Modelling of the consumption of a dye used to probe the decomposition of Nitrocellulose

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Motivations and Objectives

- Nitrocellulose is a special polymer and features properties not yet achieved with other polymers:
  > it can be used to get hard, flexible and tight films for lacquers, possible with very high gloss;
  > it is environmentally without issue, means it is a 'green' substance;
  > it is produced according to the goal of sustainability – renewable raw materials are used
  > it is used for medical and biochemical purposes: filtration, blot processes;
- NC is an energetic polymer, which burns nearly perfectly smokeless (theater NC, flash paper);
- NC has good mechanical properties which make GP grains strong and useable under high mechanical loads;
- NC shows slow intrinsic decomposition because of the weakness of the CO-NO_2 bond at all three positions of the 1-4-β-anhydroglucopyranose (AHP) rings;
- But: well manufactured NC is of good intrinsic thermal stability;
- To protect NC against autocatalytical attack by split-off NOx it must be stabilized;
- The three ring positions of AHP rings, C2, C3, C6 have different bond dissociation enthalpies;
- Therefore they should react with different rates.

- The idea is to get information about the different reaction rates in decomposition of CO-NO_2 groups;
- The reaction with a stabilizer could give this information during the initial range of decomposition.
- Clarification of the reactivity order of the three sites at the AHP ring

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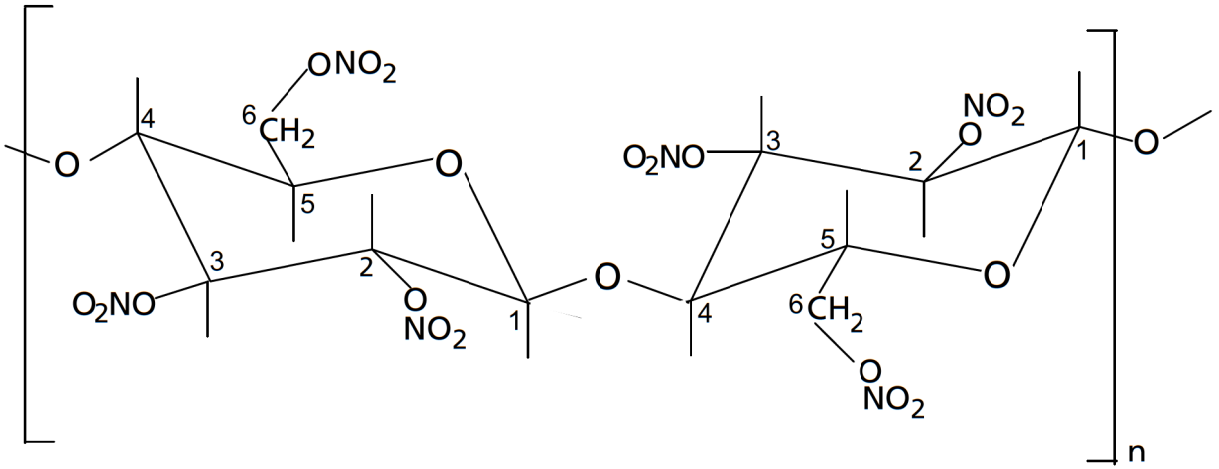
Nitrocellulose (NC)

cellulose nitrate
flash paper, flash cotton, flash string, gun cotton



1→4-O-β-D-glucosidic bond or (generally) 1→4-O-β-D-glycosidic bond

β means equatorial bond, α means axial bond. The monomer base is cellobiose.

Bond dissociation enthalpies (not energies!) of the CO-NO_2 bonds, determined by QM calculations (with Dmol^3 from Accelrys)

C2: 161 kJ/mol
C3: 133 kJ/mol
C6: 174 kJ/mol

C2 : C3 : C6
relative values
0.92 : 0.76 : 1.00

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Data of the used nitrocellulose in this work

Property	**unit**	**value**
Nitrogen content	mass-%	12.15
Mean molar mass of one anhydroglucopyranose unit	g/mol	265.95
Mean total degree of substitution (TDS)	-	2.307
Content of ONO_2 groups	mass-%	53.79
Content of NO_2 groups	mass-%	39.91
Oxygen balance	%	-37.49

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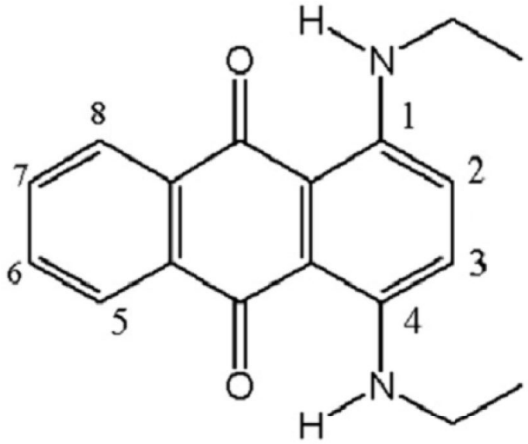
The experimental data

Mohammed Moniruzzaman in short named ‘Monir’ has made experiments with NC and an added dye.



an anthraquinone based dye was used, SB 59

1,4-bis (ethylamino) -9,10-anthraquinone

It has an activated aromatic system, radical substitution is possible.

It acts as a stabilizer.

NC films have been manufactured with 2 mass-% dye and 5 mass-% dioctyl phthalate using butanone as solvent.

The films and prior the NC have been thoroughly dried.

The decrease of the added dye was determined by UV-VIS spectroscopy.

For the initial decrease of the dye concentration a reaction type of first order was assumed at first.

But the course of the concentration decrease was different from a first order decrease.

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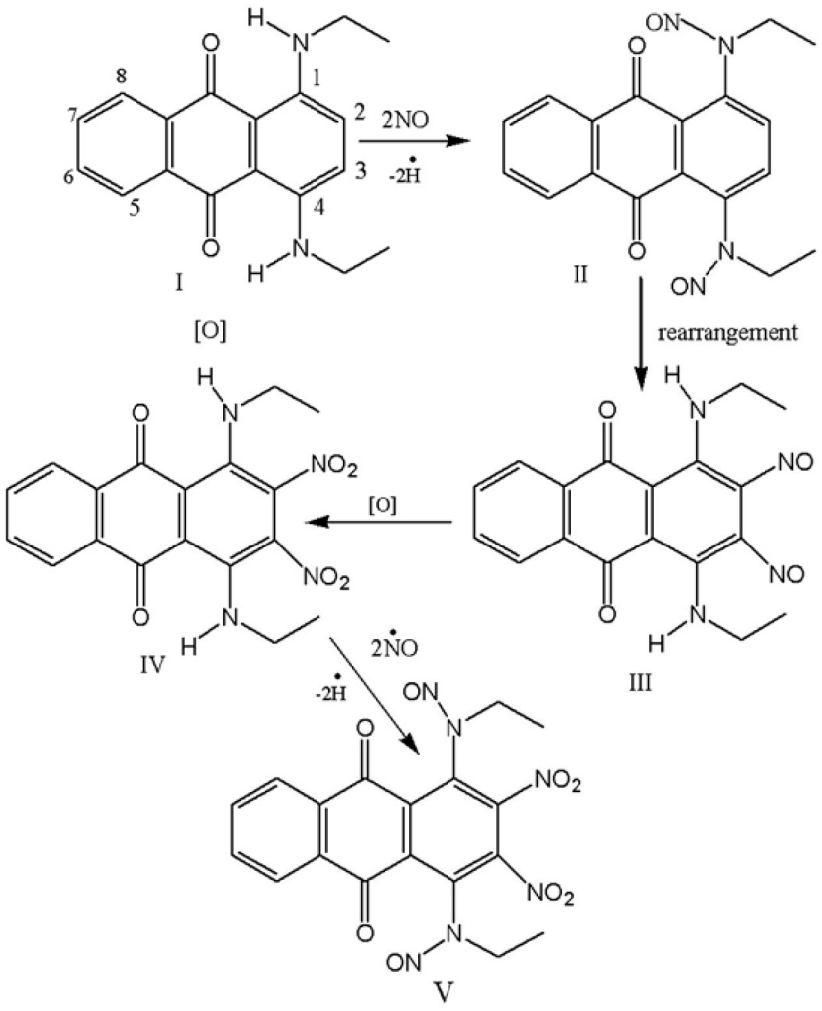
Simplified reaction scheme of the reaction between dye and NOx



