Mo isotope kinetic equations

1 Molybdenum thiolation kinetic calculations

1.1 $\mathbf{MoO_4{}^{2-} \longrightarrow MoO_3S^{2-}}$

$[\mathrm{A}]_o = \mathrm{MoO_4{}^{2-}}$

$[\mathrm{A}] = \mathrm{MoO_3S^{2-}}$

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -k_i[A] \tag{1}$$

Using separation of variables (Forier Method) I solve for [A]

$$\frac{d[A]}{[A]} = -k_i dt$$

$$\int_{[A]}^{[A]_o} \frac{1}{[A]} d[A] = \int -k_i dt$$

$$\ln[A] - \ln[A]_o = -k_i t$$

$$\ln\frac{[A]}{[A]_o} = -k_i t$$

$$[A] = [A]_o e^{-k_i t}$$

1.2 $\mathbf{MoO_3S^{2-} \longrightarrow MoO_2S_2{}^{2-}}$

$[\mathrm{B}] = \mathrm{MoO_2S_2{}^{2-}}$

$$\frac{\mathrm{d}[B]}{\mathrm{d}t} = k_i[A] - k_{ii}[B] \tag{2}$$

$$\frac{\mathrm{d}[B]}{\mathrm{d}t} + k_{ii}[B] = k_i[A]$$

Recognizing that this is a non homogeneous first order differential equation I use variation of parameters I solve for [B]. First solving the **complimentary solution**:

$$\frac{\mathrm{d}[B]}{\mathrm{d}t} + k_{ii}[B] = 0$$

$$\frac{\mathrm{d}[B]}{\mathrm{d}t} = -k_{ii}[B]$$

$$\int \frac{1}{[B]} d[B] = \int -k_{ii} dt$$

$$\ln|[B]| = -k_{ii}t + C_o$$

$$[B] = e^{-k_{ii}t + C_o}$$

$$[B] = C_o e^{-k_{ii}t}$$

Using variation of parameters, the **particular solution** is formed by multiplying the complementary solution by an unknown function C(t):

$$[B] = C(t)e^{-k_{ii}t}$$

I substitute the **particular solution** into the original equation:

$$\frac{\mathrm{d}[B]}{\mathrm{d}t} + k_{ii}[B] = k_i[A]$$

this simplifies to:

$$C'(t)e^{-k_{ii}t} = k_i[A]_o e^{-k_i t}$$
$$C'(t) = \frac{k_i[A]_o e^{-k_i t}}{e^{-k_{ii}t}}$$
$$C'(t) = k_i[A]_o e^{(k_{ii}-k_i)t}$$
$$\int C'(t)dt = k_i[A]_o \int e^{(k_{ii}-k_i)t}dt$$
$$C(t) = \frac{k_i[A]_o}{k_{ii}-k_i} e^{k_{ii}t-k_i t} + C_1$$

I set C(t) = to B as a function of time:

$$B(t) = \frac{k_i[A]_o}{k_{ii}-k_i} e^{k_{ii}t-k_i t} + C_1$$

to find C_1 I assume that [B] is 0 when the experiment begins (e.g., t=0):

$$B(0) = \frac{k_i[A]_o}{k_{ii}-k_i} e^{k_{ii}0-k_i 0} + C_1$$

$$0 = \frac{k_i[A]_o}{k_{ii}-k_i} + C_1$$

$$C_1 = -\frac{k_i[A]_o}{k_{ii}-k_i}$$

B(t) then becomes:

$$B(t) = \frac{k_i[A]_o}{k_{ii}-k_i} e^{k_{ii}t-k_i t} - \frac{k_i[A]_o}{k_{ii}-k_i}$$

substitute B(t) into **particular solution**:

$$[B] = \left(\frac{k_i[A]_o}{k_{ii}-k_i} e^{k_{ii}t-k_i t} - \frac{k_i[A]_o}{k_{ii}-k_i}\right) e^{-k_{ii}t}$$

$$[B] = \frac{k_i[A]_o}{k_{ii}-k_i}\left(e^{k_{ii}t-k_i t}e^{-k_{ii}t} - e^{-k_{ii}t}\right)$$

$$[B] = \frac{k_i[A]_o}{k_{ii}-k_i}\left(e^{-k_i t} - e^{-k_{ii}t}\right)$$

1.3 $MoO_2S_2{}^{2-} \longrightarrow MoOS_3{}^{2-}$

$[\mathrm{C}] = \mathrm{MoO_{S3}}^{2-}$

$$\frac{\mathrm{d}[C]}{\mathrm{d}t} = k_{ii}[B] - k_{iii}[C] \tag{3}$$

This can be solved using variation of parameters the same method as eq. (2)

$$\frac{\mathrm{d}[C]}{\mathrm{d}t} + k_{iii}[C] = 0$$
$$\frac{\mathrm{d}[C]}{\mathrm{d}t} = -k_{iii}[C]$$
$$\int \frac{1}{[C]} d[C] = \int -k_{iii} dt$$

$$\ln|[C]| = -k_{iii}t + C_o$$
$$[C] = e^{-k_{iii}t + C_o}$$
$$[C] = C_o e^{-k_{iii}t}$$

