CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Rhodium complex catalyzed asymmetric hydrogenation – Transfer of pre-catalysts into active species

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Precatalyst synthesis

[Rh(DIPAMP)NBD]BF$_4$ was purchased by Umicore and recrystallized once from MeOH. ^{31}P NMR *d* 50.0 ppm (d, 2P, J_{Rh-P} = 158.3 Hz).
[Rh(DIPAMP)COD]BF$_4$ was purchased by STREM and recrystallized once from MeOH. ^{31}P NMR *d* 50.9 ppm (d, 2P, J_{Rh-P} = 150.8 Hz).

[Rh(DPPE)COD]BF$_4$. In a secured 50 ml Schlenk flask Rh(acac)COD (1 mmol, 310 mg) was dissolved in 3 ml THF. At -79°C (dry ice/ethanol mixture) the ligand DPPE (1 mmol, 398 mg) dissolved in 7 ml THF was added within 30 min. At 0°C HBF$_4$ (50% in water, 62.27µl) is added via syringe and, the catalyst solution turns orange. The solution was allowed to stir for further 5 min. The catalyst complex is precipitated by addition of diethylether at room temperature. The yellow complex is filtered, washed with diethylether and dried *in vacuo*. Purification by recrystallization from MeOH yields 585 mg (84 %) of yellow crystals. ^{31}P NMR *d* 57 ppm (d, 2P, J_{Rh-P} = 149.3 Hz).

[Rh(Me-DuPHOS)COD]BF$_4$ was purchased by STREM and recrystallized once from MeOH. ^{31}P-NMR *d* 76.4 ppm (d, 2P, J_{Rh-P} = 149 Hz).
Synthesis of [Rh(Me-DuPHOS)NBD]BF$_4$. [Rh(Me-DuPHOS)(COD)]BF$_4$ (180 mg, 0.3 mmol) was dissolved in 6 ml MeOH in a secured Schlenk flask and hydrogenated for 60 min. The hydrogen was removed by freezing the solution and consecutive evacuation (3 times), addition of 150 µl (1.5 mmol) NBD and stirring over night. To the solution diethylether was slowly added and a violet solid precipitated. The precipitate was recristallyzed from MeOH, washed twice with diethylether and dried *in vacuo* yielding 160 mg (88% isolated yield) violet crystals of [Rh(Me-DuPHOS)(NBD)]BF$_4$. ^{31}P NMR *d* 75.9 ppm (d, 2P, J_{Rh-P} = 145.8 Hz).

Synthesis of [Rh(Et-DuPHOS)COD]BF$_4$. The solutions of the ligand Et-DuPHOS (1.025 g, 2.76 mmol) in 1 ml THF and of HBF$_4$ (380 µl, 54 % in diethylether) in 9 ml THF are combined while stirring. This solution is added to a solution of Rh(acac)COD (856 mg, 2.76 mmol) in 8 ml THF at 60°C. A deep red solution results, which is allowed to stir for further 5 min. The catalyst solution is cooled to room temperature and ca. 30 ml TBME are added to precipitate the catalyst. The complex is then washed with TBME and dried *in vacuo*. For purification the complex is dissolved in methanol and TBME is added until the initial precipitate appears. The precipitate is filtered. To the remaining catalyst solution TBME is added until no further clouding occurs at the surface of the stirred solution. The catalyst now precipitates. It is washed twice with TBME and dried *in vacuo* to yield 69 % of [Rh(Et-DuPHOS)(COD)]BF_4. ^{31}P NMR *d* 70.3 ppm (d, 2P, $J_{Rh\text{-}P}$ = 148.5 Hz).

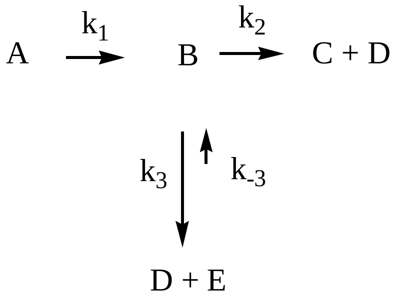
Synthesis of [Rh(BINAP)COD]BF_4 and [Rh(BINAP)NBD]BF_4. In a secured Schlenk flask 0.3 mmol (92.7 mg) Rh(acac)COD (or Rh(acac)NBD; 0.65 mmol, 192 mg) in 7ml THF were dissolved. At 0°C 1 eq. HBF_4 (50% in H_2O) was added. The ligand BINAP (1 eq.) was dissolved in a dropping funnel in 15 ml THF and was slowly added to the solution of Rh(acac)COD (or Rh(acac)NBD) at -79°C (dry ice/ethanol mixture). While warming the solution to room temperature the yellow solution turned orange. By addition of diethylether (ca. 50 ml) precipitation of the catalyst was achieved. The ether was removed via capillary. Purification of the catalysts by recrystallization from MeOH, washing with diethylether and drying *in vacuo* yielded 245 mg (78% isolated yield) [Rh(BINAP)(COD)]BF_4 (^{31}P NMR *d* 25.7 ppm (d, 2P, $J_{Rh\text{-}P}$ = 145.8 Hz)) and 455 mg (70% isolated yield) [Rh(BINAP)(NBD)]BF_4 (^{31}P NMR *d* 26.2 ppm (d, 2P, $J_{Rh\text{-}P}$ = 156.5 Hz)).

[Rh(Catasium)COD]BF_4 was purchased by Degussa and recrystallized from CH_2Cl_2. ^{31}P NMR in CD_2Cl_2 *d* 64.8 ppm (d, 2P, $J_{Rh\text{-}P}$ = 150.6 Hz).

Synthesis of [Rh(Catasium)NBD]BF_4. (The catalyst had kindly been provided by Dr. J. Holz.) 100 mg (0.267 mmol) [Rh(NBD)$_2$]BF_4 were dissolved in dichloromethane at 0°C. Via capillary a solution of 1 eq. of the ligand dissolved in 1 ml CH_2Cl_2 was slowly added at 0°C. The solution was stirred for 30 min at 0°C and then slowly (within ca. 2 h) heated to room temperature. The catalyst was precipitated with diethylether and recrystallized from ca. 1 ml dichloromethane/diethylether and 114 mg (70% isolated yield) red brown crystals were obtained. ^{31}P NMR in aceton-d_6 *d* 63.1 ppm (d, 2P, $J_{Rh\text{-}P}$ = 158.1 Hz).

Cyclooctene with a purity of > 99.5 % was purchased by FLUKA and used as received.