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Experimental data and first evaluation

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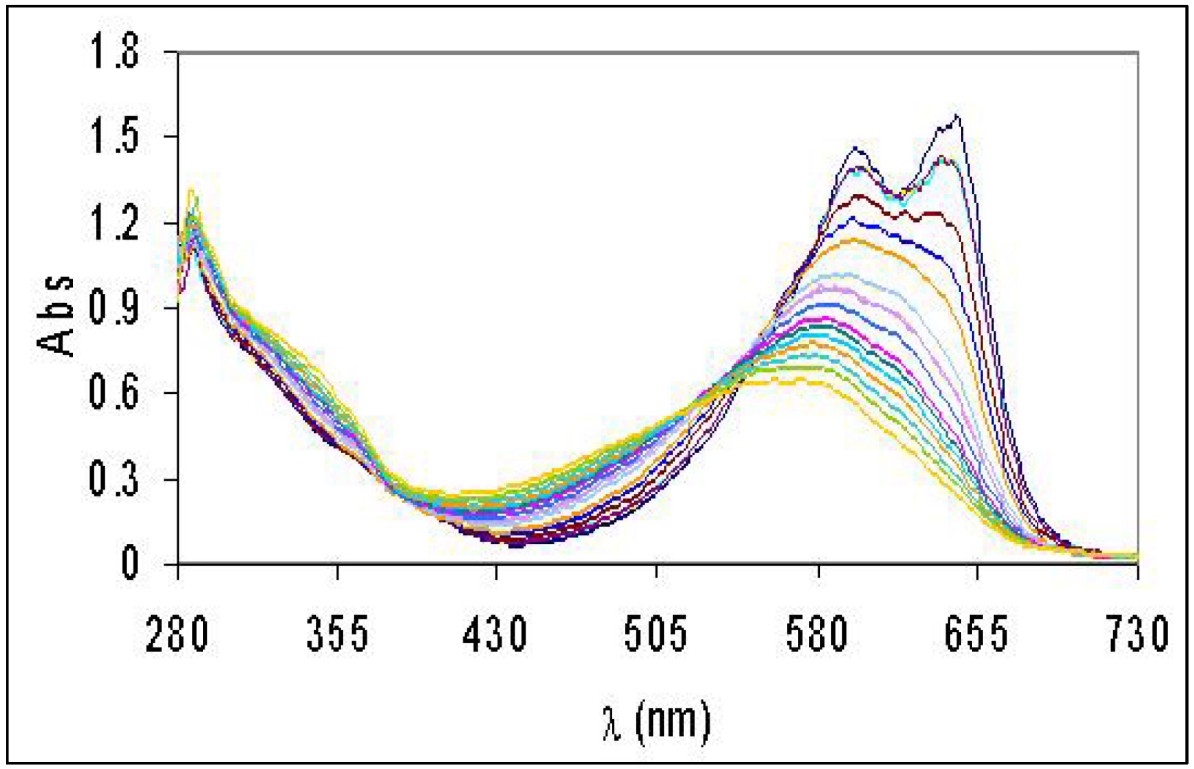
Example of UV-VIS spectra obtained from NC films with time



Ageing times and absorbance values of dye at 50°C

time [h]	A_S [-]
0	1.44
6	1.388
22.5	1.293
46.5	1.195
75	1.122
141	1
188	0.94
260	0.861
361	0.799
428	0.767
504	0.729
596	0.693
764	0.63
934	0.55

UV-visible absorption spectra of an unaged NC film and NC film aged at 50ºC as function of time.

Two isosbestic points can be seen, one at about 552 nm, the other at 380 nm. This indicates a systematic decrease of dye concentration without disturbances.

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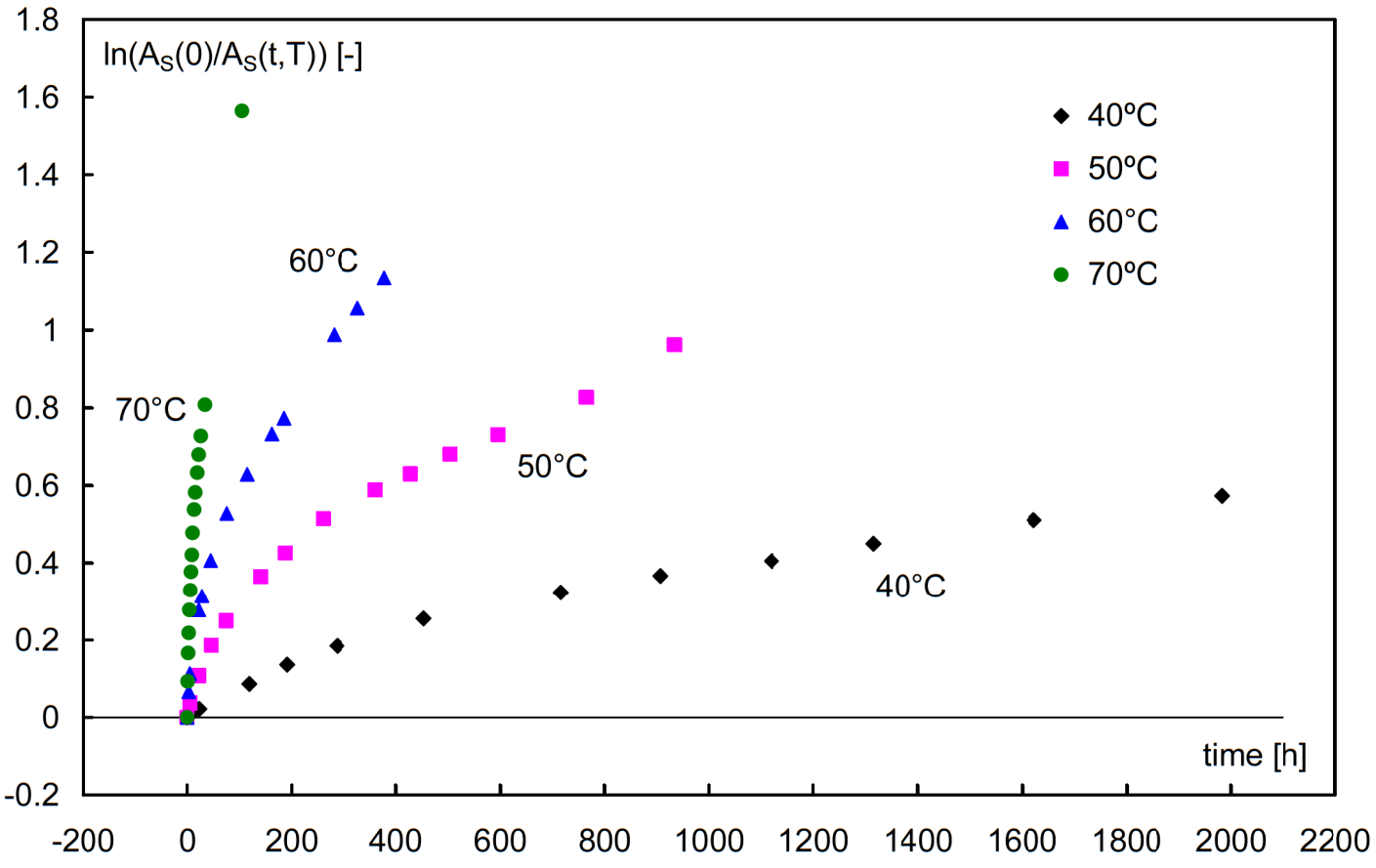
The experimental data plotted as $\ln(A_S(0)/A_S(t))$ as function of ageing time



Ageing times and absorbance values of dye at 50°C

time [h]	A_S [-]	evaluation
0	1.44	Δt_1
6	1.388	
22.5	1.293	0 - 46.5 h
46.5	1.195	
75	1.122	Δt_2
141	1	
188	0.94	75 -260 h
260	0.861	
361	0.799	Δt_3
428	0.767	
504	0.729	22 - 105 h
596	0.693	
764	0.63	
934	0.55	

Plots of logarithmic absorbance ratio $\ln(A_S(0)/A_S(t,T)) = \ln(c_S(0)/c_S(t,T)$ against aging time for NC films containing the dye SB 59, which were aged at 40ºC, 50ºC, 60ºC and 70ºC.