Using variation of parameters, the **particular solution** is formed by multiplying the complementary solution by an unknown function C(t):

$$[C] = C(t)e^{-k_{iii}t}$$

I substitute the **particular solution** into the original equation:

$$\frac{\mathrm{d}[C]}{\mathrm{d}t} + k_{iii}[C] = k_{ii}[B]$$

this simplifies to:

$$C'(t)e^{-k_{iii}t} = \frac{k_i[A]_o}{k_{ii} - k_i}\left(e^{-k_i t} - e^{-k_{ii}t}\right)$$

$$C'(t)e^{-k_{iii}t} = \frac{k_i[A]_o}{k_{ii} - k_i}e^{-k_i t} - \frac{k_i[A]_o}{k_{ii} - k_i}e^{-k_{ii}t}$$

$$C'(t) = \frac{\left(\frac{k_i[A]_o}{k_{ii}-k_i}\right)e^{-k_i t} - \left(\frac{k_i[A]_o}{k_{ii}-k_i}\right)e^{-k_{ii}t}}{e^{-k_{iii}t}}$$

$$C'(t) = \left(\frac{k_i[A]_o}{k_{ii} - k_i}\right)e^{k_{iii}t - k_i t} - \left(\frac{k_i[A]_o}{k_{ii} - k_i}\right)e^{k_{iii}t - k_{ii}t}$$

$$\int C'(t)dt = \frac{k_i[A]_o}{k_{ii} - k_i}\int e^{k_{iii}t - k_i t}dt - \frac{k_i[A]_o}{k_{ii} - k_i}\int e^{k_{iii}t - k_{ii}t}dt$$

$$C(t) = \frac{k_i[A]_o(k_{iii} - k_i)}{k_{ii} - k_i} e^{k_{iii}t - k_i t} - \frac{k_i[A]_o(k_{iii} - k_{ii})}{k_{ii} - k_i} e^{k_{iii}t - k_{ii}t} + C_2$$

to find C_2 I assume that [C] is 0 when the experiment begins (e.g., t=0):

$$C(0) = \frac{k_i[A]_o(k_{iii} - k_i)}{k_{ii} - k_i} - \frac{k_i[A]_o(k_{iii} - k_{ii})}{k_{ii} - k_i} + C_2$$

$$C_2 = \frac{k_i[A]_o(k_{iii} - k_{ii})}{k_{ii} - k_i} - \frac{k_i[A]_o(k_{iii} - k_i)}{k_{ii} - k_i}$$

$$C_2 = \frac{k_i[A]_o}{k_{ii} - k_i}\Big(k_i - k_{ii}\Big)$$

C(t) then becomes:

$$C(t) = \frac{k_i[A]_o(k_{iii} - k_i)}{k_{ii} - k_i} e^{k_{iii}t - k_i t} - \frac{k_i[A]_o(k_{iii} - k_{ii})}{k_{ii} - k_i} e^{k_{iii}t - k_{ii}t} + \frac{k_i[A]_o}{k_{ii} - k_i}(k_i - k_{ii})$$

$$C(t) = \frac{k_i[A]_o}{k_{ii} - k_i}\Big[(k_{iii} - k_i)e^{k_{iii}t - k_i t} - (k_{iii} - k_{ii})e^{k_{iii}t - k_{ii}t} + (k_i - k_{ii})\Big]$$

substitute C(t) into **particular solution**:

$$[C] = \frac{k_i[A]_o}{k_{ii} - k_i}\Big[(k_{iii} - k_i)e^{k_{iii}t - k_i t} - (k_{iii} - k_{ii})e^{k_{iii}t - k_{ii}t} + (k_i - k_{ii})\Big]e^{-k_{iii}t}$$

$$[C] = \frac{k_i[A]_o}{k_{ii} - k_i}\Big[(k_{iii} - k_i)e^{-k_i t} - (k_{iii} - k_{ii})e^{-k_{ii}t} + (k_i - k_{ii})e^{-k_{iii}t}\Big]$$

1.4 $\mathbf{MoOS_3{}^{2-} \longrightarrow MoS_4{}^{2-}}$

$[\mathrm{D}] = \mathrm{MoS_4{}^{2-}}$

$$\frac{\mathrm{d}[D]}{\mathrm{d}t} = k_{iii}[C] \tag{4}$$

$$D'(t) = k_{iii}[C]$$

$$D(t) = k_{iii}\int [C]dt$$

$$D(t) = \frac{k_i[A]_o k_{iii}}{k_{ii} - k_i}\int\Big((k_{iii} - k_i)e^{-k_i t} - (k_{iii} - k_{ii})e^{-k_{ii}t} + (k_i - k_{ii})e^{-k_{iii}t}\Big)dt$$

$$D(t) = \frac{k_i[A]_o k_{iii}}{k_{ii} - k_i}\left(\frac{(k_{iii} - k_i)}{-k_i}e^{-k_i t} - \frac{(k_{iii} - k_{ii})}{-k_{ii}}e^{-k_{ii}t} + \frac{(k_i - k_{ii})}{-k_{iii}}e^{-k_{iii}t}\right) + C_3$$

to find C_3 I assume that [D] is 0 when the experiment begins (e.g., t=0):

$$0 = \frac{k_i[A]_o k_{iii}}{k_{ii} - k_i}\left(\frac{(k_{iii} - k_i)}{-k_i} - \frac{(k_{iii} - k_{ii})}{-k_{ii}} + \frac{(k_i - k_{ii})}{-k_{iii}}\right) + C_3$$

$$D(t) = \frac{k_i[A]_o k_{iii}}{k_{ii} - k_i}\left(\frac{(k_{iii} - k_i)}{-k_i}e^{-k_i t} - \frac{(k_{iii} - k_{ii})}{-k_{ii}}e^{-k_{ii} t} + \frac{(k_i - k_{ii})}{-k_{iii}}e^{-k_{iii} t}\right) - \frac{k_i[A]_o k_{iii}}{k_{ii} - k_i}\left(\frac{(k_{iii} - k_i)}{-k_i} - \frac{(k_{iii} - k_{ii})}{-k_{ii}} + \frac{(k_i - k_{ii})}{-k_{iii}}\right)$$