

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

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Abstract

A non-destructive UV-Vis spectroscopic method together with a dye was used to study the ageing of nitrocellulose (NC). The method involves determining the change of absorbance of a dye with time mixed with NC in a thin film. During the ageing of the NC two secondary and one primary CO-NO₂ groups at the anhydroglucopyranose (AHP) ring positions C2, C3 and C6 undergo decomposition and this leads to NO_x formation. The NO_x nitrates the dye and the decrease in the concentration of the original un-nitrated dye is followed by UV-Vis spectroscopy. The reaction of the dye with NO_x was monitored by periodically recording the absorption spectra of the films. The graphs of the logarithmic absorbance as function of ageing time produced non-linear plots. However, splitting the data into three time intervals was found to give rise to three linear regions with three distinct rate constants. A simplified data description was therefore made at first, using segmented data. Thereafter, the data were evaluated with extended modelling using (i) a first order description, (ii) a second order description and (iii) a nth order description. This modelling considered the data as a whole; no splitting of data in segmented time intervals and no single temperature evaluation has been made. In this way directly the Arrhenius parameters were obtained, together with the three relative partial degrees of substitution for the three AHP sites. The results from these extended and complete evaluations agree satisfactorily with each other and with quantum chemical calculations of the bond dissociation enthalpies of the CO-NO₂ bonds at the three ring positions. The Arrhenius expressions derived from the experimental data obtained at 40°C, 50°C, 60°C and 70°C gave three activation energy values, which are seen to correspond to the homolytic breakdown of CO-NO₂ groups at the C2, C3 and C6 AHP ring positions on NC. Based on all data and literature results the order of stability of the CO-NO₂ groups was concluded to be C6 > C2 > C3, with regard to bond dissociation energies and activation energies. However, the order of 'stability' with respect to the rate of conversion (loss of NO₂) at the three individual positions is C6 > C3 > C2. Comparing the Arrhenius lines of the three rate constants crossing points have been identified, which are in the temperature range 75°C to 87°C. At lower temperatures the activation energy values are between 103 and 119 kJ/mol, above between 163 to 191 kJ/mol. Such a change in apparent activation energy was also found experimentally and now these findings are supported by the presented modelling.

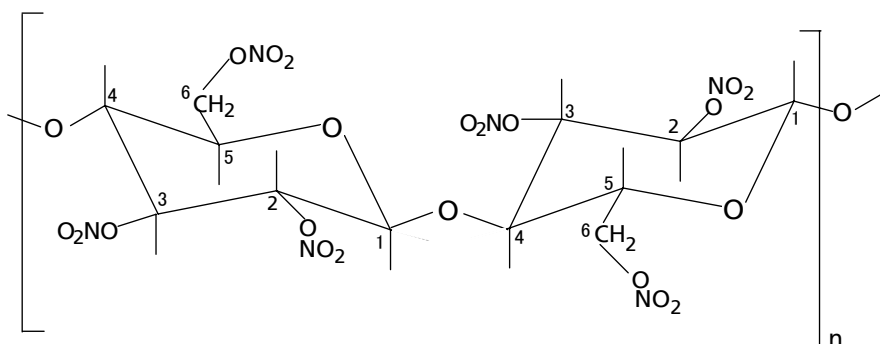
Key Words: Nitrocellulose; activation energies at individual ring positions; modelling of decomposition; UV-Vis spectroscopy; order of stability; change in activation energy.

1. Introduction

In the literature a few investigations exist, which deal with the different stability of the nitrate ester group at the three anhydroglucopyranose (AHP) ring sites of nitrocellulose numbered 2 and 3 for the two secondary C-atom sites and 6 for the primary C atom site, see viewgraph below. The following could be found: one quantum mechanical calculation /1/ and four investigations with C-13 NMR on the relative change of nitrate ester group concentrations: (i) by nitration at 90°C /3/, (ii) by denitration and by nitration at 75 to 80°C /4/, (iii) by nitration at 110°C /5/ and (iv) by thermal degradation at 110°C /5/. In the recent publication of the authors /2/ the activation energies and pre-exponential factors of the thermal degradation have been determined.

Nitrocellulose (NC)

Other names: 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.

What is known on the stability and reactivity of the three AHP ring sites

M.A. Bohn, 2008 /1/

Bond dissociation **enthalpies (not energies!)** of the CO-NO₂ bonds, determined by QM calculations (with Dmol³ from Accelrys)

C2: 161 kJ/mol	C2 : C3 : C6	Found order: C6 > C2 > C3
C3: 133 kJ/mol	relative values	
C6: 174 kJ/mol	0.92 : 0.76 : 1.00	

T.K. Wu, 1980 /3/

C-13 NMR, determination of the ratios of equilibrium constants K_i for nitration at the three ring sites, 90°C mixed acid. Found order for nitration: C6 > C2 > C3

D.T. Clark, P.J. Stephenson, F. Heatley, 1981 /4/

C-13 NMR, determination of equilibrium constants of nitration and denitration in T-range 75°C to 80°C. The final degree of nitration is thermodynamically controlled not kinetically.

Found order for nitration: C6 > C2 > C3 Found order for denitration: C3 > C2 > C6

H.R. Leider, A.J. Pane, 1987 /5/

C-13 NMR, determination of degradation rates at the three sites, at 110°C over 15 days.

Found order for degradation: C6 > C3 > C2

Determination of the ratios of equilibrium constants K_i for nitration at the three ring sites, 110°C mixed acid.

Found order for nitration: C6 > C2 > C3

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 (used as 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-NO₂ 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 NO_x 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-NO₂ 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 should be achieved.