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Plot of $\ln(A_S(0)/A_S(t)) = \ln(c_S(0)/c_S(t))$ against aging time, samples aged at 70 ºC

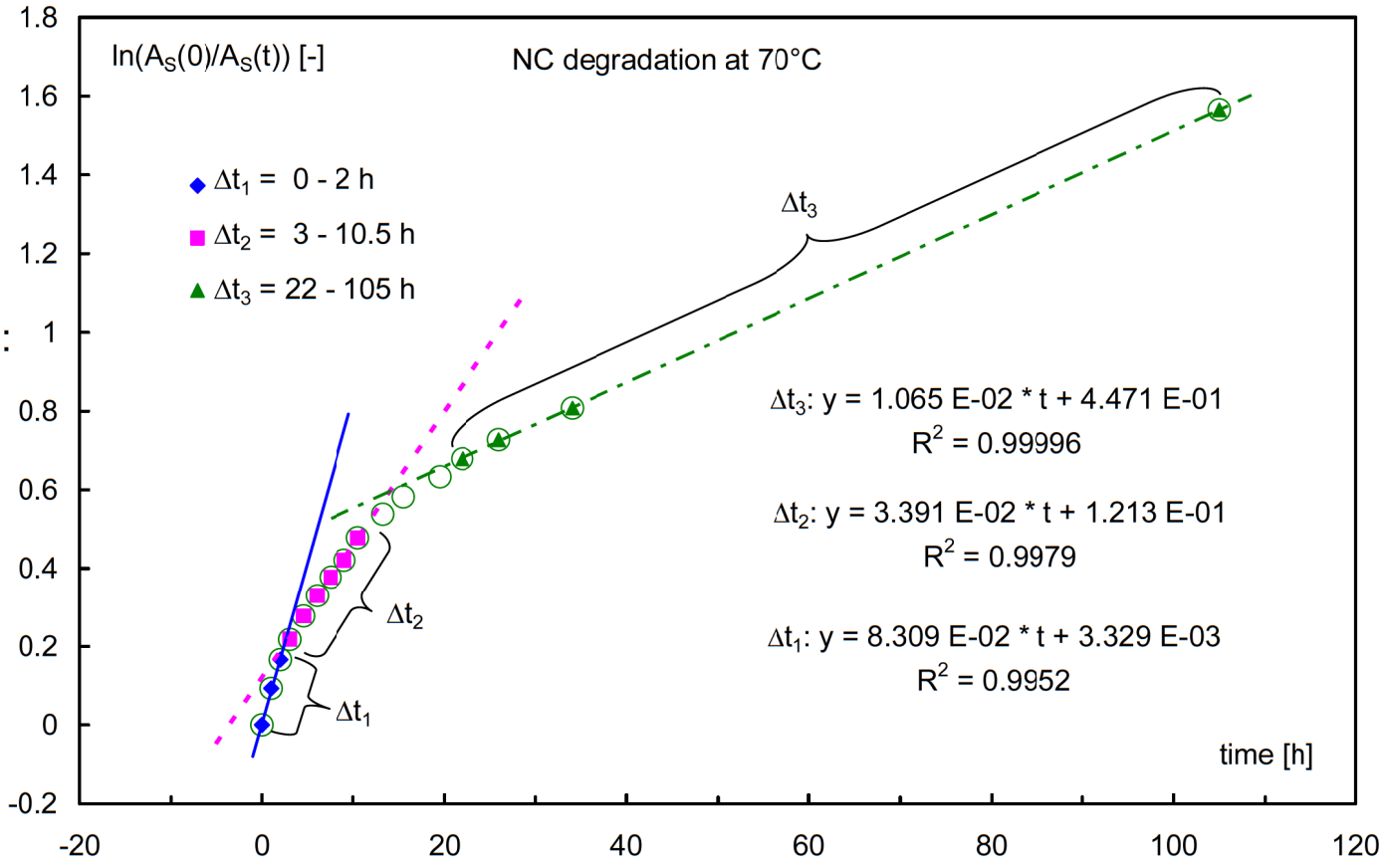
Segmental evaluation

time intervals of evaluation at 70°C:

(i) $\Delta t1$ = 0 - 2 h, first part

(ii) $\Delta t2$ = 3 - 10.5 h, second part

(iii) $\Delta t3$ = 22 - 105 h, third part



The big open circles indicate all data obtained at 70°C,

the full symbols indicate the parts used for evaluation.

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Kinetic description of concentration change of dye with reaction time

$$\ln\left(\frac{I_{S,0}(\lambda,T)}{I_S(\lambda,0,T)}\right) = A_S(\lambda,0,T) = c_S(0,T)\cdot d(T)\cdot \varepsilon_S(\lambda,T)$$

$$\ln\left(\frac{I_{S,0}(\lambda,T)}{I_S(\lambda,t,T)}\right) = A_S(\lambda,t,T) = c_S(t,T)\cdot d(T)\cdot \varepsilon_S(\lambda,T)$$

$$\frac{A_S(\lambda,t,T)}{A_S(\lambda,0,T)} = \frac{c_S(t,T)}{c_S(0,T)}$$

$$\frac{c_S(t,T)}{c_S(0,T)} = \exp\left(-k_S(T)\cdot t\right)$$

$$\ln\left(\frac{c_S(0,T)}{c_S(t,T)}\right) = \ln\left(\frac{A_S(\lambda,0,T)}{A_S(\lambda,t,T)}\right) = k_S(T)\cdot t$$

A_S = absorbance of the non-nitrated dye
ε_S = absorptivity of the non-nitrated dye
λ = wavelength
T = temperature
t = time
c_S = concentration of the non-nitrated dye
k_S = reaction rate constant of first order reaction

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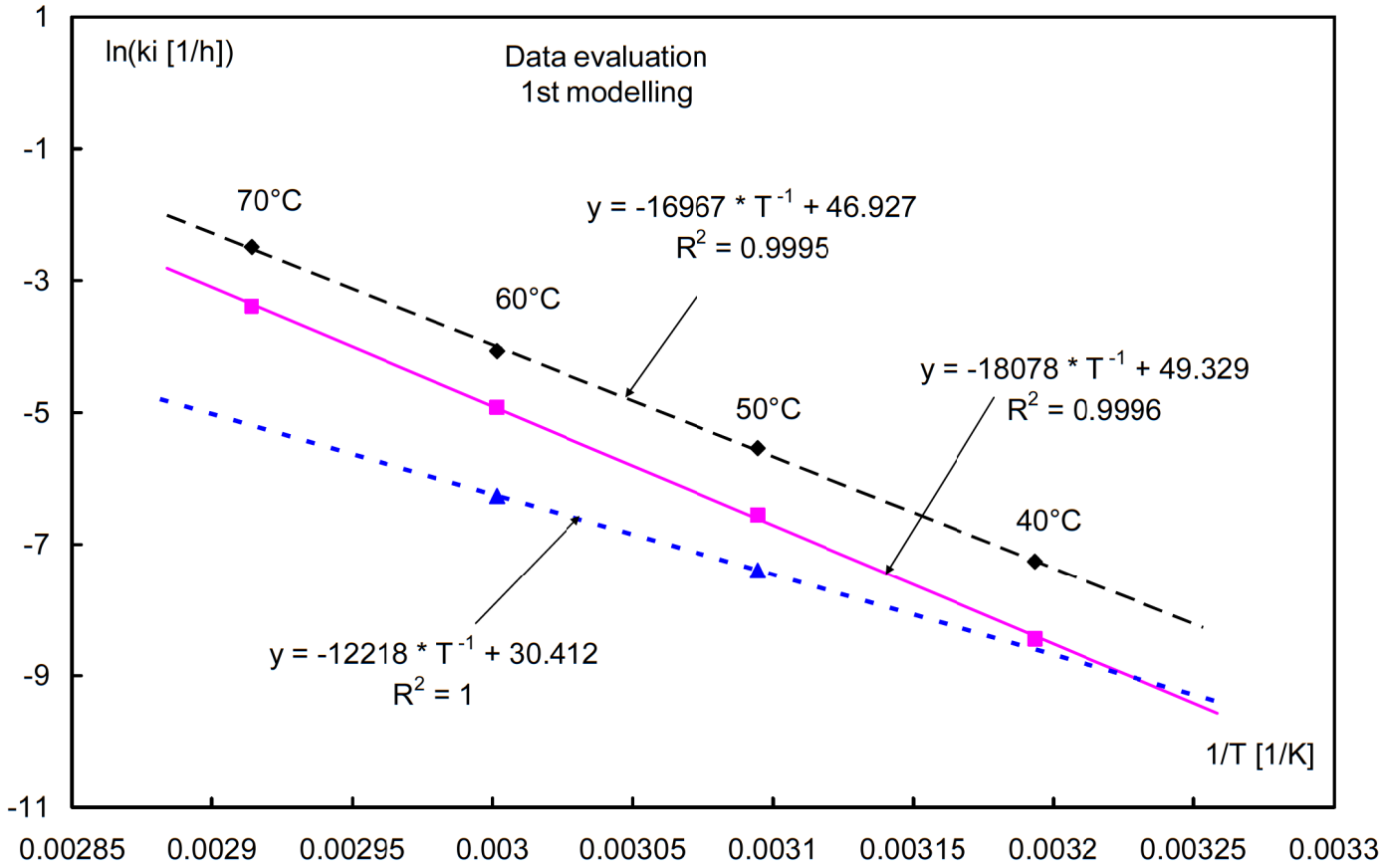
Arrhenius plots of reaction rate constants – first modelling