Reaction Sequence Corresponding to Scheme 1 for Highly Stable Diolefin Complexes:



A: diolefin complex

B: monoolefin complex

C: alkane

D: solvate complex

E: monoolefin

k_1 and k_2 are pseudo-first-order rate constants in case of a constant hydrogen pressure

Rate Equations:

$$\frac{d[A]}{dt} = -k_1[A] \tag{1}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] - k_3[B] + k_{-3}[D][E] \tag{2}$$

$$\frac{d[C]}{dt} = -k_2[B] \tag{3}$$

$$\frac{d[D]}{dt} = k_2[B] + k_3[B] - k_{-3}[D][E] \tag{4}$$

$$\frac{d[E]}{dt} = k_3[B] - k_{-3}[D][E] \tag{5}$$

Equilibrium assumption :

$$\begin{aligned} K_D &= \frac{[D][E]}{[B]} \\ [E] &= \frac{K_D[B]}{[D]} \\ \frac{d[E]}{dt} &= \frac{K_D}{[D]}\frac{d[B]}{dt} - [B]\frac{K_D}{[D]^2}\frac{d[D]}{dt} \end{aligned} \tag{6}$$

Addition of (5) + (1) and subtraction of (4) - (5) yields:

$$\begin{aligned} \frac{d[B]}{dt} + \frac{d[E]}{dt} &= k_1[A] - k_2[B] \\ \frac{d[D]}{dt} - \frac{d[E]}{dt} &= k_2[B] \end{aligned} \tag{7}$$

Substitution of (6) into (7):

$$\begin{aligned} \left(1+\frac{K_D}{[D]}\right)\frac{d[B]}{dt} - [B]\frac{K_D}{[D]^2}\frac{d[D]}{dt} &= k_1[A] - k_2[B] \\ \left(1+[B]\frac{K_D}{[D]^2}\right)\frac{d[D]}{dt} - \frac{K_D}{[D]}\frac{d[B]}{dt} &= k_2[B] \end{aligned} \tag{8}$$

The position of the equilibrium is at the side of the solvate complex (cf. ref. 25 of the main part), i.e. $K_D >> 1$*, and therefore it also follows (especially in case of diluted solutions ([D] is very small) with application of UV/Vis-spectroscopy):*

$$\frac{K_D}{[D]} >> 1 \tag{9}$$

Eqn. (8.1) can be simplified using (9):

$$\left(\frac{K_D}{[D]}\right)\frac{d[B]}{dt} - [B]\frac{K_D}{[D]^2}\frac{d[D]}{dt} \approx k_1[A] - k_2[B] \tag{10}$$

Addition of (10) and (8.2) finally results to:

$$\frac{d[D]}{dt} \approx k_1[A] \tag{11}$$

The solutions are:

$$\begin{aligned} [A] &= [A]_0 e^{-k_1 t} \\ [D] &\approx [A]_0 (1 - e^{-k_1 t}) \end{aligned} \tag{12}$$

From the stoichiometry it follows:

$$\begin{aligned} [A]_0 - [A] &= [B] + [D] \\ 1 - \frac{[A]}{[A]_0} &= \frac{[B]}{[A]_0} + \frac{[D]}{[A]_0} \end{aligned}$$

Substituting the solutions (12) for [A] and [D] leads to the conclusion:

$$\frac{[B]}{[A]_0} << 1 \tag{13}$$

In other words, the concentration of [B] is very small, and a simple first-order reaction law is obtained for [A] and [D], even without further assumptions concerning the ratio of k_2 and k_3.

First order reaction: $\mathbf{a} \xrightarrow{k_1} \mathbf{b}$

Using the reaction variable x it follows:

$a = a_0 - x$ and $b = b_0 + x$

$$\frac{dA_\lambda}{dt} = q_\lambda \cdot k_1 \cdot (a_0 - \frac{(A_\lambda - A_{\lambda,0})}{q_\lambda}) = k_1 \cdot (a_0 \cdot q_\lambda - A_\lambda + A_{\lambda,0}) \ (x = \frac{(A_\lambda - A_{\lambda,0})}{q_\lambda}) \quad [1]$$

Substituting $q_\lambda = d \cdot (\varepsilon_{b,\lambda} - \varepsilon_{a,\lambda})$:

$$\frac{dA_\lambda}{dt} = k_1 \cdot (a_0 \cdot \varepsilon_{b,\lambda} \cdot d - a_0 \cdot \varepsilon_{a,\lambda} \cdot d - A_\lambda + A_{\lambda,0})$$

Since $A_{\lambda,\infty} = a_0 \cdot \varepsilon_{b,\lambda} \cdot d$ and $A_{\lambda,0} = a_0 \cdot \varepsilon_{a,\lambda} \cdot d$:

$\frac{dA_\lambda}{dt} = k_1 \cdot (A_{\lambda,\infty} - A_\lambda)$, which can be rearranged to $\frac{dA_\lambda}{dt} = k_1 \cdot A_{\lambda,\infty} - k_1 \cdot A_\lambda$

I.e., a plot of dA_λ/dt vs. A_λ produces straight lines with a negative slope corresponding to the pseudo-rate constant to be established.

The rate law mentioned above can be solved

$$\ln\left[\frac{(A_{\lambda,\infty} - A_{\lambda})}{(A_{\lambda,\infty} - A_{\lambda,0})}\right] = -k_1 \cdot t$$

and finally rearranged to give:

$$A_{\lambda} = A_{\lambda,\infty} - (A_{\lambda,\infty} - A_{\lambda,0}) \cdot e^{-(k_1 \cdot t)}$$

I.e., a non-linear fit of the extinction as a function of time can be used as well to determine the pseudo-rate constant.

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[1] H.-H. Perkampus, R. Kaufmann, *„Kinetische Analyse mit Hilfe der UV-Vis-Spektroskopie“* VCH Verlagsgesellschaft mbH, Weinheim, **1991**.

There is another possibility for this derivation:

Starting from the known expression for the first order rate law

$$\ln\left[\frac{(A_{\lambda,\infty} - A_{\lambda})}{(A_{\lambda,\infty} - A_{\lambda,0})}\right] = -k_1 \cdot t \quad \text{it follows:}$$

$$A_{\lambda,\infty} - A_{\lambda} = (A_{\lambda,\infty} - A_{\lambda,0}) \cdot e^{-(k_1 \cdot t)} \quad \text{or}$$

$$A_{\lambda} = A_{\lambda,\infty} - (A_{\lambda,\infty} - A_{\lambda,0}) \cdot e^{-(k_1 \cdot t)} \quad (A_{\lambda} = A_{\lambda,\infty} + \left(A_{\lambda,0} - A_{\lambda,\infty}\right) e^{-k_1 t})$$

(or $-A_{\lambda,0} \cdot e^{-(k_1 \cdot t)} = A_{\lambda,\infty} - A_{\lambda,\infty} \cdot e^{-(k_1 \cdot t)} - A_\lambda$, respectively).