2. Used materials and sample preparations

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

Most of the presented material is recently published in /2/

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

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

Polymer Degradation and Stability 102 (2014) 49 – 58

Calculation of some characterizing properties of NC

n	average degree of substitution of the three nitrable sites per AHP ring
N	average nitrogen content in mass-%
M	molar mass of one nitrated AHP in g/mol
NE	content of nitrate ester groups in mass-%

n(N)	to calculate n with given N	n is a value between 0 and 3
N(n)	to calculate N with given n	in mass-%
M(n)	to calculate M with given n	in g/mol
M(N)	to calculate M with given N	in g/mol
NE(n)	to calculate nitrate content with given n	in mass-%
NE(N)	to calculate nitrate content with given N	in mass-%

$$N(n) = \frac{14.0067 \cdot [\text{g/mol}] \cdot n \cdot 100 \cdot [\text{mass} - \%]}{162.1406 \cdot [\text{g/mol}] + n \cdot 44.99756 \cdot [\text{g/mol}]}$$

$$n(N) = \frac{162.1406 \cdot [\text{g/mol}] \cdot N \cdot [\text{mass} - \%]}{100 \cdot [\text{mass} - \%] \cdot 14.0067 \cdot [\text{g/mol}] - N \cdot [\text{mass} - \%] \cdot 44.99756 \cdot [\text{g/mol}]}$$

$$M(n) = 162.1406 \cdot [\text{g/mol}] + n \cdot 44.99756 \cdot [\text{g/mol}]$$

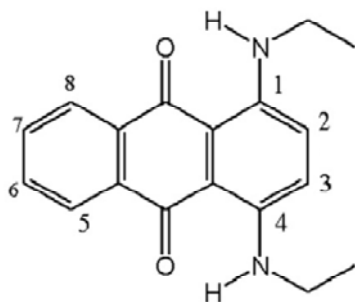
$$M(N) = 162.1406 \cdot [\text{g/mol}] \cdot \left(1 + \frac{N \cdot [\text{mass} - \%] \cdot 44.99756 \cdot [\text{g/mol}]}{100 \cdot [\text{mass} - \%] \cdot 14.0067 \cdot [\text{g/mol}] - N \cdot [\text{mass} - \%] \cdot 44.99756 \cdot [\text{g/mol}]} \right)$$

$$NE(n) = 100 \cdot [\text{mass} - \%] \cdot 62.004 \cdot [\text{g/mol}] \cdot n / M(n)$$

$$NE(N) = 100 \cdot [\text{mass} - \%] \cdot 62.004 \cdot [\text{g/mol}] \cdot n(N) / M(N)$$

Used dye and manufacturing of the NC films

Mohammed Moniruzzaman 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.

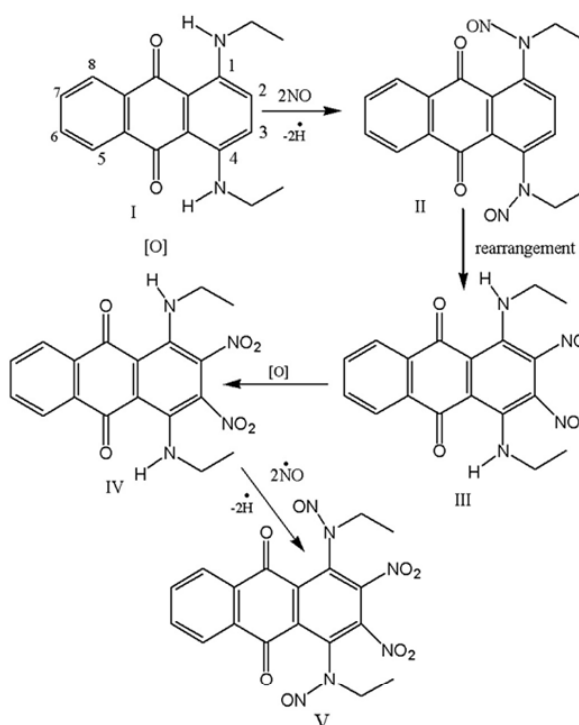
For the initial decrease of the dye concentration a reaction type of first order was assumed at first.