Arrhenius plot of the reaction rate constants of NC decomposition at C2, C3 and C6, monitored by the dye SB 59.
The rate constants have been extracted from the linear parts of the first order plots.

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Results of data evaluation by segmental application of three 1st order reactions

1st modelling - segmental evaluation with three first order reactions: > single description of 'single' (assumed) reactions with $\ln(c_S(0)/c_S(t,T))$, > one first order reaction, > for each temperature alone and applied segmental on the three parts of each curves, > equal weighting by A_i for each C_i position on AHP rings.			
AHP Ring position	**2**	**3**	**6**
weighting by A_i	1	1	1
Ea [kJ mol^{-1}]	141.1 ± 3	101.6 ± 12	150.3 ± 3
Log(Z [h^{-1}])	20.380 ± 0.4	13.208 ± 1.5	21.423± 0.4
R^2	0.9995	0.988	0.9996
Quantum mechanical calculation of bond dissociation enthalpies (BDEnt)			
BDEnt [kJ mol^{-1}]	161	133	174

The segmental application assumes implicitly a type of consecutive decomposition (means one after the other) of the nitrate ester groups at the three ring positions.

But the three sites decompose in parallel.

$$NC_{236} \xrightarrow{k_2} NC_{36} + P$$

$$NC_{36} \xrightarrow{k_3} NC_6 + P$$

$$NC_6 \xrightarrow{k_6} NC\text{-}B + P$$

$$F + P \xrightarrow{k_F} F\text{-}P$$

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Extended modelling of the data

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Parallel reaction scheme and rate equations - 1

$$NC_2 \xrightarrow{k_2} B_2 + P$$

$$NC_3 \xrightarrow{k_3} B_3 + P$$

$$NC_6 \xrightarrow{k_6} B_6 + P$$

$$S + P \xrightarrow{k_F} S\text{-}P$$

$$\frac{dS(t)}{dt} = -k'_F \cdot S(t) \cdot P(t)$$

$$\frac{dNC(t)}{dt} = \frac{dNC_2(t)}{dt} + \frac{dNC_3(t)}{dt} + \frac{dNC_6(t)}{dt} = -k_2 \cdot NC_2(t) - k_3 \cdot NC_3(t) - k_6 \cdot NC_6(t)$$

$$NC(t) = NC_2(0) \cdot \exp(-k_2 \cdot t) + NC_3(0) \cdot \exp(-k_3 \cdot t) + NC_6(0) \cdot \exp(-k_6 \cdot t)$$

$$NC(0) = NC_2(0) + NC_3(0) + NC_6(0)$$

Normalization

$$\frac{NC(t)}{NC(0)} = \frac{NC_2(0)}{NC(0)} \cdot \exp(-k_2 \cdot t) + \frac{NC_3(0)}{NC(0)} \cdot \exp(-k_3 \cdot t) + \frac{NC_6(0)}{NC(0)} \cdot \exp(-k_6 \cdot t)$$

$$NCr(t) = A_2 \cdot \exp(-k_2 \cdot t) + A_3 \cdot \exp(-k_3 \cdot t) + A_6 \cdot \exp(-k_6 \cdot t)$$

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Parallel reaction scheme and rate equations - 2

$$\frac{d\left(\frac{S(t)}{S(0)}\right)}{dt} = -k_F \cdot \frac{S(t)}{S(0)}$$

Assumption
during the initial decomposition period the concentration of P is kept small and nearly constant by the action of the dye: P(t) = Po.
Then it can be fused with k'_F to the new constant k_F: $k_F = k'_F \cdot Po$

$$\frac{dSr(t)}{dt} = -k_F \cdot Sr(t) = \frac{dNCr(t)}{dt}$$

The normalized decrease of the dye is equal to the normalized decrease of NC

$$Sr(t) - 1 = NCr(t) - 1$$

$$Sr(t) = A_2 \cdot \exp(-k_2 \cdot t) + A_3 \cdot \exp(-k_3 \cdot t) + A_6 \cdot \exp(-k_6 \cdot t)$$

$$Sr(0) = 1 = \frac{NC_2(0)}{NC(0)} + \frac{NC_3(0)}{NC(0)} + \frac{NC_6(0)}{NC(0)}$$

$$Sr(0) = 1 = A_2 + A_3 + A_6$$

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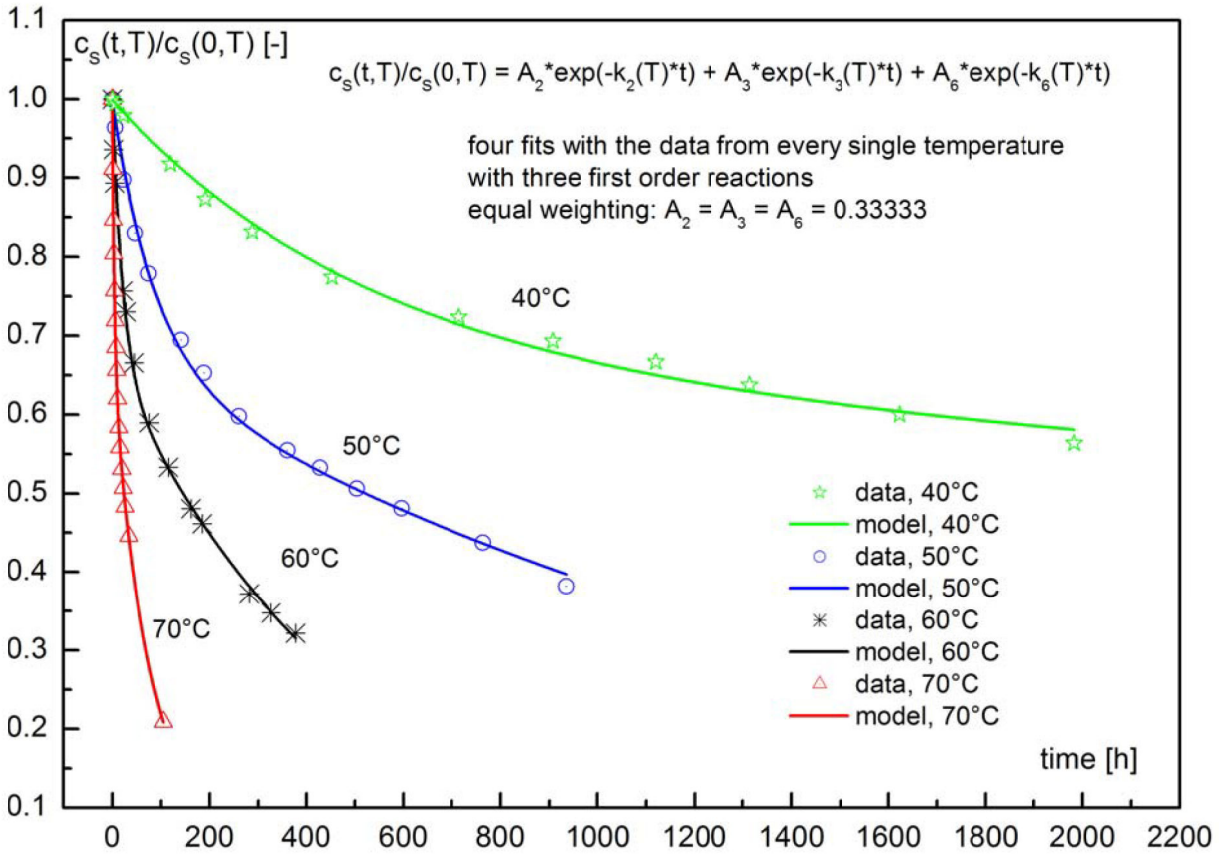
Use of three first order reactions, applied at each temperature alone