After rearrangement

$$A_\lambda = A_{\lambda,\infty} - A_{\lambda,\infty} \cdot e^{-(k_1 \cdot t)} + A_{\lambda,0} \cdot e^{-(k_1 \cdot t)}$$

and derivation with respect to time

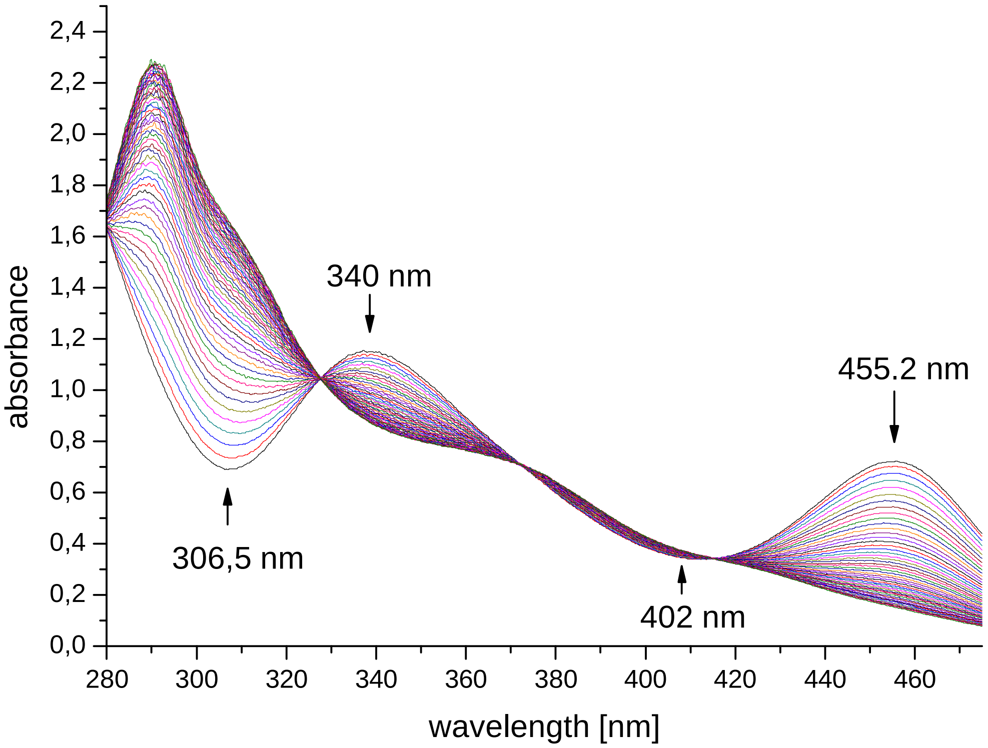
$$\frac{dA_\lambda}{dt} = k_1 \cdot A_{\lambda,\infty} \cdot e^{-(k_1 \cdot t)} - k_1 \cdot A_{\lambda,0} \cdot e^{-(k_1 \cdot t)}$$

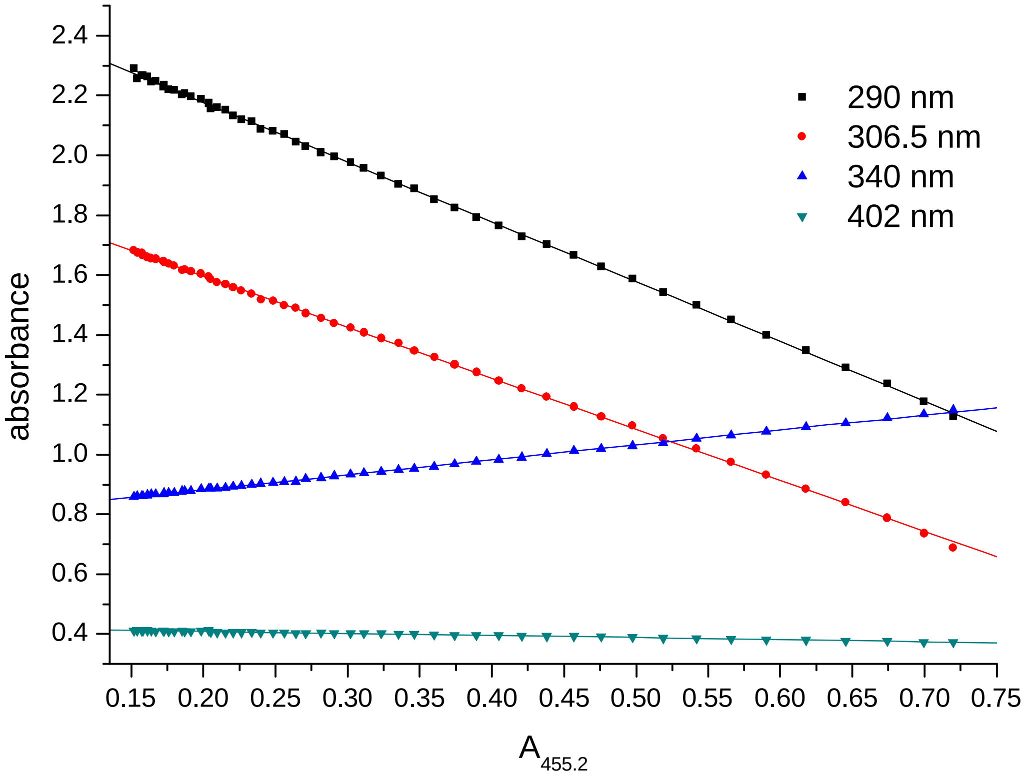
the substitution $-A_{\lambda,0} \cdot e^{-(k_1 \cdot t)} = A_{\lambda,\infty} - A_{\lambda,\infty} \cdot e^{-(k_1 \cdot t)} - A_\lambda$ finally leads to:

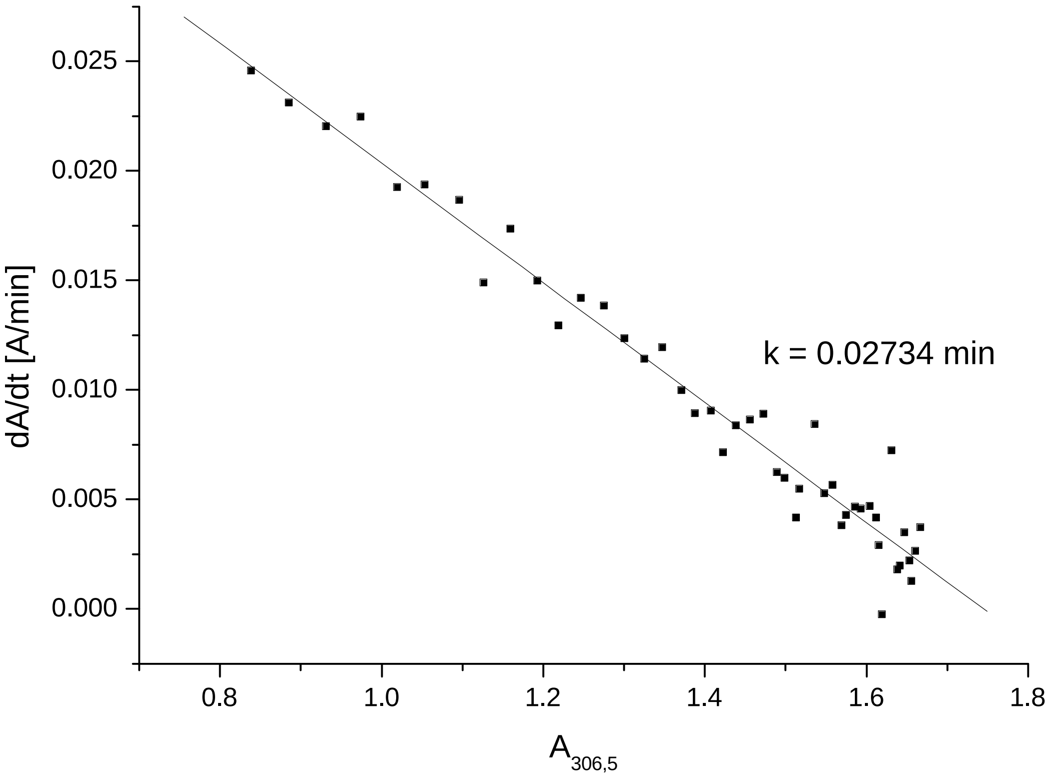
$$\frac{dA_\lambda}{dt} = k_1 \cdot A_{\lambda,\infty} \cdot e^{-(k_1 \cdot t)} + k_1 \cdot (A_{\lambda,\infty} - A_{\lambda,\infty} \cdot e^{-(k_1 \cdot t)} - A_\lambda) = k_1 \cdot A_{\lambda,\infty} - k_1 \cdot A_\lambda$$