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

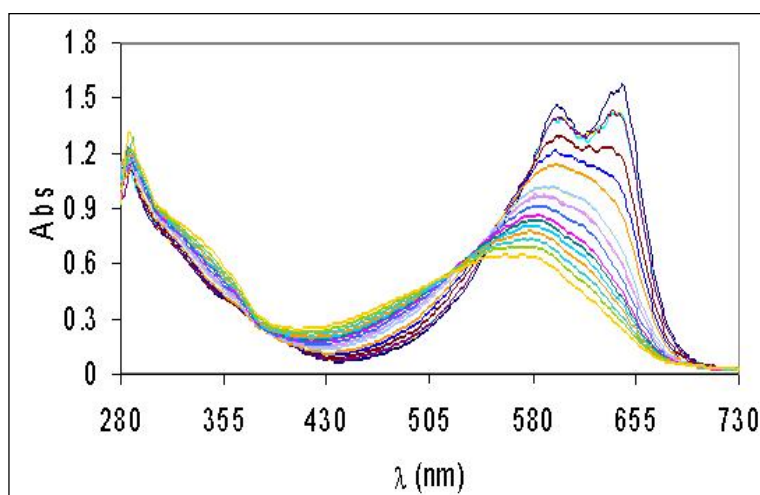
3. Results

3.1 Reaction scheme of nitration of the dye, UV-Vis spectra and absorbance-time courses

Simplified reaction scheme of the reaction between dye and NOx



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

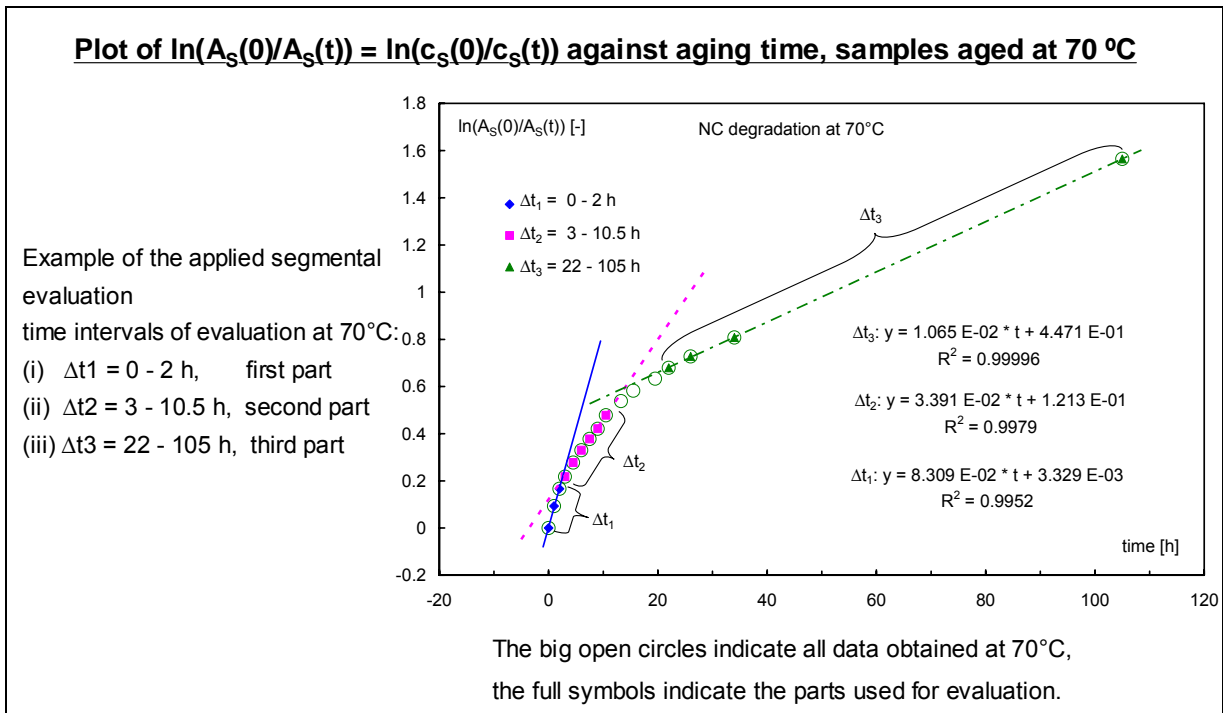
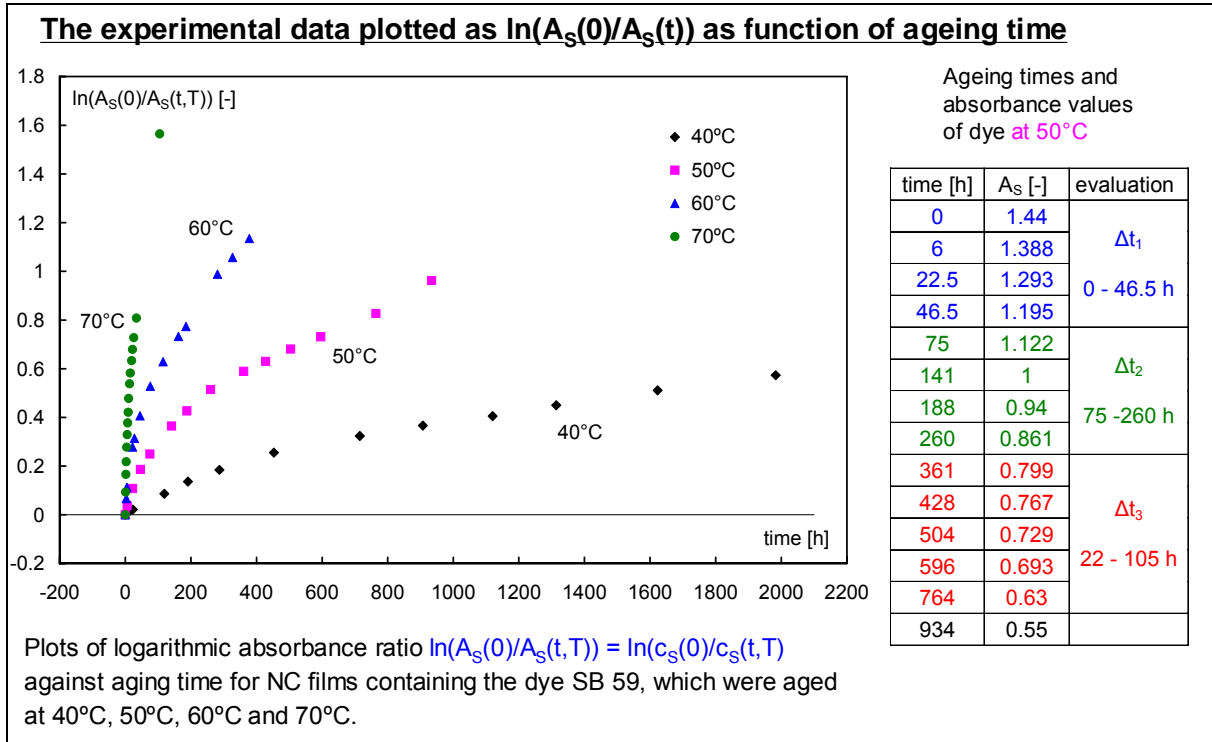


Ageing times and absorbance values of dye at 50°C

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 50°C 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.