Description of the decrease of the dye concentration with three reactions of first order, applied for each temperature alone, but all three reactions fitted at once. **Equal weighting**: $A_2 = A_3 = A_6 = 0.33333$.

$$\frac{c_S(t,T)}{c_S(0)} = Sr(t,T) = A_2 \cdot \exp(-k_2(T) \cdot t) + A_3 \cdot \exp(-k_3(T) \cdot t) + A_6 \cdot \exp(-k_6(T) \cdot t)$$

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Results of data evaluation by application of three 1st order reactions

modelling with three first order reactions, using all data at each temperature: > single temperature description, but all three segments at each temperature at once, > three first order reactions, > for each temperature alone, > equal weighting by A_i for each C_i position on AHP rings.			
AHP Ring position	**2**	**3**	**6**
weighting by A_i	0.33333	0.33333	0.33333
Ea [kJ mol^{-1}]	139.0 ± 3	134.1 ± 9	157.4 ± 12
lg(Z [h^{-1}])	20.483 ± 0.6	18.316 ± 1.4	22.121 ± 1.9
R^2	0.9988	0.9917	0.9890
Quantum mechanical calculation of bond dissociation enthalpies (BDEnt)			
BDEnt [kJ mol^{-1}]	161	133	174

Direct determination of the three sets of rate constants.

The Arrhenius parameters were determined via separate Arrhenius plots

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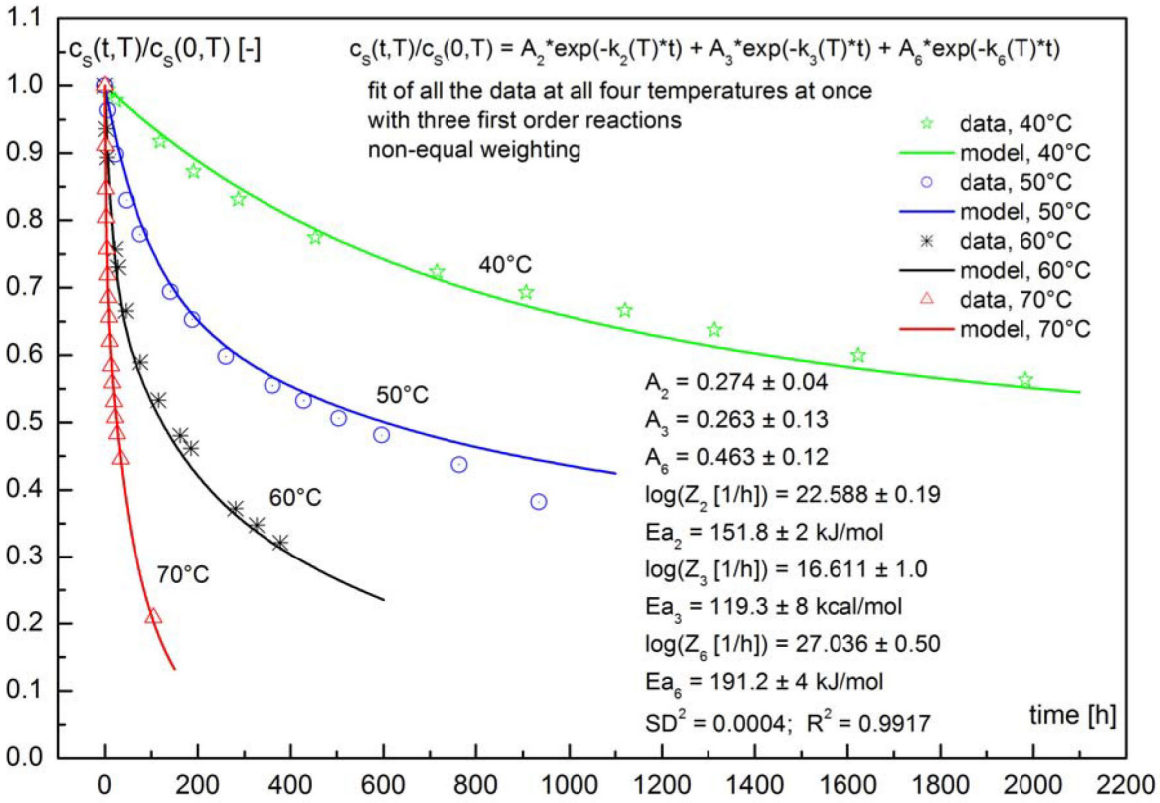
Use of three first order reactions, unequal weighting, all data at once



Description of the decrease of the dye concentration with three first order reactions.
Fitting of all data at once with unequal weighting.

$$\frac{c_S(t,T)}{c_S(0)} = Sr(t,T) = A_2 \cdot \exp(-k_2(T) \cdot t) + A_3 \cdot \exp(-k_3(T) \cdot t) + A_6 \cdot \exp(-k_6(T) \cdot t)$$

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Results of data evaluation by three 1st order reactions, all data at once

modelling with three first order reactions, using all data at all temperatures at once: > all temperature all data description, > three first order reactions, > unequal weighting by A_i for each C_i position on AHP rings.			
AHP Ring position	**2**	**3**	**6**
weighting by A_i	0.274 ± 0.04	0.263 ± 0.13	0.463 ± 0.12
Ea [kJ mol^{-1}]	151.8 ± 2	119.3 ± 8	191.2 ± 4
lg(Z [h^{-1}])	22.588 ± 0.2	16.611 ± 1.0	27.036 ± 0.5
R^2	0.9917	-	-
Quantum mechanical calculation of bond dissociation enthalpies (BDEnt)			
BDEnt [kJ mol^{-1}]	161	133	174

Direct determination of the three sets of Arrhenius parameters and the three weighting factors

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The order of the reactions of the decrease in nitrate ester groups

It is plausible that the split-off of NO_2 from a nitrate ester group occurs according to a reaction of first order.
However, the active species in nitration may result from NO_2 radicals combining to give N_2O_4.
This would then lead to a reaction of second order.
Note: in order to fulfil the radical neutrality, two radicals must be always involved in aromatic radically nitration, also in case of N-NO formation. The second radical involved may be also one from the NC backbone. Then the reaction is monomolecular with respect to NO_2

The corresponding rate equation for stabilizer consumption is then:

$$\frac{dS(t)}{dt} = -k'_F \cdot S(t) \cdot P(t) \cdot P(t)$$

One split-off NO_2 snoops around. It still can recombine at the split-off site.
Accidentally it encounters a second one and forms N_2O_4.
The second NO_2 may come from the same AHP ring or a neighbouring one.

By forming N_2O_4 both NO_2 are lost for the NC, which has formally degraded by second order.
N_2O_4 is the attacking species in the stabilizer reaction, which is formally still bimolecular.
It can be seen as tri-molecular, but with coordinated two NO_2 molecules, so more bimolecular.

