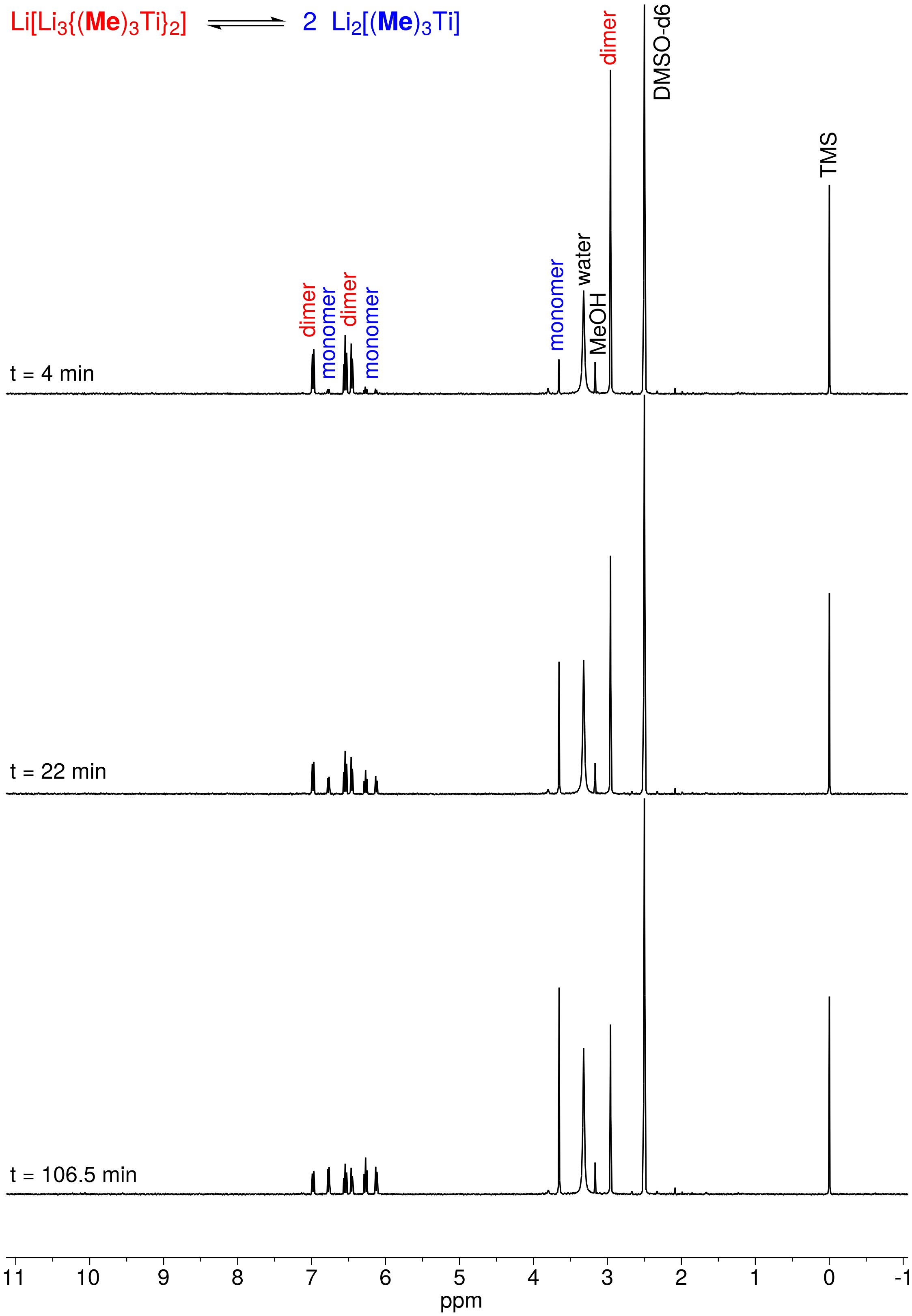
Kinetic investigation of the dissociation of dinuclear hierarchically assembled titanium(IV) helicates

David Van Craen,[a] Marcel Schlottmann,[a] Wolfgang Stahl,[a] Christoph Räuber,[a] Markus Albrecht,*[a]

Table of Content:

Stacked ^{1}H NMR of the equilibration process of $Li[Li_3\{(Me)_3Ti\}_2]$ at 25 °C