3.2 Segmented data evaluation with three first order reactions

The first step modelling used a segmental / segmented description of the data. The first order description was applied step wise along the curves for the segments with linear or nearly linear course of the data in logarithmic presentation. The development of this description is shown in the next viewgraph.

Kinetic description of concentration change of dye with reaction time using a first order decrease of the dye concentration

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

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

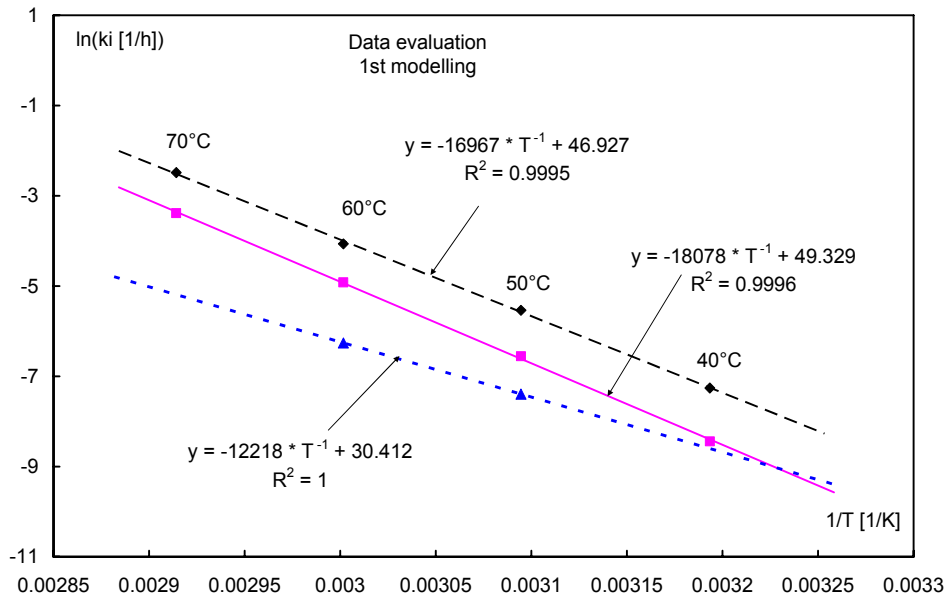
$$\frac{A_S(\lambda, t, T)}{A_S(\lambda, 0, T)} = \frac{c_S(t, T)}{c_S(0, T)}$$

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

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

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

Arrhenius plots of reaction rate constants obtained by segmental modelling



Arrhenius plot of the three reaction rate constants for NC decomposition at ring positions C2, C3 and C6, obtained from data monitored by the dye SB 59.

The rate constants have been extracted from the linear parts of the first order plots using segmental application of three first order reactions.

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

1st modelling - segmental evaluation with three first order reactions:

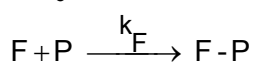
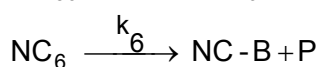
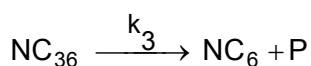
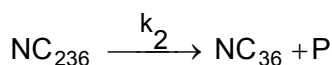
- > single description of 'single' (assumed) reactions with $\ln(C_s(0)/C_s(t,T))$,
- > one first order reaction,
- > for each temperature alone and applied segmental on the three parts of each curves,
- > equal weighting by A_i for each C_i position on AHP rings.

AHP Ring position	2	3	6
weighting by A_i	1	1	1
E_a [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 above presented segmented modeling has some drawbacks, inspite of the relatively good result obtained. The drawbacks are summarized in the following viewgraph. From this it follows that the modelling of the data must be further developed. The segmented modelling cannot describe correctly the data. This is shown in section 3.3.

Implicit consequences of the data evaluation by segmental application of three first order reactions

The segmental or segmented application assumes implicitly a consecutive decomposition (means one site after the other) of the nitrate ester groups at the three ring positions. This is expressed in the following reaction scheme. Further on this type of modelling imposes a full substitution of all ring positions in the sample, which means a nitrogen content of 14.14 mass-% or at least an equal substitution.



Consecutive reaction scheme for decomposing the nitrate ester groups at the three ring positions.

But the three sites decompose in parallel and the used NC is not completely nitrated and very probably also not equally substituted at the three AHP ring sites.

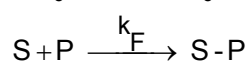
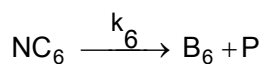
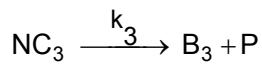
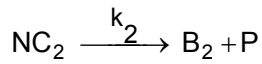
It is even more complicated in that each ring position will have an own averaged partial degree of substitution (PDS).

3.3 Extended data evaluation with three reactions in parallel

With regard to the above explained drawbacks of this more or less simplified modelling in section 3.2, the description with three reactions in parallel was worked out, see section 3.3.1, which also considers non-equal partial degrees of substitution at the three AHP ring sites.