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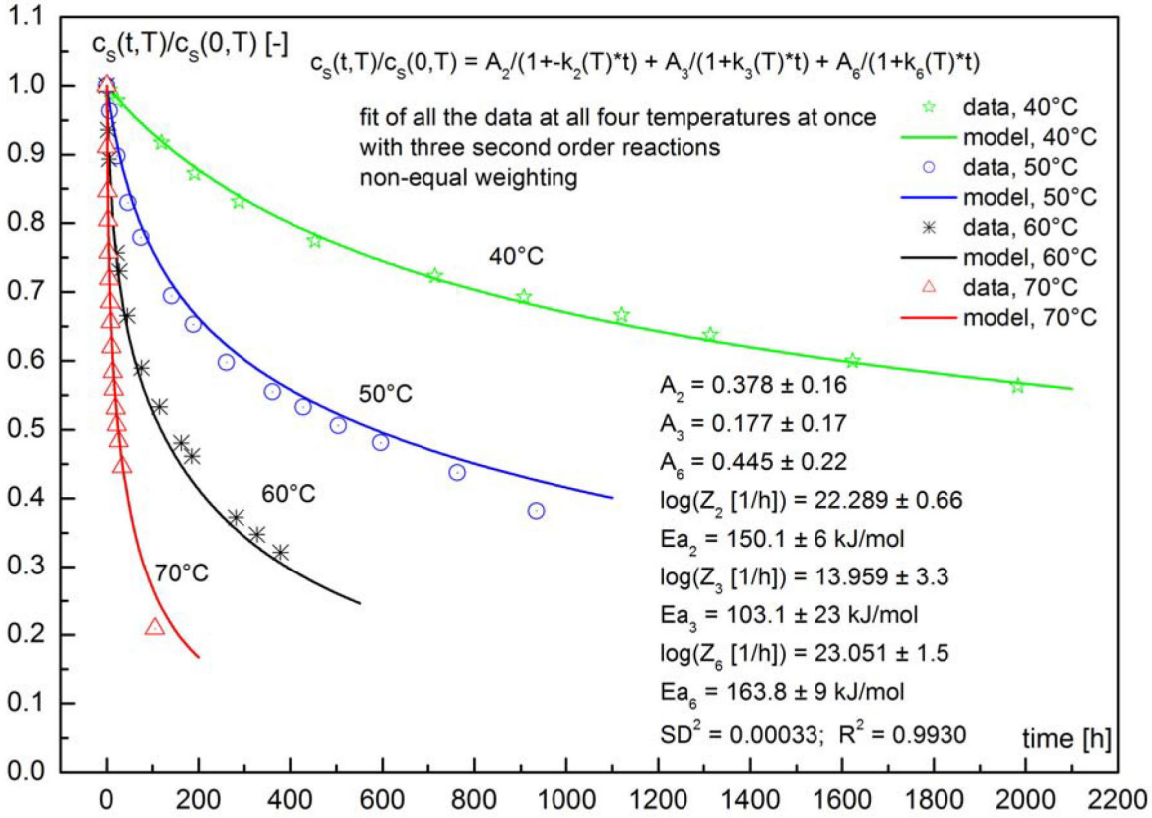
Use of three second order reactions, unequal weighting, all data at once



Description of the decrease of the dye concentration with three second order reactions.
Fitting of all data at once with unequal weighting.

$$\frac{c_S(t,T)}{c_S(0)} = Sr(t,T) = A_2/(1+k_2(T)\cdot t) + A_3/(1+k_3(T)\cdot t) + A_6/(1+k_6(T)\cdot t)$$

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Results of data evaluation by three 2nd order reactions, all data at once

modelling with three second order reactions, using all data at all temperatures at once: > all temperature all data description, > three 2nd order reactions, > unequal weighting by A_i for each C_i position on AHP rings.			
AHP Ring position	**2**	**3**	**6**
weighting by A_i	0.378 ± 0.16	0.177 ± 0.17	0.445 ± 0.22
Ea [kJ mol^{-1}]	150.1 ± 6	103.1 ± 23	163.8 ± 9
lg(Z [h^{-1}])	22.289 ± 0.66	13.959 ± 3.3	23.051 ± 1.5
n	2	2	2
R^2	0.9930	-	-
Quantum mechanical calculation of bond dissociation enthalpies (BDEnt)			
BDEnt [kJ mol^{-1}]	161	133	174

Direct determination of the three sets of Arrhenius parameters and the three weighting factors.

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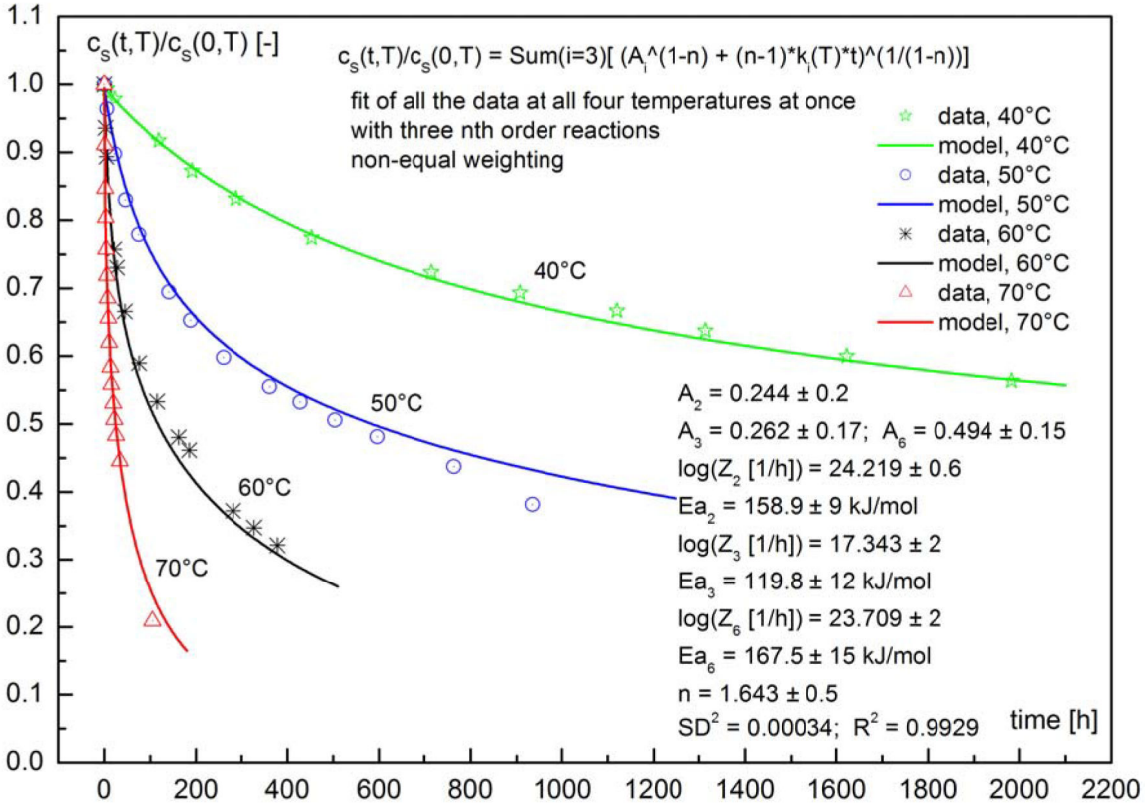
Use of three nth order reactions, unequal weighting, all data at once



Description of the decrease of the dye concentration with three nth order reactions and fitting all data at once, unequal weighting.

$$\frac{c_S(t,T)}{c_S(0)} = Sr(t,T) = \sum_{i=2,3,6} (A_i^{(1-n)} + (n-1)\cdot k_i(T)\cdot t)^{1/(1-n)}$$

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Results of data evaluation by three nth order reactions, all data at once

modelling with three nth order reactions, using all data at all temperatures at once: > all temperature all data description, > three nth order reactions, > unequal weighting by A_i for each C_i position on AHP rings.			
AHP Ring position	**2**	**3**	**6**
weighting by A_i	0.244 ± 0.2	0.262 ± 0.17	0.494 ± 0.15
Ea [kJ mol^{-1}]	158.9 ± 9	119.8 ± 12	167.5 ± 15
lg(Z [h^{-1}])	24.219 ± 0.60	17.343 ± 2	23.709 ± 2
n	1.643 ± 0.5	1.643 ± 0.5	1.643 ± 0.5
R^2	0.9929	-	-
Quantum mechanical calculation of bond dissociation enthalpies (BDEnt)			
BDEnt [kJ mol^{-1}]	161	133	174

Direct determination of the three sets of Arrhenius parameters and the three weighting factors and of one reaction order n, equal for the three nth order reactions.

