Kinetic investigation of the dissociation of dinuclear hierarchically assembled titanium(IV) helicates

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Stacked $^1$H NMR of the equilibration process of $\text{Li}[\text{Li}_3(\text{Me}_3\text{Ti})_2]$ at 25 °C

$\text{Li}[\text{Li}_3(\text{Me}_3\text{Ti})_2] \rightleftharpoons 2 \text{Li}_2(\text{Me}_3\text{Ti})$

$t = 4 \text{ min}$

$t = 22 \text{ min}$

$t = 106.5 \text{ min}$
Solution of the kinetic approach of an A to 2 B equilibrium

\[
A \overset{k_1}{\underset{k_2}{\longrightarrow}} 2B
\]

The following reaction with the given starting conditions is investigated:

\[
a(t = 0) = a_0
\]
\[
b(t = 0) = 0
\]

The time dependent change of \(a\) is described as:

\[
\frac{da}{dt} = -k_1a + k_2b^2
\]

Regarding to the equilibrium with the equilibrium concentrations:

\[
\lim_{t \to \infty} \frac{da}{dt} = 0
\]

\[
K = \frac{1}{K_{dim.}} = \frac{b_\infty^2}{a_\infty} = \frac{k_1}{k_2}
\]

These equations allow to describe the kinetic approach:

\[
\frac{da}{dt} = -k_2(Ka - b^2)
\]

Including the starting conditions and the stoichiometry for \(b\):

\[
b = 2(a_0 - a)
\]

\[
\frac{da}{dt} = -k_2[-4a^2 + (K + 8a_0)a - 4a_0^2]
\]

Integration via separation of the variables gives:

\[
\int_{a_0}^{a} \frac{da}{-4a^2 + (K + 8a_0)a - 4a_0^2} = -k_2t
\]

The integral can be described as:

\[
\int_{a_0}^{a} \frac{da}{-4a^2 + (K + 8a_0)a - 4a_0^2} = \int \frac{dx}{px^2 + qx + r}
\]

With: \(x = a\)

\[
p = -4
\]
\[
q = K + 8a_0
\]
\[
r = -4a_0^2
\]
Transforming the integral into:

\[ \int \frac{dx}{px^2 + qx + r} = \frac{1}{p} \int \frac{dx}{x^2 + \frac{q}{p} + \frac{r}{p}} = \frac{1}{p} \int \frac{dx}{(x-x_1)(x-x_2)} \]

With:

\[ x^2 + \frac{q}{p} + \frac{r}{p} = 0 \]

\[ x_1 = -\frac{q}{2p} + \frac{\sqrt{q^2 - 4pr}}{2p} \]

\[ x_2 = -\frac{q}{2p} - \frac{\sqrt{q^2 - 4pr}}{2p} \]

It is necessary that \( q^2 - 4pr \geq 0 \) because \( x_1 \) and \( x_2 \) are real.

Partial fraction decomposition results in:

\[ \frac{1}{(x-x_1)(x-x_2)} = \frac{A}{x-x_1} + \frac{B}{x-x_2} \]

With:

\[ A = -B = \frac{1}{x_1-x_2} = \frac{p}{\sqrt{q^2 - 4pr}} \]

Integration gives:

\[
\int \frac{dx}{(x-x_1)(x-x_2)} = \frac{1}{x_1-x_2} \left( \int \frac{dx}{x-x_1} - \int \frac{dx}{x-x_2} \right) = \frac{1}{x_1-x_2} \left[ \ln(|x-x_1|) - \ln(|x-x_2|) \right] \\
= \frac{1}{x_1-x_2} \ln \left| \frac{x-x_1}{x-x_2} \right| = \frac{p}{\sqrt{q^2 - 4pr}} \ln \left| \frac{2px+q+\sqrt{q^2 - 4pr}}{2px+q+\sqrt{q^2 - 4pr}} \right|
\]

Thus the solution for the previous simplified integral is:

\[
\int \frac{dx}{px^2 + qx + r} = \frac{1}{p} \int \frac{dx}{(x-x_1)(x-x_2)} = \frac{1}{\sqrt{q^2 - 4pr}} \ln \left| \frac{2px+q+\sqrt{q^2 - 4pr}}{2px+q+\sqrt{q^2 - 4pr}} \right|
\]

Reintroducing the previous substituted following terms: \( x = a \)

\[ p = -4 \]

\[ q = K + 8a_0 \]

\[ r = -4a_0^2 \]
With respect to the integration limits:

\[
\int_{a_0}^{a} \frac{da}{-4a^2 + (K + 8a_0)a - 4a_0^2} = \frac{1}{Q} \ln \left| \frac{-8a + K + 8a_0 - Q}{-8a + K + 8a_0 + Q} \right| - \frac{1}{Q} \ln \left| \frac{K - Q}{K + Q} \right|
\]