3.3.1 Establishing the model

Parallel reaction scheme and rate equations - 1



NC_k : concentration of nitrate ester groups at position k

The stabilizer reaction is bimolecular

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

$$\frac{d\text{NC}(t)}{dt} = \frac{d\text{NC}_2(t)}{dt} + \frac{d\text{NC}_3(t)}{dt} + \frac{d\text{NC}_6(t)}{dt} = -k_2 \cdot \text{NC}_2(t) - k_3 \cdot \text{NC}_3(t) - k_6 \cdot \text{NC}_6(t)$$

$$\text{NC}(t) = \text{NC}_2(0) \cdot \exp(-k_2 \cdot t) + \text{NC}_3(0) \cdot \exp(-k_3 \cdot t) + \text{NC}_6(0) \cdot \exp(-k_6 \cdot t)$$

$$\text{NC}(0) = \text{NC}_2(0) + \text{NC}_3(0) + \text{NC}_6(0)$$

Normalization by concentration of nitrate ester groups at time t = 0

$$\frac{\text{NC}(t)}{\text{NC}(0)} = \frac{\text{NC}_2(0)}{\text{NC}(0)} \cdot \exp(-k_2 \cdot t) + \frac{\text{NC}_3(0)}{\text{NC}(0)} \cdot \exp(-k_3 \cdot t) + \frac{\text{NC}_6(0)}{\text{NC}(0)} \cdot \exp(-k_6 \cdot t)$$

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

Parallel reaction scheme and rate equations - 2

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

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

Assumption:

during the initial decomposition period the concentration of P is kept small and nearly constant by the action of the dye: $\text{P}(t) = \text{P}_0$.

Then it can be fused with k'_F to the new constant k_F : $k_F = k'_F \cdot \text{P}_0$

Normalization of dye or stabilizer concentration with its initial concentration.

$$\frac{d\text{Sr}(t)}{dt} = -k_F \cdot \text{Sr}(t) = \frac{d\text{NCr}(t)}{dt}$$

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

$$\text{Sr}(t) - 1 = \text{NCr}(t) - 1$$

Integration of the rate equation results in this relation between normalized concentrations of stabilizer and NC.

It follows with $\text{Sr}(t) = \text{NCr}(t)$

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

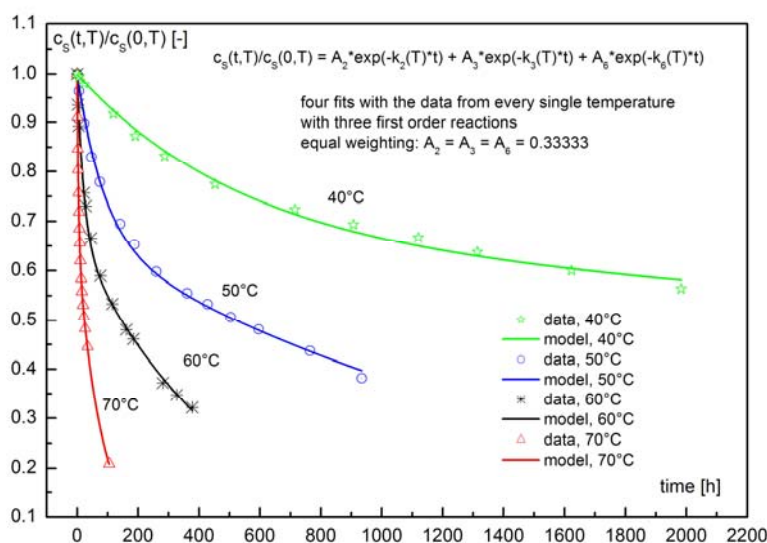
$$\text{Sr}(0) = 1 = \frac{\text{NC}_2(0)}{\text{NC}(0)} + \frac{\text{NC}_3(0)}{\text{NC}(0)} + \frac{\text{NC}_6(0)}{\text{NC}(0)}$$

$$\text{Sr}(0) = 1 = A_2 + A_3 + A_6$$

The modelling is applied with increasing complexity, starting in section 3.3.2 with a first level.

3.3.2 Modelling with three parallel first order reactions at once and equal weighting of the three sites, but applied for each temperature alone

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



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

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

Results of data evaluation by application of three parallel 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 in parallel,
- > for each temperature alone,
- > equal weighting by A_i for each C_i position on AHP rings.

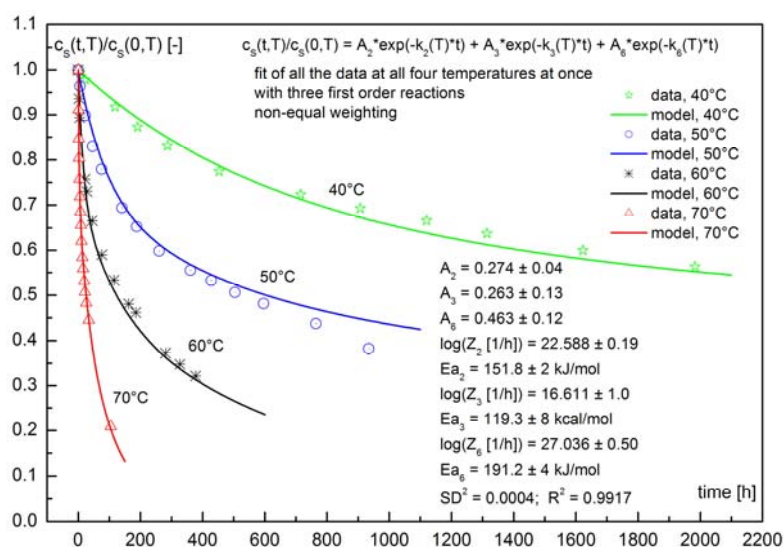
AHP Ring position	2	3	6
weighting by A_i	0.33333	0.33333	0.33333
E_a [kJ mol ⁻¹]	139.0 ± 3	134.1 ± 9	157.4 ± 12
$\lg(Z$ [h ⁻¹])	20.483 ± 0.6	18.316 ± 1.4	22.121 ± 1.9
R^2	0.9988	0.9917	0.9890
Quantum mechanical calculation of bond dissociation enthalpies (BDEnt)			
BDEnt [kJ mol ⁻¹]	161	133	174

Direct determination of the three sets of rate constants.