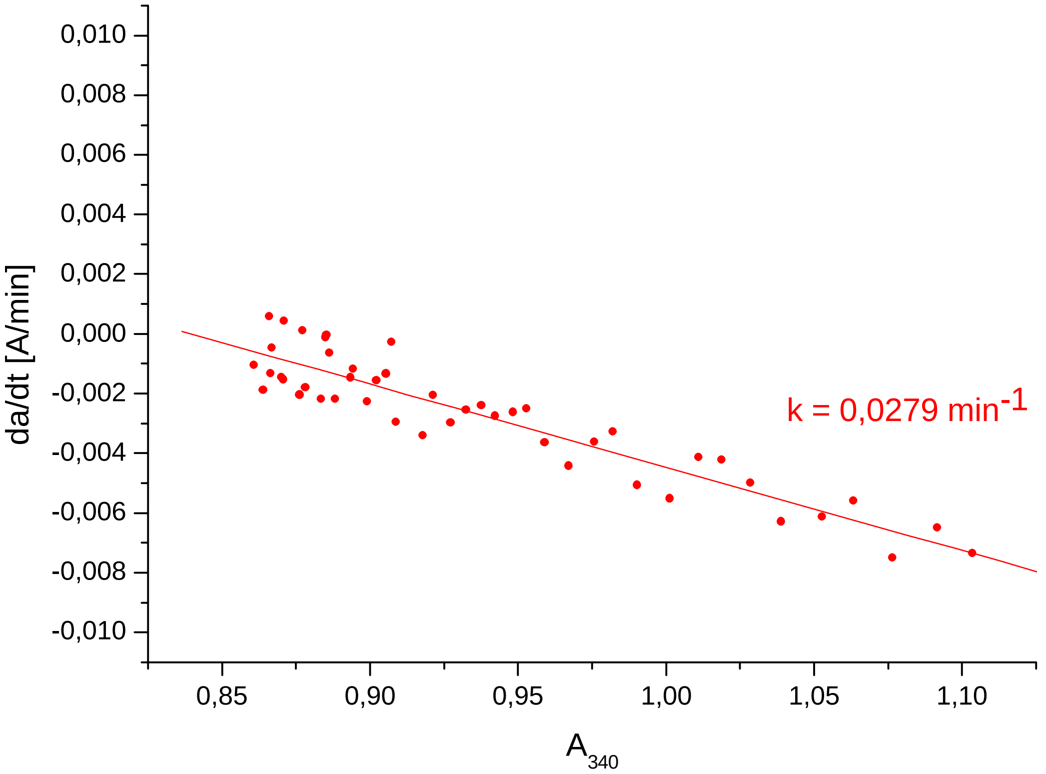
$\frac{dA_?}{dt}$ obviously linearly depends on A_λ itself, $-k_1$ being the slope of a linear plot.

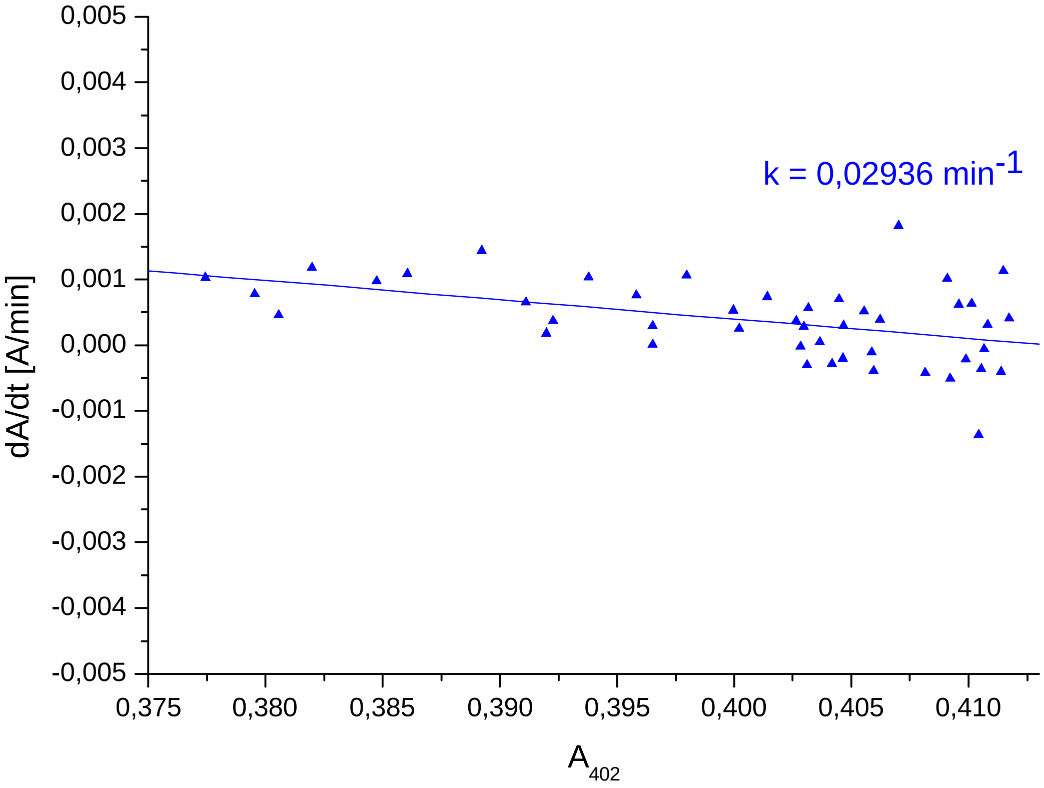
Results from the UV/Vis-spectroscopic, stoichiometric hydrogenation of [Rh(Et-DuPHOS)COD]BF_4 (0.0196 mmol catalyst, 40.0 ml MeOH, 25.0°C, scanning time = 2 min, 120 nm/min, d= 0.5 cm)