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Summary of the best results – all temperature all data modelling

Modelling with three second order reactions in parallel				
Ring position	**2**	**3**	**6**	**A_i weighted average**
Weighting by A_i	0.378	0.177	0.445	1
Ea [kJ mol^{-1}]	150	103	164	147.9
lg(Z [h^{-1}])	22.289	13.959	23.051	21.154
Modelling with three first order reactions in parallel				
Weighting by A_i	0.274	0.263	0.463	1
Ea [kJ mol^{-1}]	152	119	191	161.5
lg(Z [h^{-1}])	22.588	16.611	27.036	23.075
BDEnth [kJ/mol]	160.8	133.0	174.4	-

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Arrhenius lines and decrease of partial concentrations

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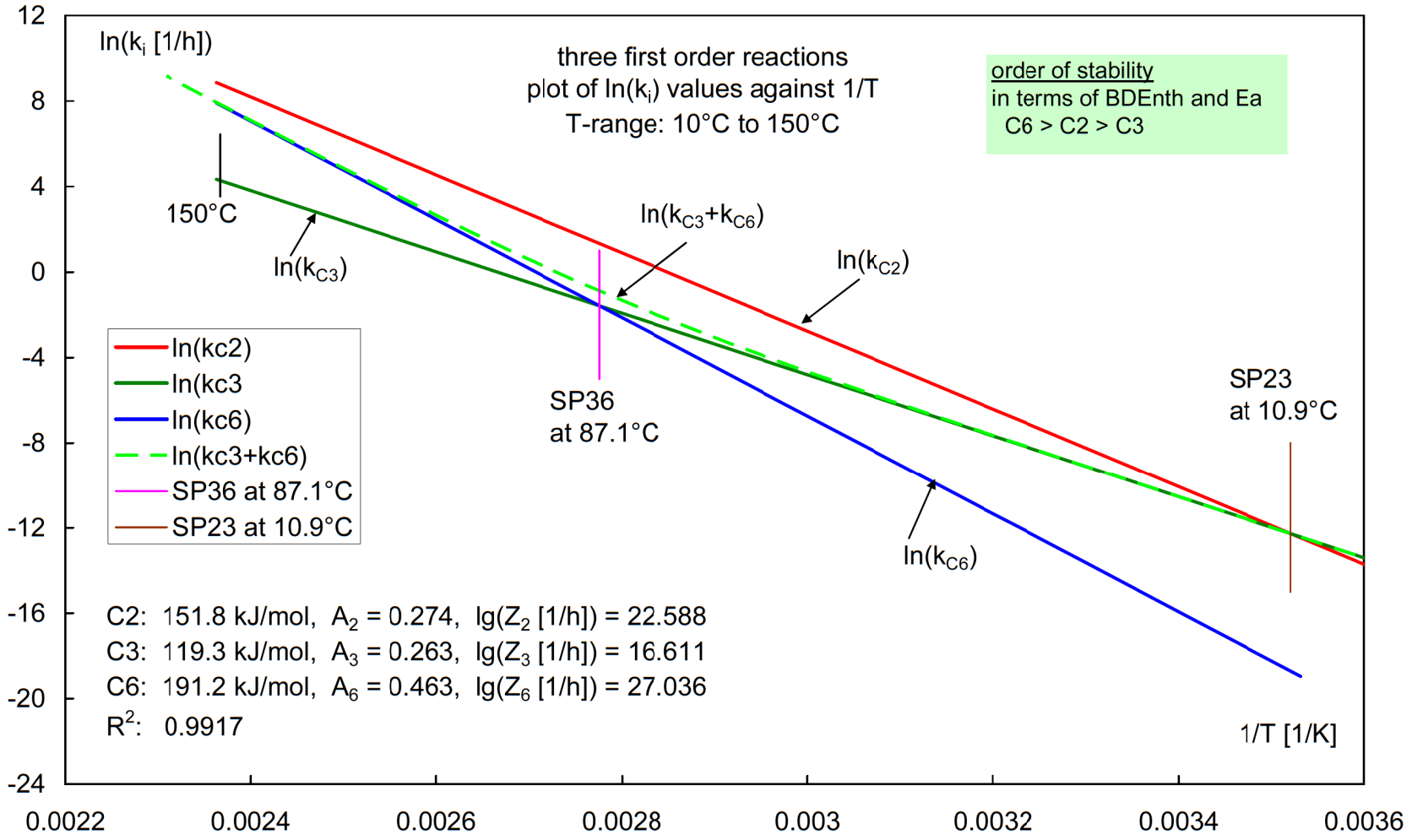
Crossings of the Arrhenius lines of the three 1st order reactions



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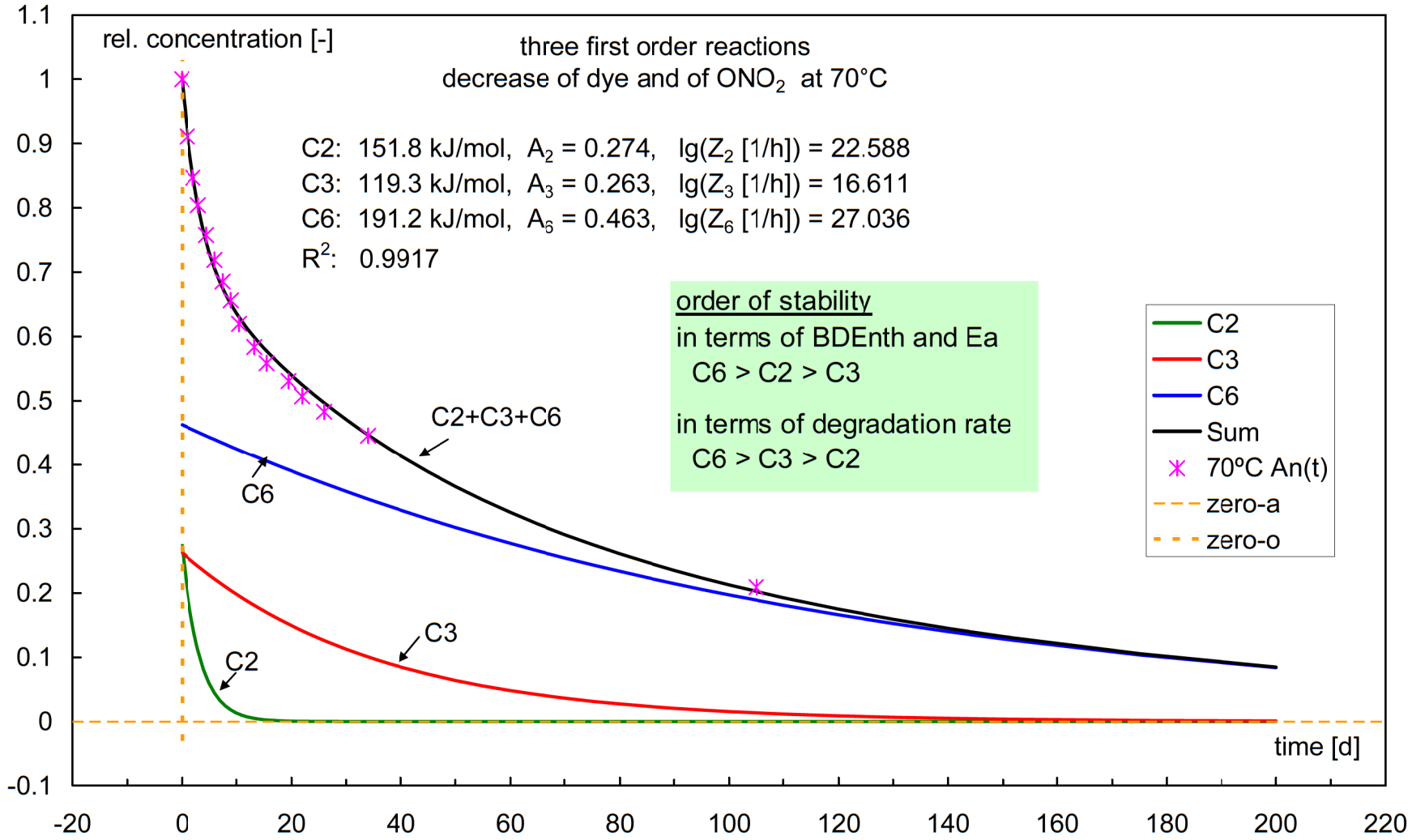
Relative concentration courses with best fit of three 1st order reactions