Solution of the kinetic approach of an A to 2 B equilibrium

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\,B$$

The following reaction with the given starting conditions is investigated:

$$\boldsymbol{a(t=0) = a_0}$$

$$\boldsymbol{b(t=0) = 0}$$

The time dependend change of ***a*** is described as:

$$\frac{da}{dt} = -k_1 a + k_2 b^2$$

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:

$$\int_{a_0}^{a} \frac{da}{-4a^2 + (K + 8a_0)a - 4a_0^2} = -k_2 t$$

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:

$$y = -k_2 t + c$$

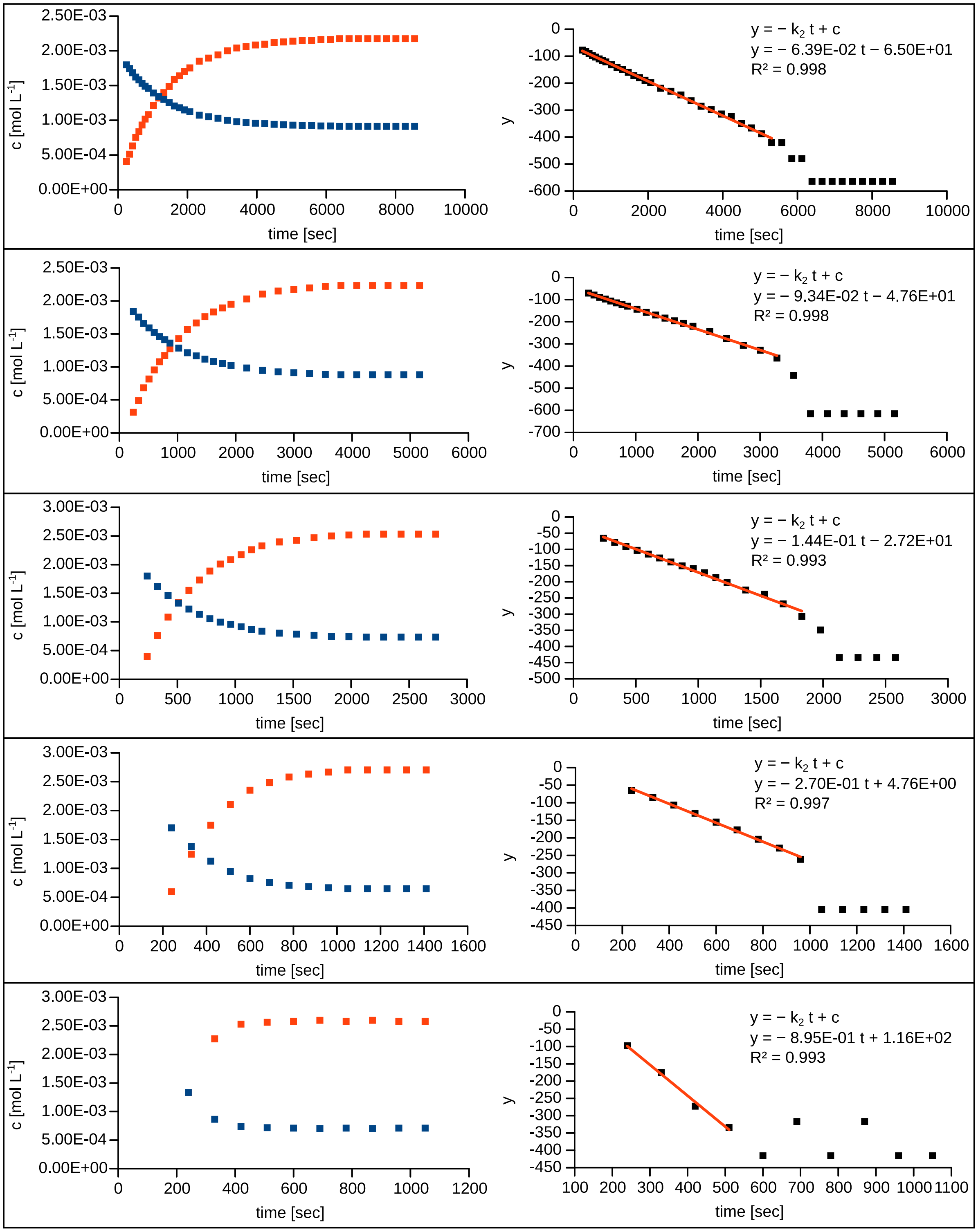
With

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

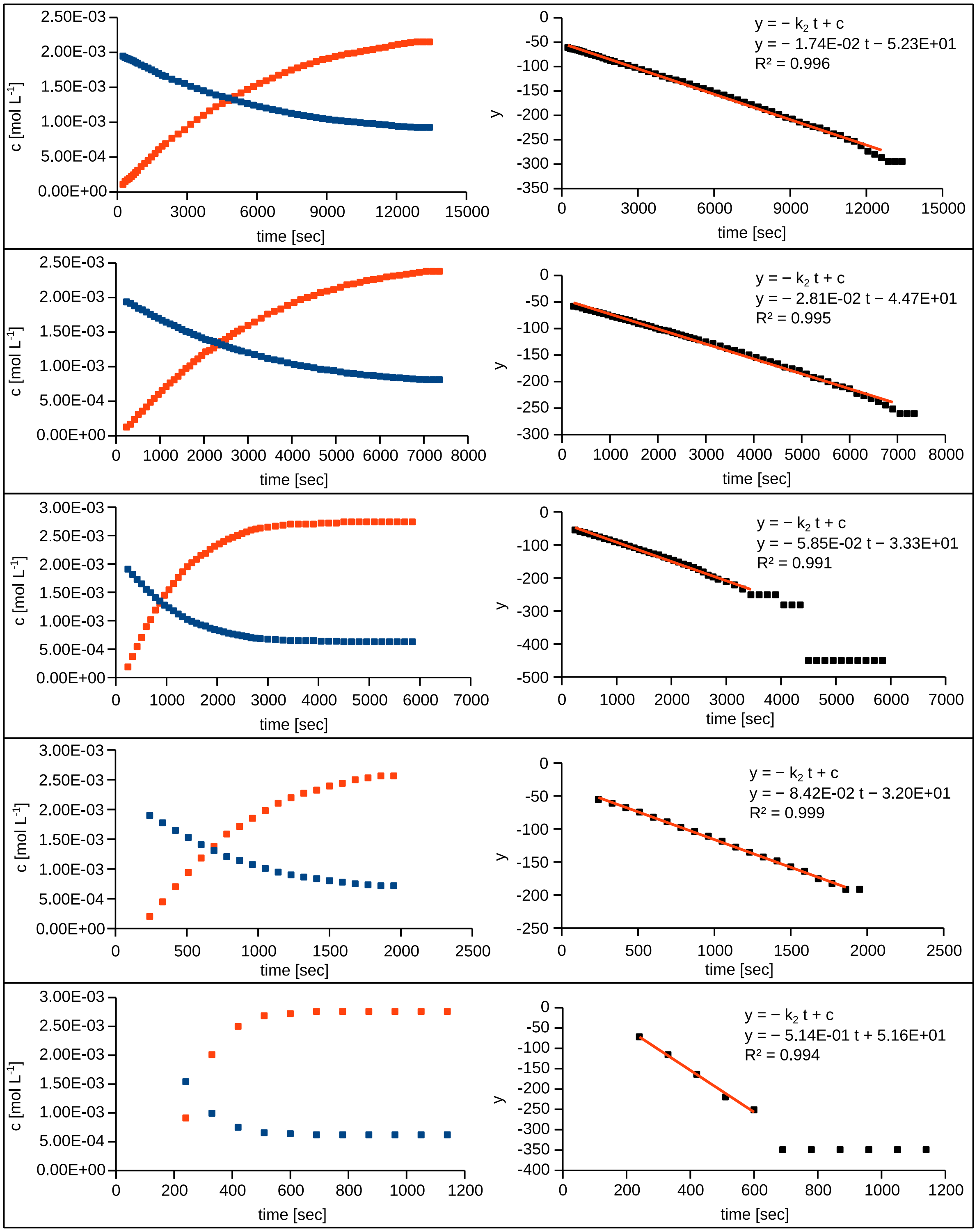
$$c = \frac{1}{Q} ln \left|\frac{K - Q}{K + Q}\right|$$

$Q = \sqrt{K(K + 16a_0)}$ while $K(K + 16a_0) \geq 0$ because $K \geq 0$ and $a_0 \geq 0$