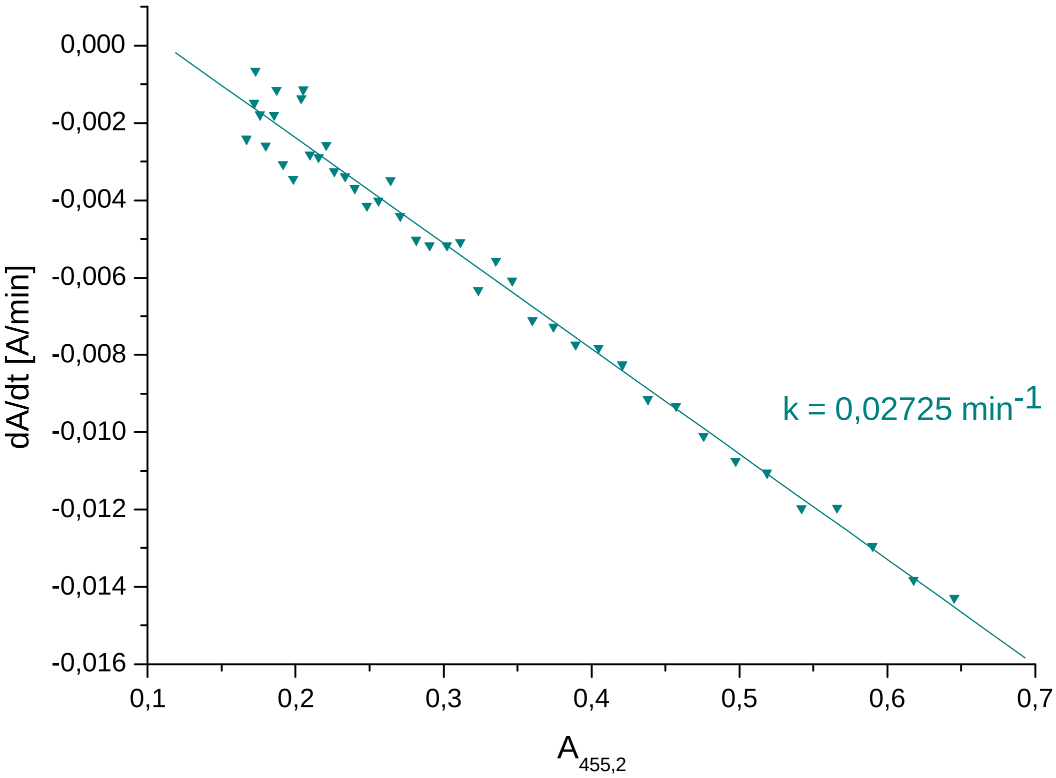

absorbance
2,4
2,2
2,0
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
280
300
320
340
360
380
400
420
440
460
wavelength [nm]
340 nm
455.2 nm
306,5 nm
402 nm

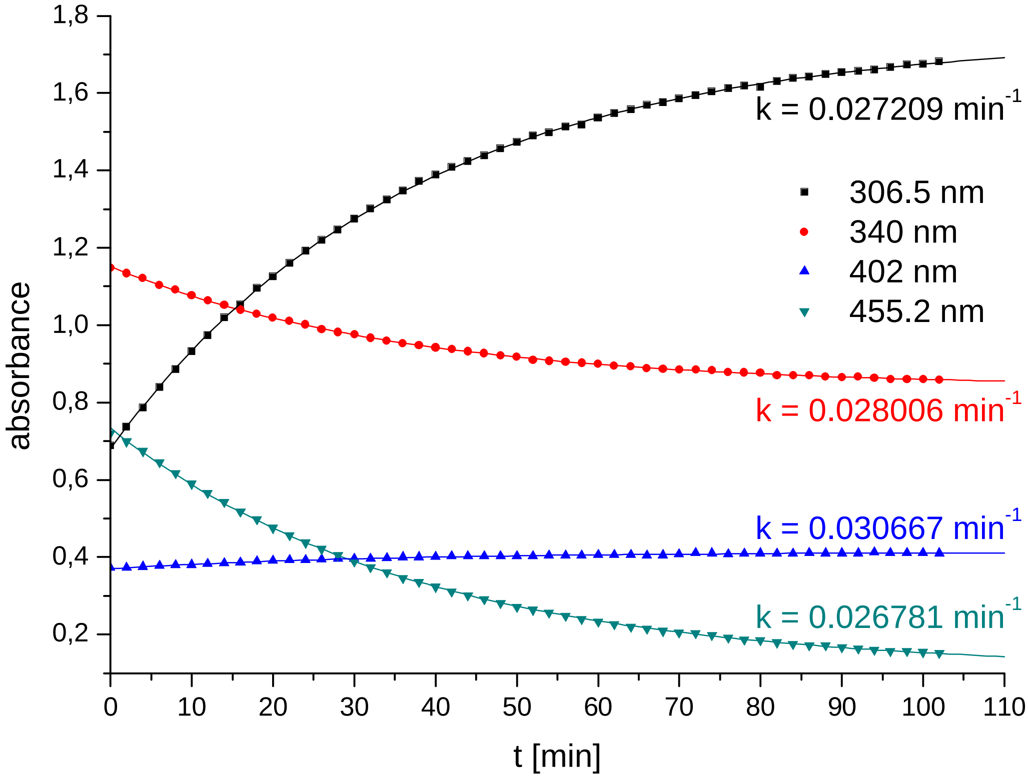

absorbance
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
$A_{455.2}$
■ 290 nm
● 306.5 nm
▲ 340 nm
▼ 402 nm


0.025
0.020
0.015
0.010
0.005
0.000
dA/dt [A/min]
0.8
1.0
1.2
1.4
1.6
1.8
$A_{306,5}$
k = 0.02734 min