The Arrhenius parameters were determined via separate Arrhenius plots

3.3.3 Modelling with three first order reactions at once and unequal weighting of the three sites, and applied with the data of all temperature at once

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



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

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

Results of data evaluation by three parallel 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 in parallel,
- > 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
E_a [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

3.3.4 The order of reactions in nitrate ester decrease and in stabilizer nitration

The reaction between stabilizer and NO or NO₂ is of second order and can be modelled in detail considering this fact /6/. But also the decrease of nitrate ester groups can appear as a second order reaction, which is explained in the following viewgraph. Leider and Pane give a first hint in 1981 /7/ in that they found a correlation between decrease in nitrate ester content and the nitrogen gas development, which implies a decrease of second order for the nitrate ester content in the NC.

The order of the reactions: decrease in nitrate ester groups and stabilizer nitration

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 with respect to stabilizer nitration reaction.

Note: in order to fulfil the radical neutrality, two radicals must be always involved in aromatic radical nitration, also in case of N-NO formation.

Assuming N_2O_4 , the corresponding rate equation for stabilizer consumption is:

$$\frac{dS(t)}{dt} = -k'_F \cdot S(t) \cdot [P(t) \cdot P(t)] \quad \text{The } [P(t) \cdot P(t)] \text{ is seen as one species.}$$

How to imagine the molecular processes:

One split-off NO_2 snoops around. It still can recombine at the split-off site at the AHP ring..

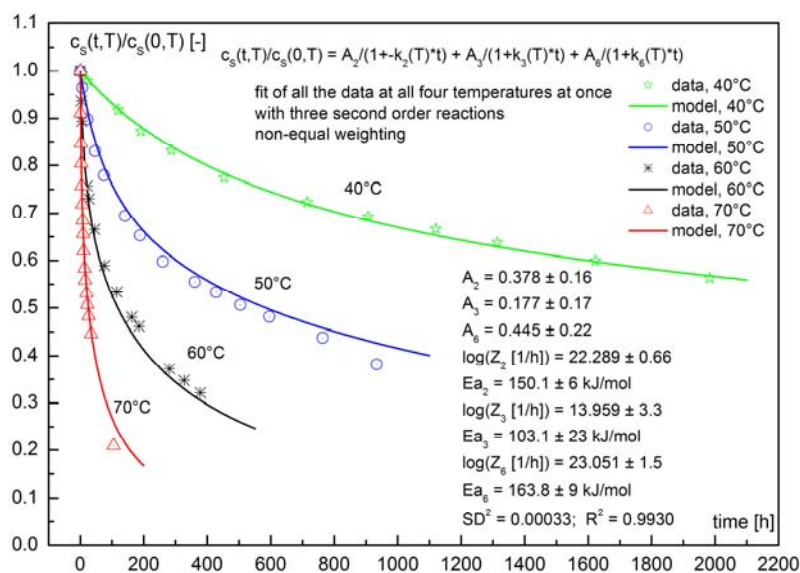
Accidentally it encounters a second one and forms N_2O_4 , which is radically neutral.

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 now formally degraded by second order. N_2O_4 is the attacking species in the stabilizer reaction, which is formally still bimolecular, because the two NO_2 radicals are spatially coordinated.

3.3.4.1 Modelling with three second order reactions

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.

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

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.

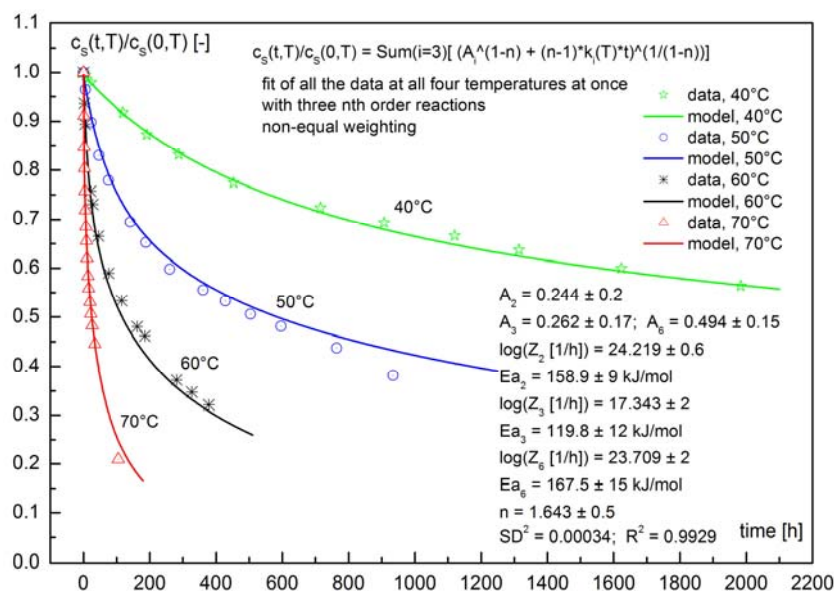
AHP Ring position	2	3	6
weighting by A_i	0.378 ± 0.16	0.177 ± 0.17	0.445 ± 0.22
E_a [kJ mol ⁻¹]	150.1 ± 6	103.1 ± 23	163.8 ± 9
$\lg(Z$ [h ⁻¹])	22.289 ± 0.66	13.959 ± 3.3	23.051 ± 1.5
n	2	2	2
R^2	0.9930	-	-
Quantum mechanical calculation of bond dissociation enthalpies (BDEnt)			
BDEnt [kJ mol ⁻¹]	161	133	174

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

3.3.4.2 Modelling with three nth order reactions

An nth order reaction could provide with an average between first and second order. Indeed, the found common reaction order is with this data $n = 1.643$. As a whole the description is not better than with $n = 2.00$.