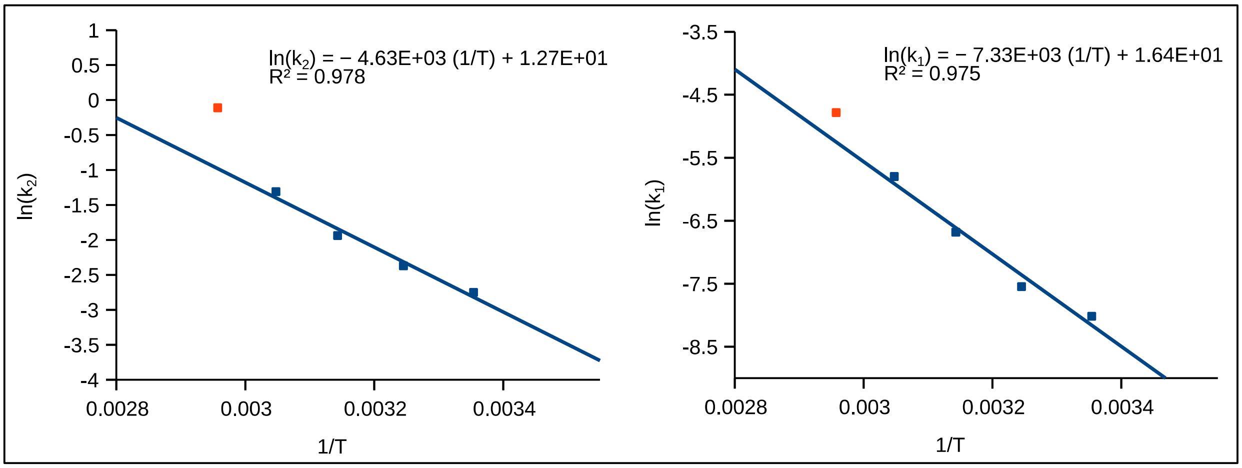
Kinetic of $Li[Li_3\{(\mathbf{Me})_3Ti\}_2]$ for 25 °C to 65 °C



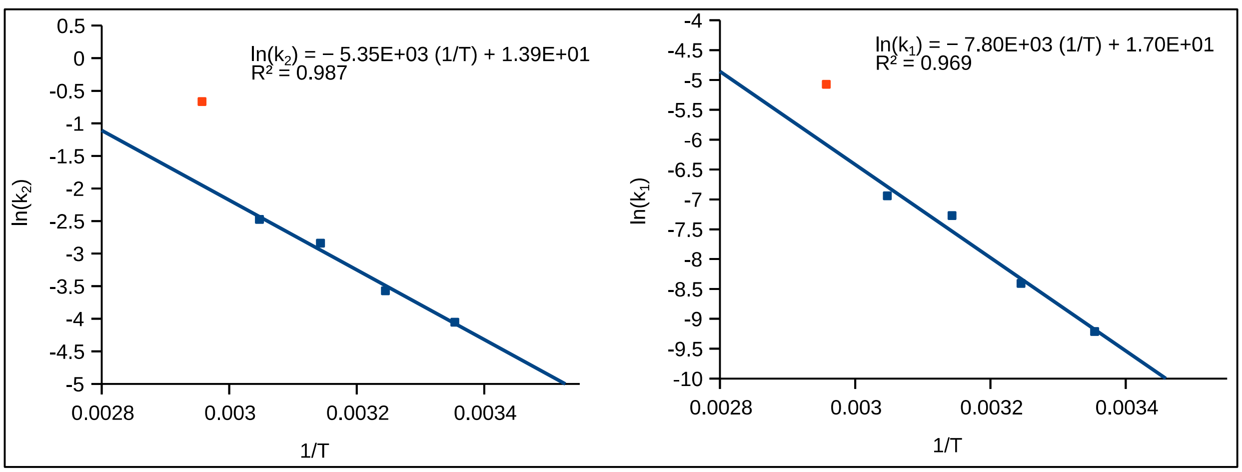
Kinetic of Li[Li$_3${(**cyBu**)$_3$Ti}$_2$] for 25 °C to 65 °C



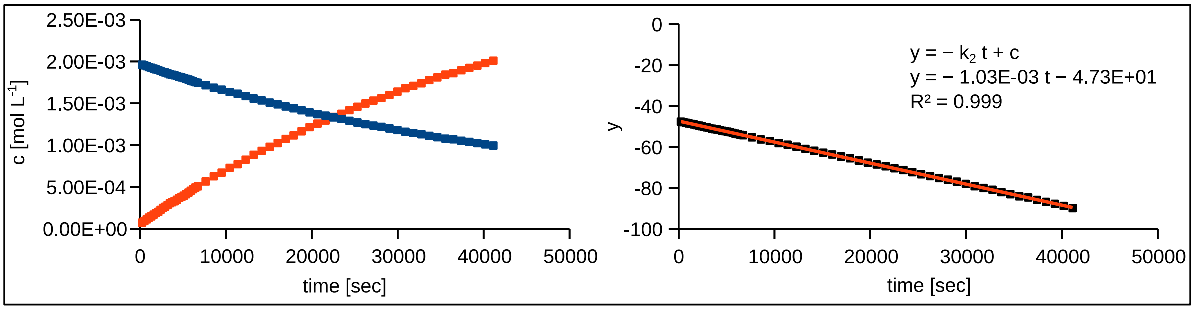
Arrhenius plots of Li[Li$_3${(**Me**)$_3$Ti}$_2$]