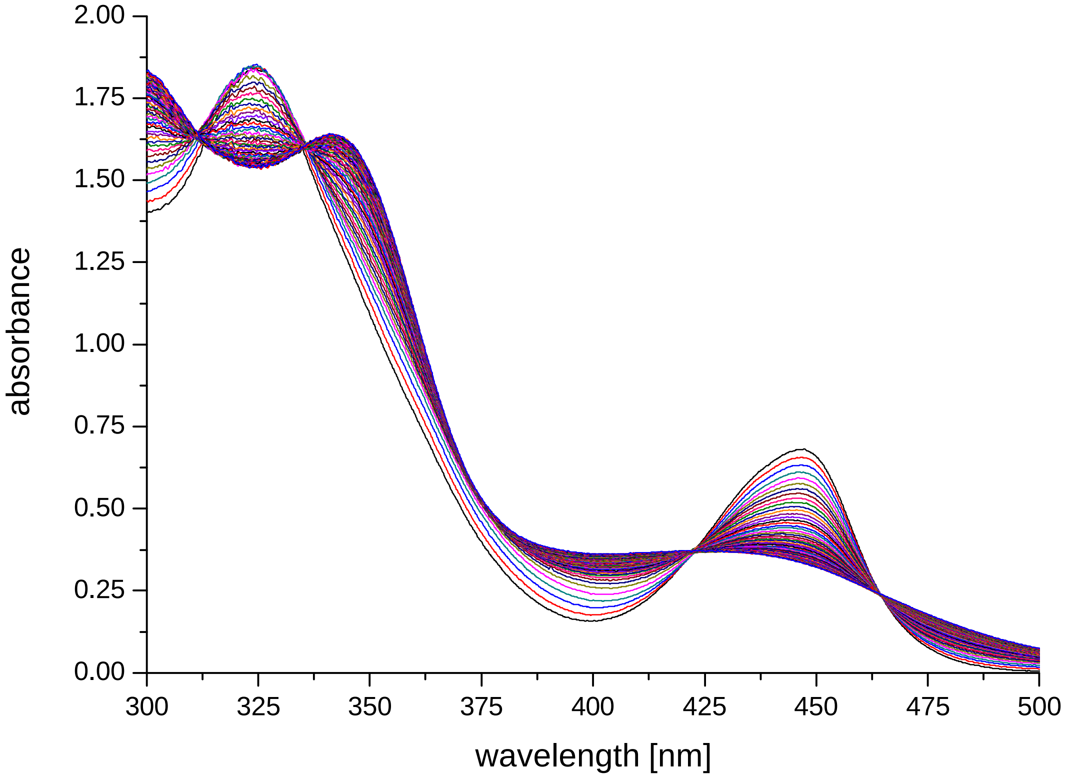

0,010
0,008
0,006
0,004
0,002
0,000
-0,002
-0,004
-0,006
-0,008
-0,010
da/dt [A/min]
0,85
0,90
0,95
1,00
1,05
1,10
A_{340}
k = 0,0279 min^{-1}

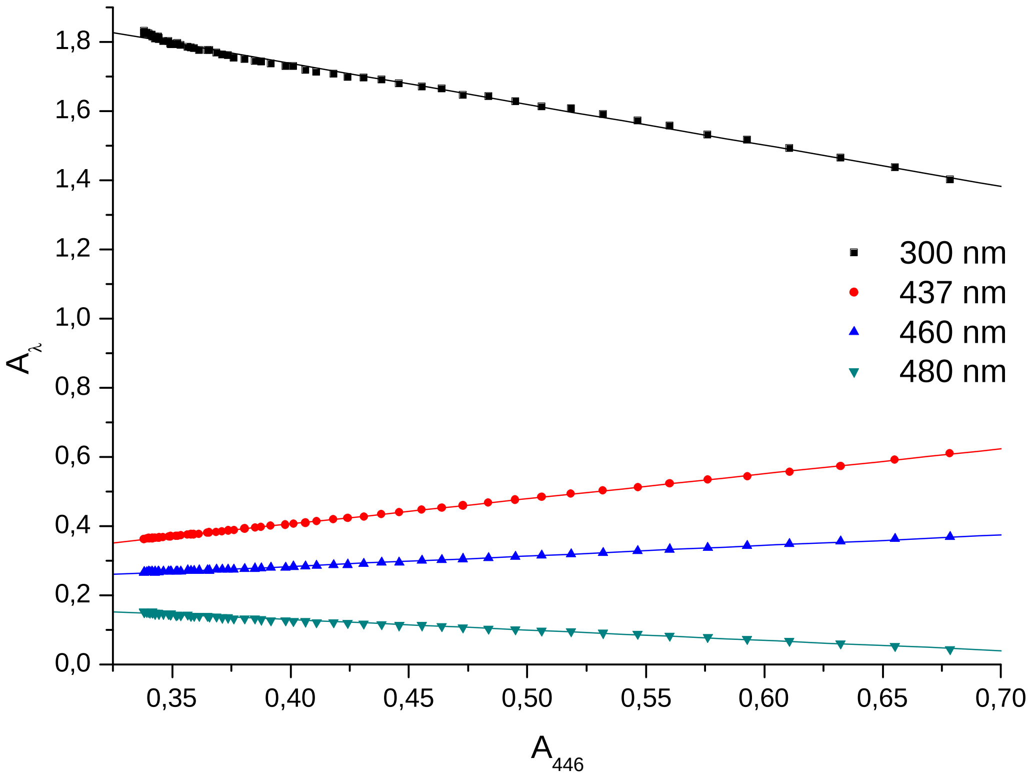

k = 0,02936 min^{-1}
dA/dt [A/min]
0,005
0,004
0,003
0,002
0,001
0,000
-0,001
-0,002
-0,003
-0,004
-0,005
0,375
0,380
0,385
0,390
0,395
0,400
0,405
0,410
A$_{402}$


dA/dt [A/min]
0,000
-0,002
-0,004
-0,006
-0,008
-0,010
-0,012
-0,014
-0,016
0,1
0,2
0,3
0,4
0,5
0,6
0,7
$A_{455,2}$
k = 0,02725 min^{-1}