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.

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

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
E_a [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.

3.4 Summary of best modelling results

The best modelling is achieved using all data at all temperatures at once. In this way directly the Arrhenius parameters are obtained. The following table lists the best modelling results, which were obtained with three second order reactions in parallel and with three first order reactions in parallel. The weighting factors have been determined also by free parameter fitting. A comparison of the obtained activation energies with the bond dissociation enthalpies is given also. The order of stability in the sense of bond strength and activation energy is therewith: C6 > C2 > C3.

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
E_a [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
E_a [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	-

3.5 Discussion of the order of stability and reactivity of the three AHP ring sites

The order of stability and reactivity was and is still a matter of discussion. In order to shed light on this problem, the Arrhenius lines obtainable with the determined Arrhenius parameter from section 3.4 are constructed and compared. As expected, the difference in activation energy and pre-factor expresses in such a way that cross-points are formed. This means the apparent activation energy changes around these cross-points and a two mechanistic reaction behaviour is established. Such behaviour was reported already several times in the literature /9, 10/ and finally has found entrance in test regulations for NC-based materials /11, 12/. The following two viewgraphs are taken from /10/ and the next one illustrates the situation of apparent activation energies resulting by crossing of Arrhenius lines.

Stabilizer consumption: activation energy E_a as function of temperature

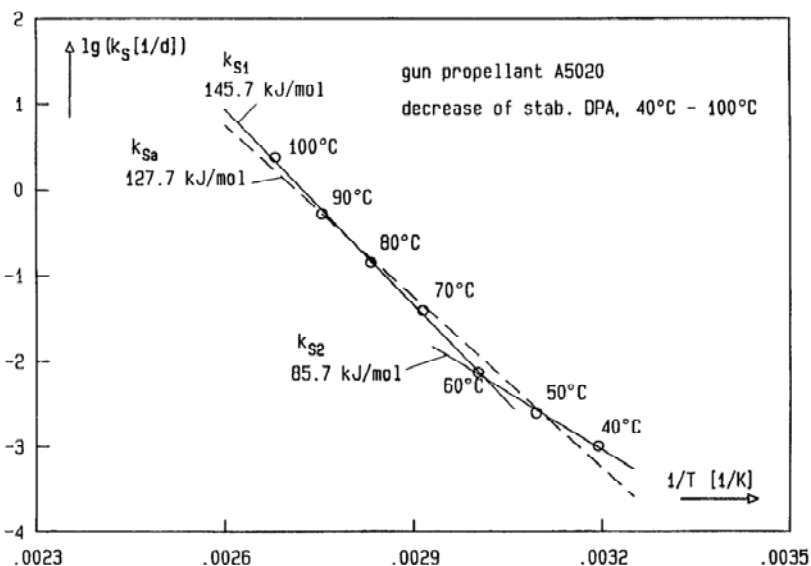
Decrease of stabilizer DPA in single base GP A5020 (20 mm machine gun).

Observed change in E_a at about 65°C.

This is explained as mechanistic change in the apparent decomposition, means what is primary recognizable; but both processes occur in parallel.

The higher temperature range is dominated by more thermolytical (=homolytical bond scission forming radicals) ester group decomposition.

The lower temperature range is dominated by more hydrolytical ester group decomposition.



Molar mass decrease of NC: activation energy E_a as function of temperature

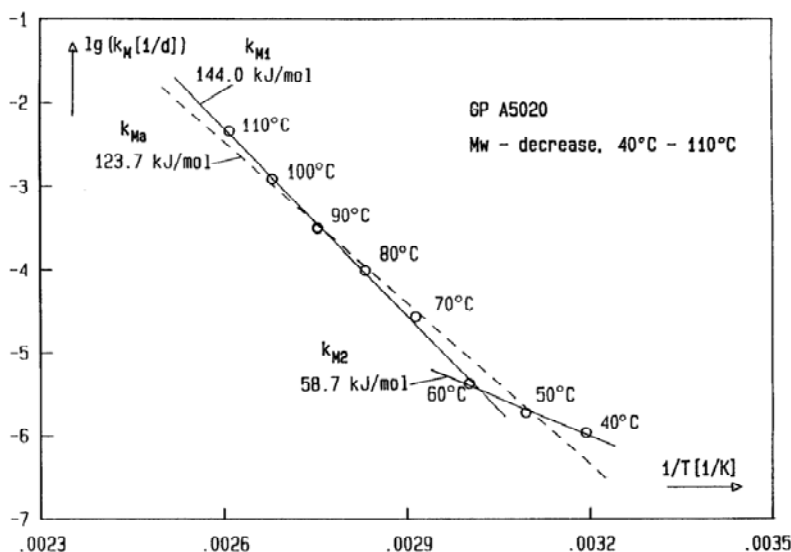
Decrease of molar mass of NC in single base GP A5020 (20mm machine gun).

