k_1 & s+k_2 & 0 \\ 0 & -k_2 & s \end{vmatrix} = (s+k_1)(s+k_2)s$$

$$F(a) = \frac{1}{\Delta}\begin{vmatrix} a_0 & 0 & 0 \\ b_0 & s+k_2 & 0 \\ c_0 & -k_2 & s \end{vmatrix} = \frac{a_0(s+k_2)s}{(s+k_1)(s+k_2)s} = \frac{a_0}{(s+k_1)}$$

$$F(b) = \frac{1}{\Delta}\begin{vmatrix} s+k_1 & a_0 & 0 \\ -k_1 & b_0 & 0 \\ 0 & c_0 & s \end{vmatrix} = \frac{a_0 k_1}{(s+k_1)(s+k_2)} + \frac{b_0}{(s+k_2)}$$

$$F(c) = \frac{1}{\Delta}\begin{vmatrix} s+k_1 & 0 & a_0 \\ -k_1 & s+k_2 & b_0 \\ 0 & -k_2 & c_0 \end{vmatrix} = \frac{a_0 k_1 k_2}{s(s+k_1)(s+k_2)} + \frac{b_0 k_2}{s(s+k_2)} + \frac{c_0}{s}$$

Modeling Complex Kinetics by Numerical Integration

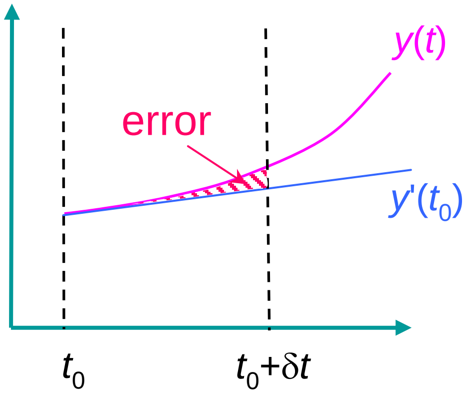
$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \qquad \frac{da}{dt} = -k_1 a \qquad \frac{db}{dt} = k_1 a - k_2 b \qquad \frac{dc}{dt} = k_2 b$$

If the concentrations ***a***, ***b*** and ***c*** are known at a specific time t_i, we can estimate their values for some small increase in time δt.

$$\delta a = -k_1 a \delta t \qquad a(t_i + \delta t) = a(t_i) + \delta a = a(t) - k_1 a(t_i)\delta t$$

$$\delta b = k_1 a \delta t - k_2 b \delta t \qquad b(t_i + \delta t) = b(t_i) + k_1 a(t_i)\delta t - k_2 b(t_i)\delta t$$

$$\delta c = k_2 b \delta t \qquad c(t_i + \delta t) = c(t_i) + k_2 b(t_i)\delta t$$



This is the Euler method of numerical integration:

Suppose $y' = f(t, y)$ and δt is a small increment in t.

$$y(t_0 + \delta t) = y(t_0) + y'(t_0)\delta t$$

$$y(t_{n+1}) = a(t_n) + y'(t_n)\delta t$$

Errors accumulate unless δt is extremely small. Runge-Kutta methods are better.

Runge-Kutta Methods for Numerical Integration

Suppose $y' = f(t,y)$ which can be expressed as a Taylor series.

$$f(x) = \sum_{n=0}^{\infty} \frac{f^n(x_0)}{n!}(x - x_0)^n$$

By using the substitution $\Delta = x - x_0$ we get

$$f(x_0 + \Delta) = f(x_0) + f'(x_0)\Delta + \tfrac{1}{2} f''(x_0)\Delta^2 + \tfrac{1}{6} f'''(x_0)\Delta^3 + \dots$$

or $$y(t + \delta t) = y(t) + y'(t)\delta t + \tfrac{1}{2} y''(t)\delta t^2 + \tfrac{1}{6} y'''(t)\delta t^3 + \dots$$

The second derivative (and higher) is approximated by the finite difference:

$$y''(t) \approx \frac{\delta y'}{\delta t} = \frac{y'(t + \delta t) - y'(t)}{\delta t}$$

The fourth-order Runge-Kutta solution is

$$y_{n+1} = y_n + \tfrac{1}{6}(a + 2b + 2c + d)$$

where

$$\left.\begin{aligned}
a &= f(t_n, y_n) \cdot \delta t \\
b &= f(t_n + \tfrac{1}{2}\delta t, y_n + \tfrac{1}{2}a) \cdot \delta t \\
c &= f(t_n + \tfrac{1}{2}\delta t, y_n + \tfrac{1}{2}b) \cdot \delta t \\
d &= f(t_n + \delta t, y_n + c) \cdot \delta t
\end{aligned}\right\}$$