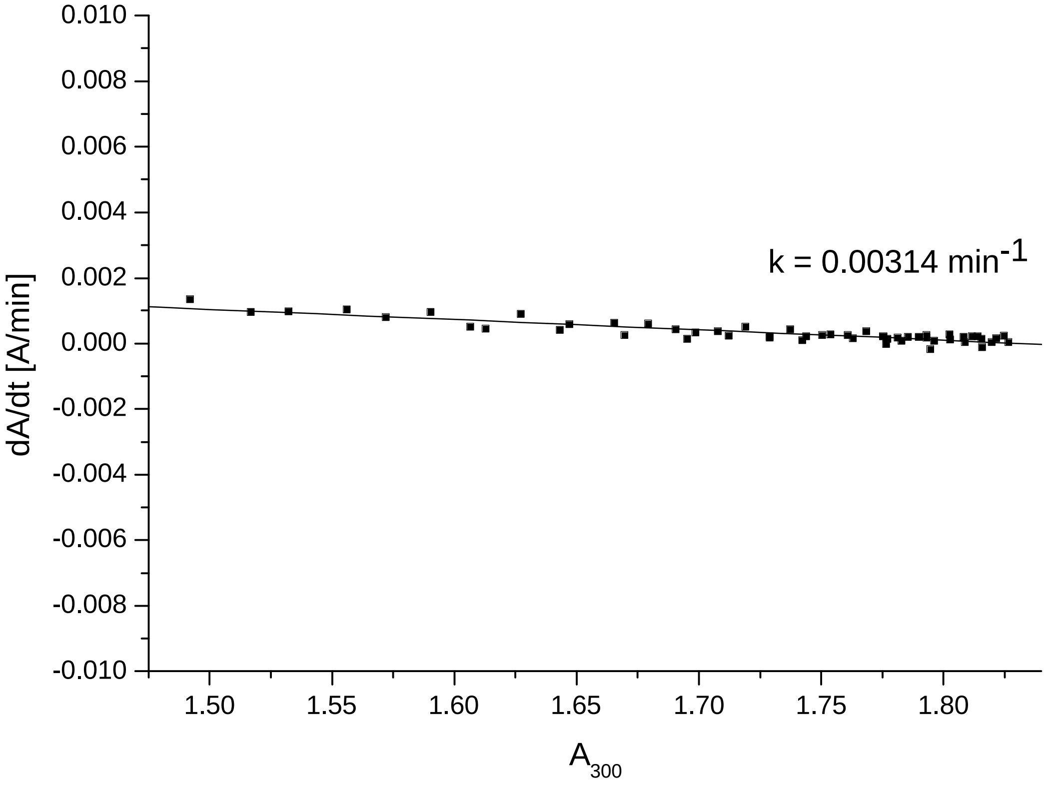

1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
absorbance
0
10
20
30
40
50
60
70
80
90
100
110
t [min]
k = 0.027209 min^{-1}
306.5 nm
340 nm
402 nm
455.2 nm
k = 0.028006 min^{-1}
k = 0.030667 min^{-1}
k = 0.026781 min^{-1}

Results from the UV/Vis-spectroscopic, stoichiometric hydrogenation of [Rh(DPPE)COD]BF_4 ((0.019 mmol catalyst, 40.0 ml MeOH, 25.0°C, scanning time = 20 min, 60 nm/min, d= 0.5 cm)