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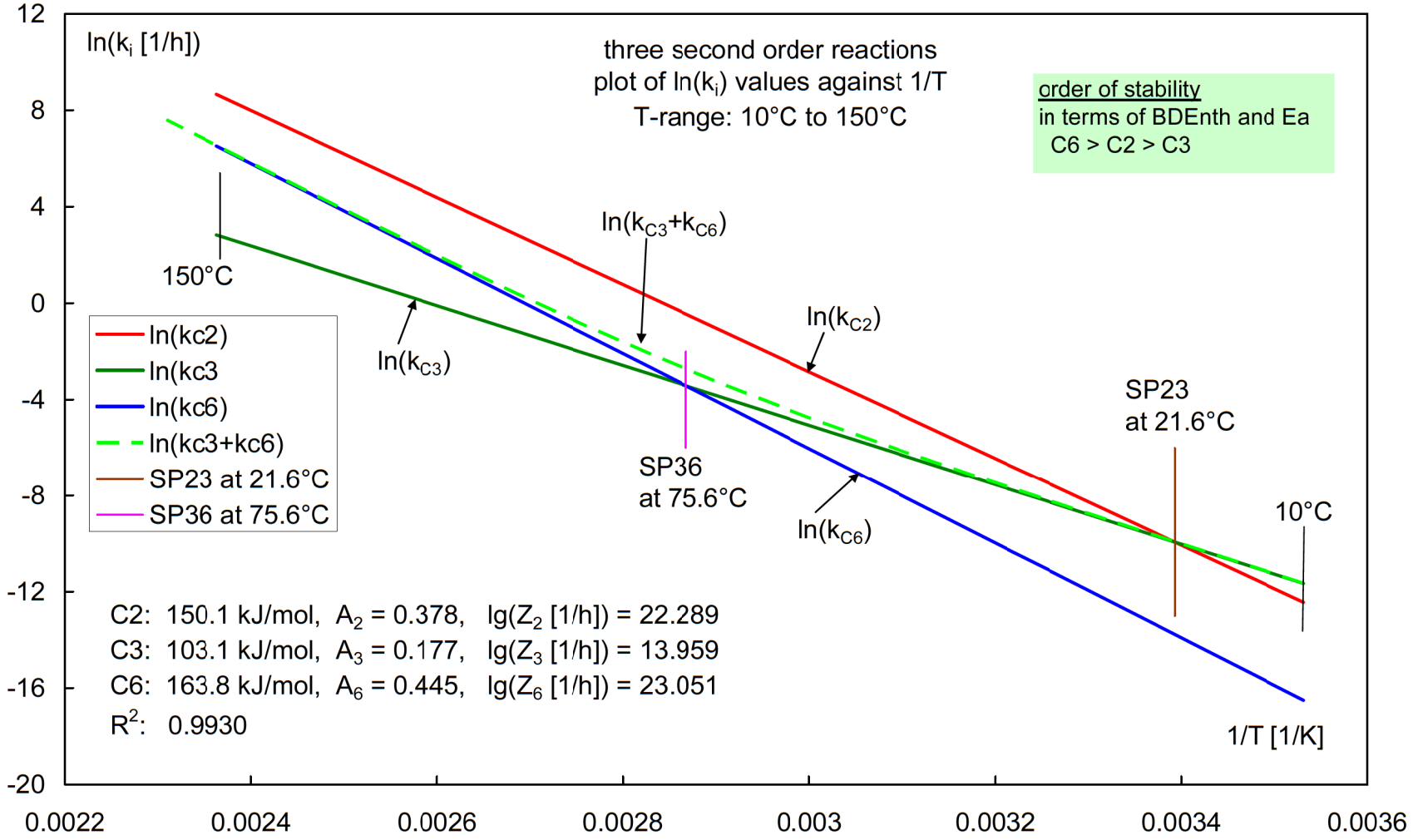
Crossings of the Arrhenius lines of the three 2nd order reactions



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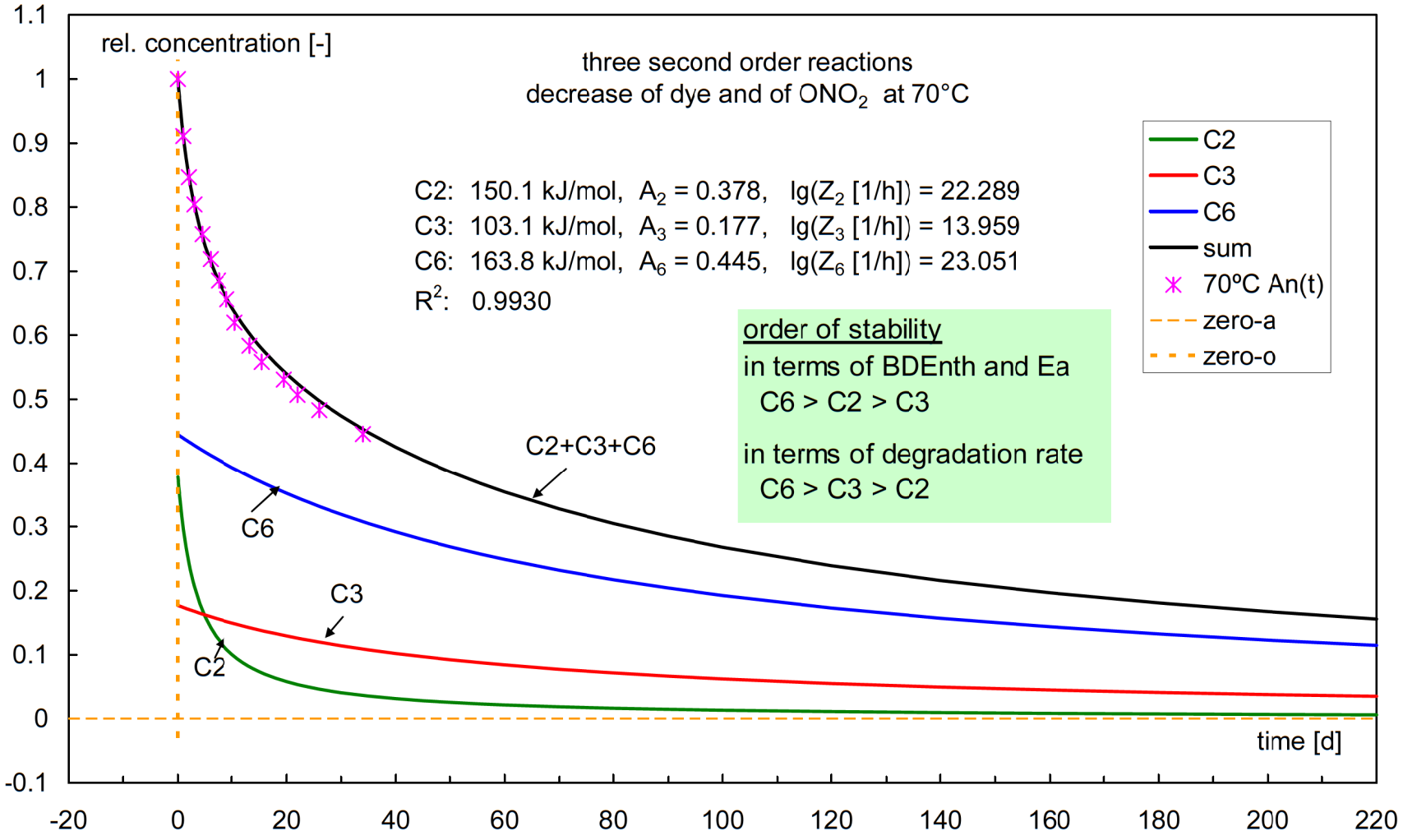
Relative concentration courses with best fit of three 2nd order reactions



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Conclusions

The stabilization of a NC film with an aromatic dye molecule (has activated benzene rings) revealed a step-wise reaction behaviour.

During the initial period of decomposition the approximation of first order for the stabilizer decrease is possible.

The different partial degrees of substitution at the three sites are considered by the modelling.

Modelling using all data at all temperatures at once is preferred – it provides directly with the Arrhenius parameters.

One can have the situation of a second order reaction for formal NC decrease via N_2O_4

The order of stability of the three sites are twofold

> with regard to activation energy and bond dissociation enthalpy: C6 > C2 > C3

> with regard to degradation rates of the three sites: C6 > C3 > C2

This solves the discrepancy between the two opinions in the literature.

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Most of the presented material is recently published in

Polymer Degradation and Stability 102 (2014) 49 – 58.

Activation energies for the decomposition of nitrate ester groups at the anhydroglucopyranose ring positions C2, C3 and C6 of nitrocellulose using the nitration of a dye as probe.

Mohammed Moniruzzaman, John M. Bellerby, Manfred A. Bohn

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What comes next?

The next tasks will be:

> the use of a reaction scheme incorporating the bimolecular stabilizer reaction;

> the elaboration of the N_2O_4 hypothesis as reacting species.

See you on the next NC-Symposium in 2016

In Canada or in Europe.

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