This term results in the final linear equation for the determination of \(k_2\):

\[
y = -k_2 t + c
\]

With

\[
y = \frac{1}{Q} \ln \left| \frac{-8a + K + 8a_0 - Q}{-8a + K + 8a_0 + Q} \right|
\]

\[
c = \frac{1}{Q} \ln \left| \frac{K - Q}{K + Q} \right|
\]

\[
Q = \sqrt{K(K + 16a_0)} \text{ while } K(K + 16a_0) \geq 0 \text{ because } K \geq 0 \text{ and } a_0 \geq 0 \]
Kinetic of Li[Li$_3$((Me)$_2$Ti)$_2$] for 25 °C to 65 °C

25°C

\[ y = -k_2 \cdot t + c \]
\[ y = -6.39 \cdot 10^{-2} \cdot t - 6.50 \cdot 10^1 \]
\[ R^2 = 0.998 \]

35°C

\[ y = -k_2 \cdot t + c \]
\[ y = -9.34 \cdot 10^{-2} \cdot t - 4.76 \cdot 10^1 \]
\[ R^2 = 0.998 \]

45°C

\[ y = -k_2 \cdot t + c \]
\[ y = -1.44 \cdot 10^{-1} \cdot t - 2.72 \cdot 10^1 \]
\[ R^2 = 0.993 \]

55°C

\[ y = -k_2 \cdot t + c \]
\[ y = -2.70 \cdot 10^{-1} \cdot t + 4.76 \cdot 10^0 \]
\[ R^2 = 0.997 \]

65°C

\[ y = -k_2 \cdot t + c \]
\[ y = -8.95 \cdot 10^{-1} \cdot t + 1.16 \cdot 10^2 \]
\[ R^2 = 0.993 \]
Kinetic of Li[[cyBu]_2Ti]_3 for 25 °C to 65 °C

- **25°C**
  - Equation: \( y = -k_2 t + c \)
  - Equation: \( y = -1.74 \times 10^{-2} t - 5.23 \times 10^1 \)
  - \( R^2 = 0.996 \)

- **35°C**
  - Equation: \( y = -k_3 t + c \)
  - Equation: \( y = -2.81 \times 10^{-2} t - 4.47 \times 10^1 \)
  - \( R^2 = 0.995 \)

- **45°C**
  - Equation: \( y = -k_4 t + c \)
  - Equation: \( y = -5.85 \times 10^{-2} t - 3.33 \times 10^1 \)
  - \( R^2 = 0.991 \)

- **55°C**
  - Equation: \( y = -k_5 t + c \)
  - Equation: \( y = -8.42 \times 10^{-2} t - 3.20 \times 10^1 \)
  - \( R^2 = 0.999 \)

- **65°C**
  - Equation: \( y = -k_6 t + c \)
  - Equation: \( y = -5.14 \times 10^{-2} t + 5.16 \times 10^1 \)
  - \( R^2 = 0.994 \)
Arrhenius plots of Li[Li$_2$((Me)$_3$Tl)$_2$]

\[
\ln(k) = -4.63 \times 10^3 \frac{1}{T} + 1.27 \times 10^1
\]
\[R^2 = 0.978\]

Arrhenius plots of Li[Li$_3$((cyBu)$_3$Tl)$_2$]

\[
\ln(k) = -5.35 \times 10^3 \frac{1}{T} + 1.39 \times 10^1
\]
\[R^2 = 0.987\]
Error estimation

The errors of the dimerization constants were obtained via a propagation of the NMR uncertainty (± 5 % for the integration).

The errors of the rate constants were obtained via comparison of the two different kinetic methods. The rate constants obtained from solving the kinetic approach \( y = -k_2 t + c \) are compared to those obtained by the initial slope \( \ln(c_{d}/c_{d,t=0}) \). This approach allows the direct estimation of the uncertainties of the shown rate constants.

Example for Li[Li₃{(Me)₃Ti}₂]:

Rate constants obtained by solving the kinetic approach: \( k_1 = 3.295 \cdot 10^{-4}; k_2 = 6.392 \cdot 10^{-2} \)

Rate constants obtained by the initial slope: \( k_1 = 3.756 \cdot 10^{-4}; k_2 = 7.287 \cdot 10^{-2} \)

Estimated errors obtained by comparison: \( \Delta k_1 = \pm 0.461 \cdot 10^{-4}; \Delta k_2 = \pm 0.895 \cdot 10^{-2} \)

The errors for the activation energies were obtained from the linear regression.