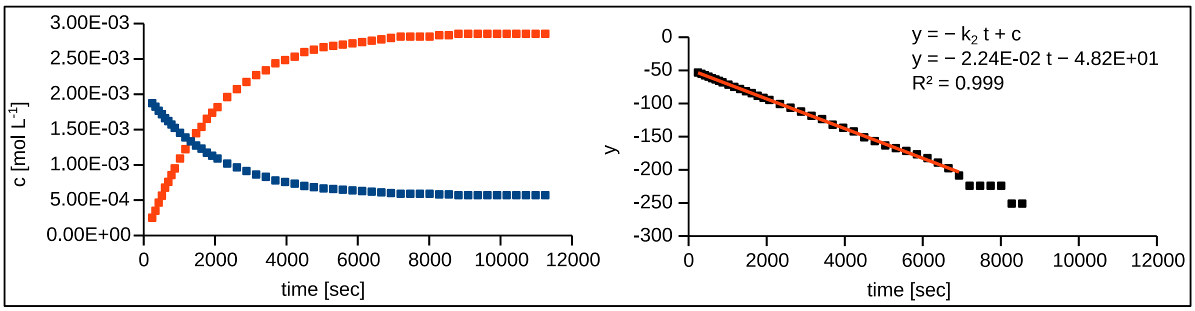
Arrhenius plots of Li[Li$_3${(**cyBu**)$_3$Ti}$_2$]



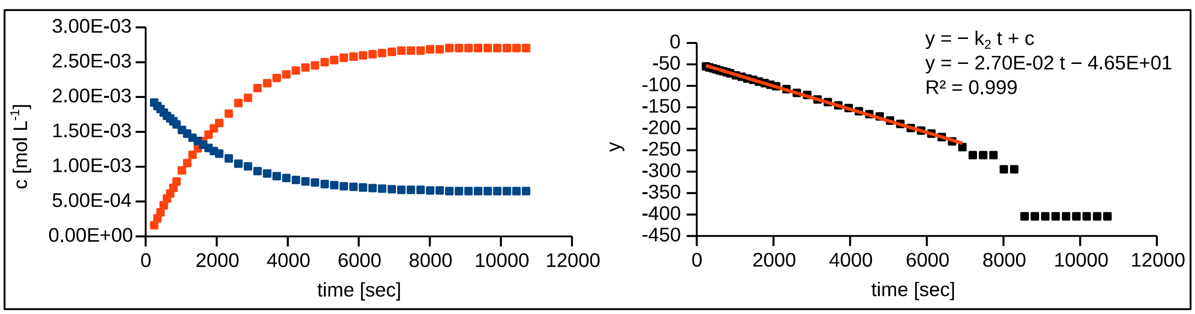
Kinetic of Li[Li_3{(**3-Pent**)$_3$Ti}$_2$] at 25 °C



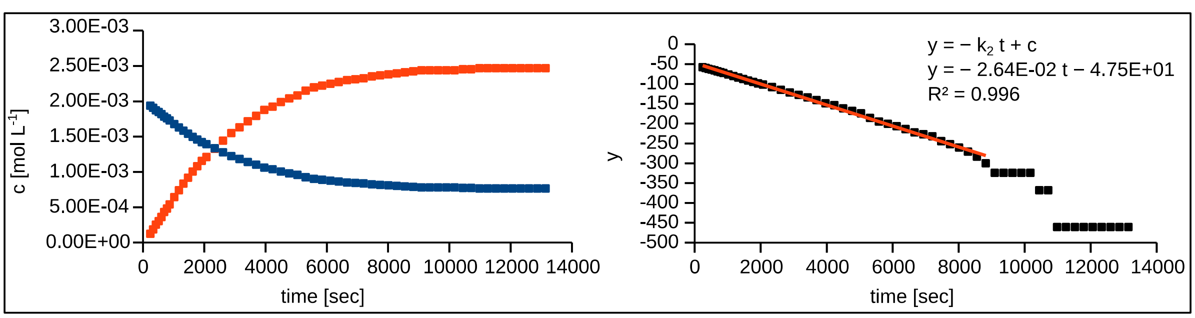
Kinetic of Li[Li_3{(**3,5-F_2-Bz**)$_3$Ti}$_2$] at 25 °C



Kinetic of Li[Li_3{(**3,5-Cl_2-Bz**)$_3$Ti}$_2$] at 25 °C



Kinetic of Li[Li_3{(**3,5-Br_2-Bz**)$_3$Ti}$_2$] at 25 °C



Error estimation

The errors of the dimerization constants were obtained via a propagation of the NMR uncertainty ($\pm$ 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 $Li[Li_3\{(\mathbf{Me})_3Ti\}_2]$:

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.