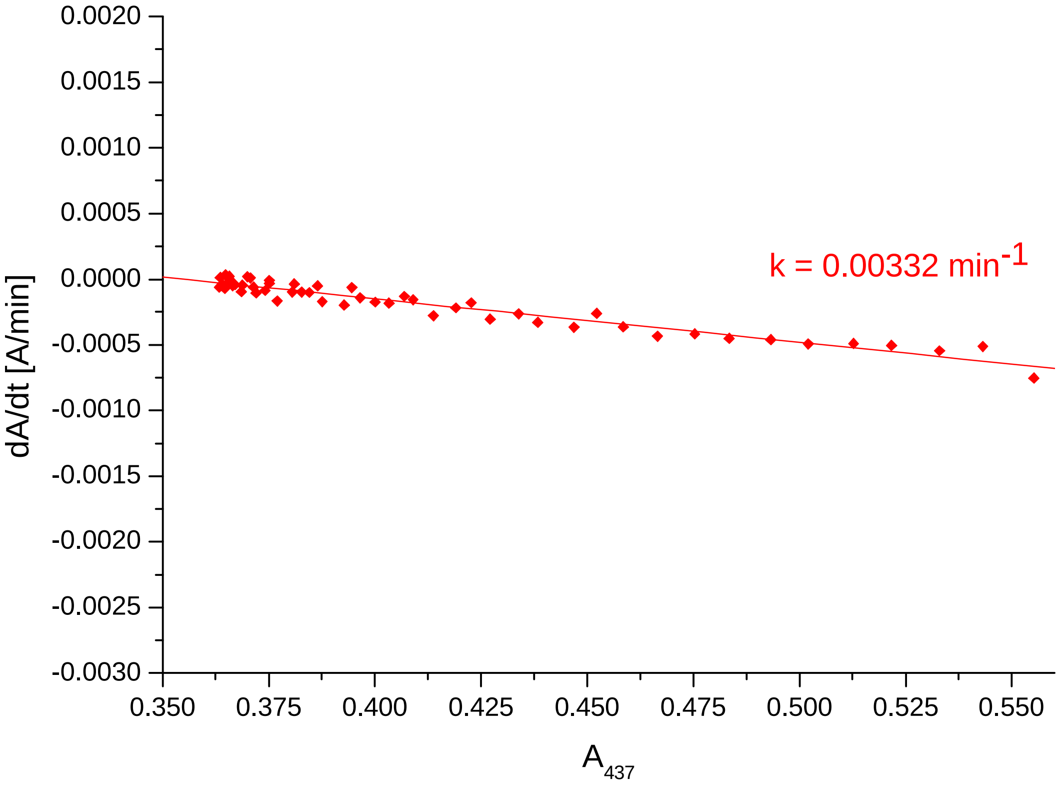


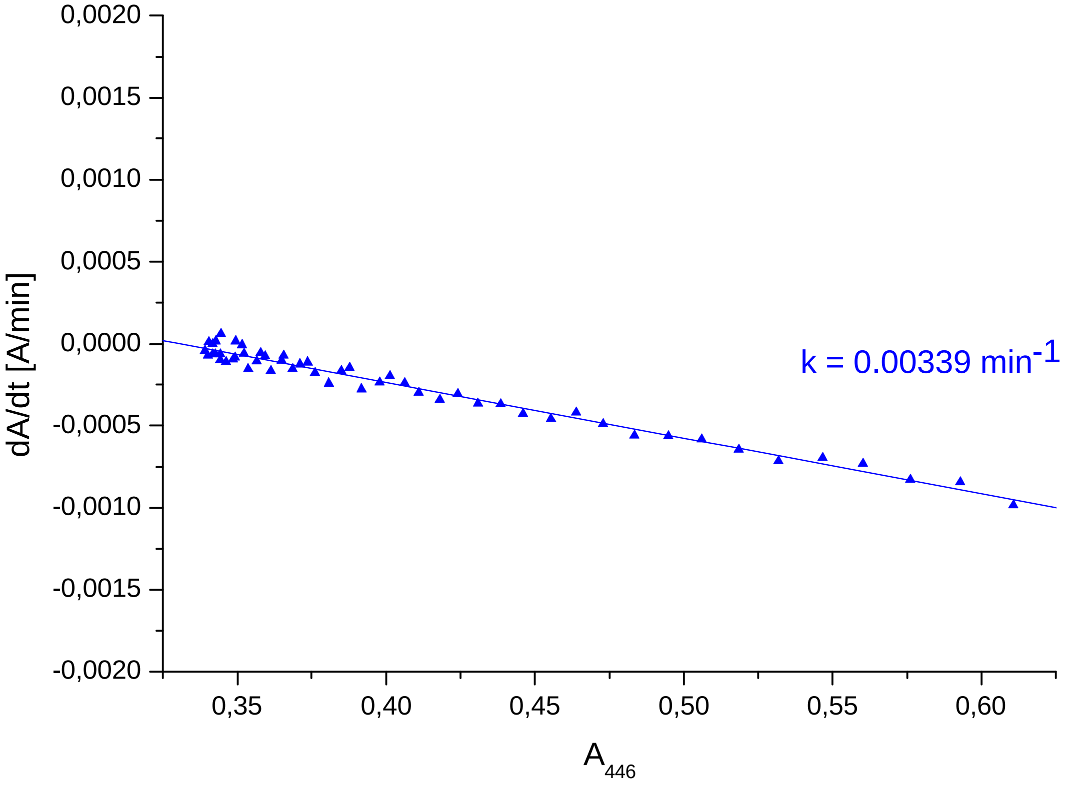


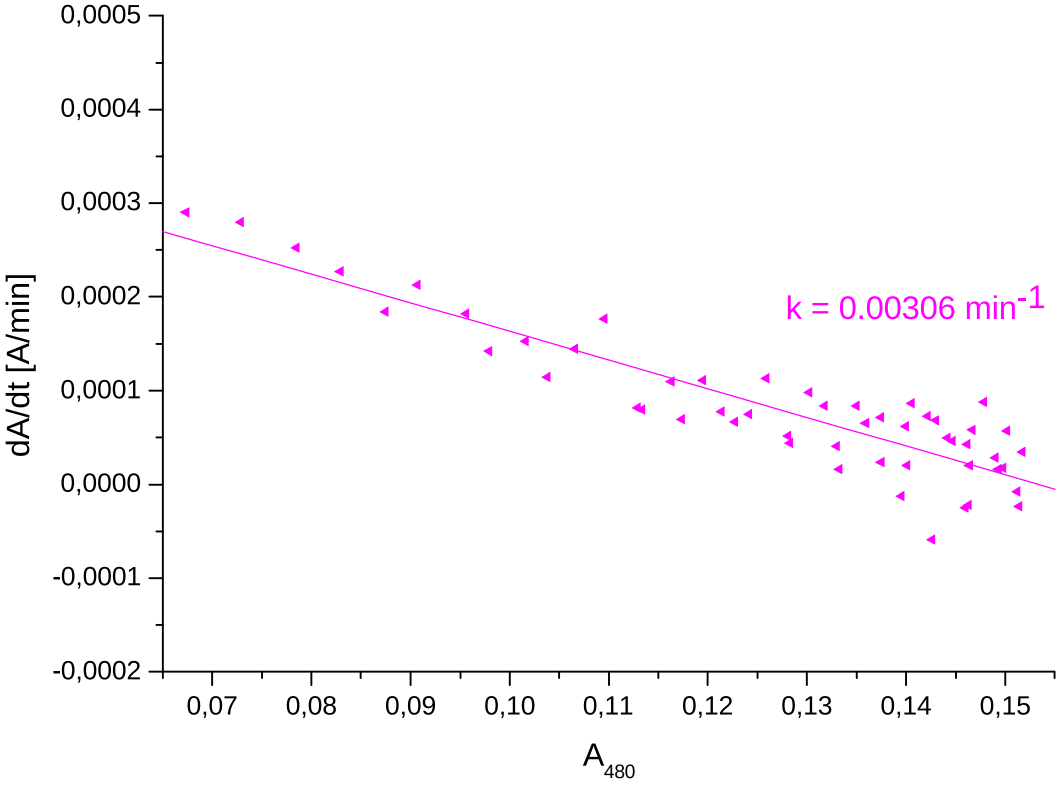
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
A_λ
0,35
0,40
0,45
0,50
0,55
0,60
0,65
0,70
A_{446}
300 nm
437 nm
460 nm
480 nm

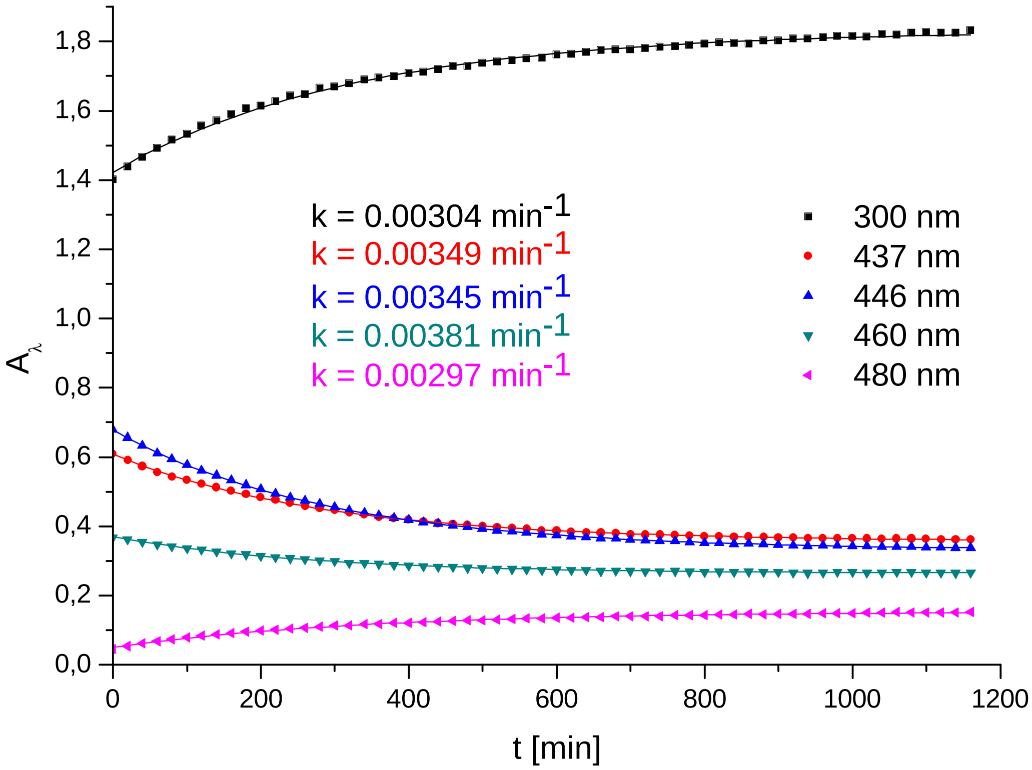


0.010
0.008
0.006
0.004
0.002
0.000
-0.002
-0.004
-0.006
-0.008
-0.010
dA/dt [A/min]
1.50
1.55
1.60
1.65
1.70
1.75
1.80
A_{300}
k = 0.00314 min^{-1}


0.0020
0.0015
0.0010
0.0005
0.0000
-0.0005
-0.0010
-0.0015
-0.0020
-0.0025
-0.0030
dA/dt [A/min]
0.350
0.375
0.400
0.425
0.450
0.475
0.500
0.525
0.550
A_{437}
k = 0.00332 min^{-1}


0,0020
0,0015
0,0010
0,0005
0,0000
-0,0005
-0,0010
-0,0015
-0,0020
dA/dt [A/min]
0,35
0,40
0,45
0,50
0,55
0,60
A_{446}
k = 0.00339 min^{-1}


0,0005
0,0004
0,0003
0,0002
0,0001
0,0000
-0,0001
-0,0002
dA/dt [A/min]
0,07
0,08
0,09
0,10
0,11
0,12
0,13
0,14
0,15
A_{480}
k = 0.00306 min^{-1}



k = 0.00304 min-1
k = 0.00349 min-1
k = 0.00345 min-1
k = 0.00381 min-1
k = 0.00297 min-1
300 nm
437 nm
446 nm
460 nm
480 nm
Aλ
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
200
400
600
800
1000
1200
t [min]