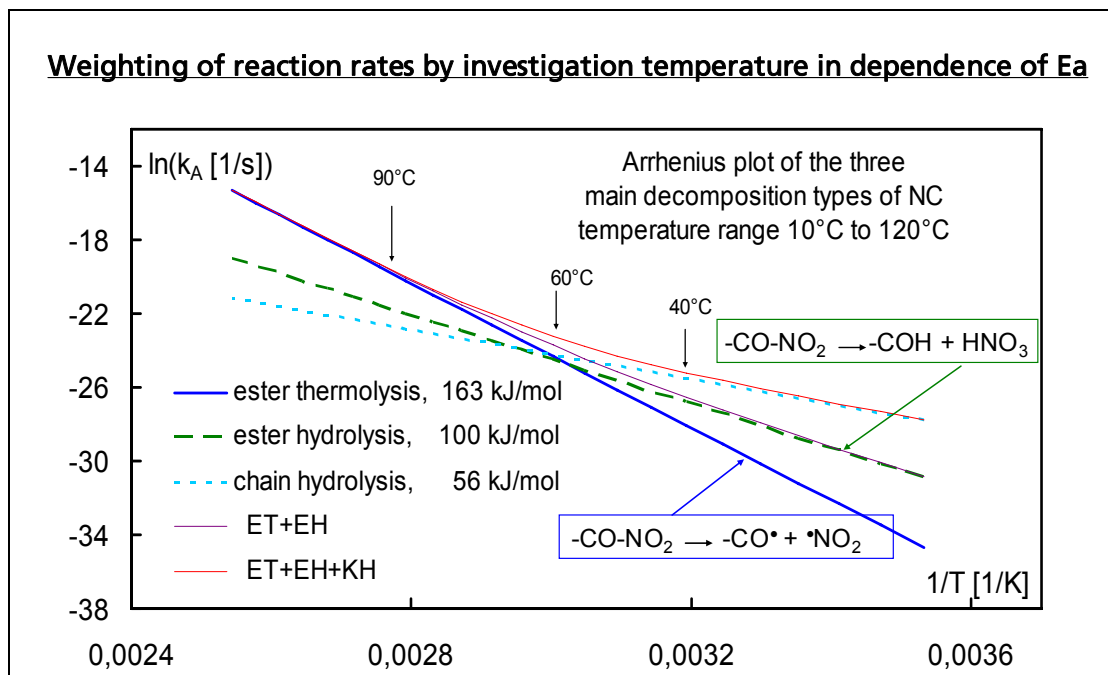
Observed change in E_a at about 65°C.

As with stabilizer decrease this is explained as mechanistic change in the apparent decomposition, means what is primary recognizable; but both processes occur in parallel.

The higher temperature range is dominated by more thermolytical (=homolytical bond scission forming radicals) ester group decomposition with consecutive chain scission.

The lower temperature range is dominated by more hydrolytical NC chain splitting.





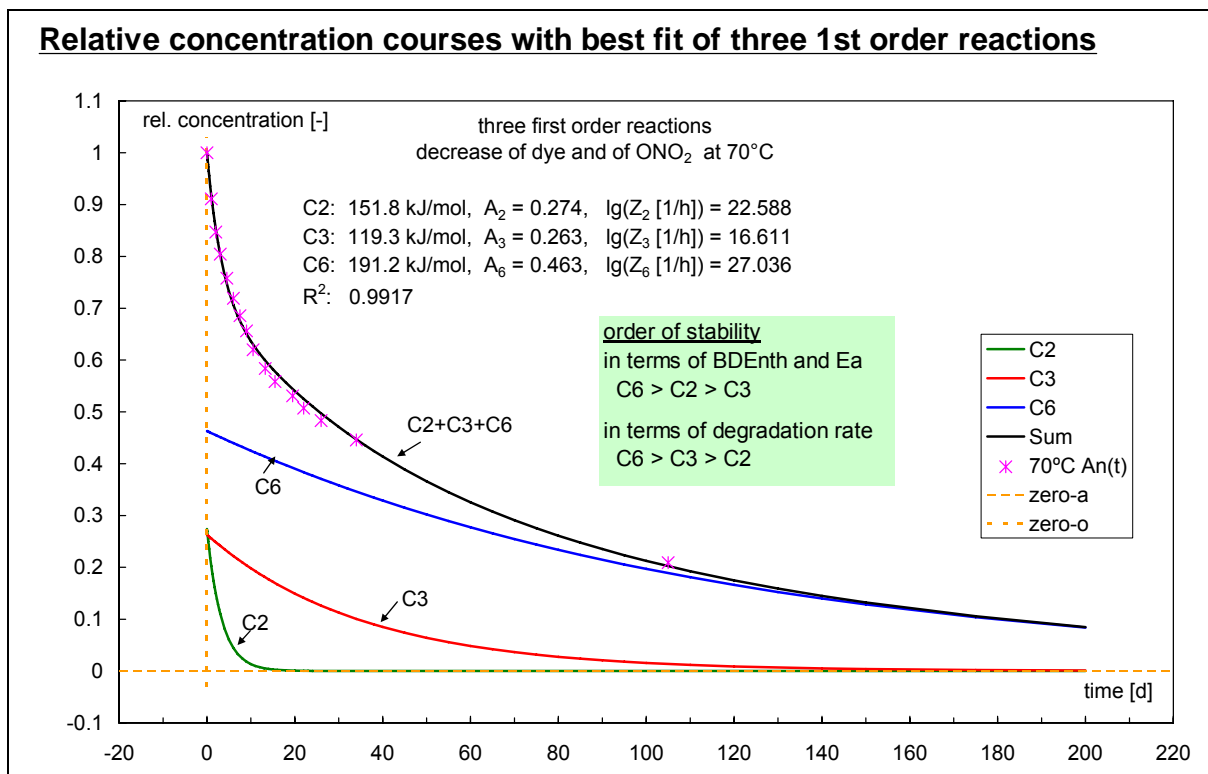
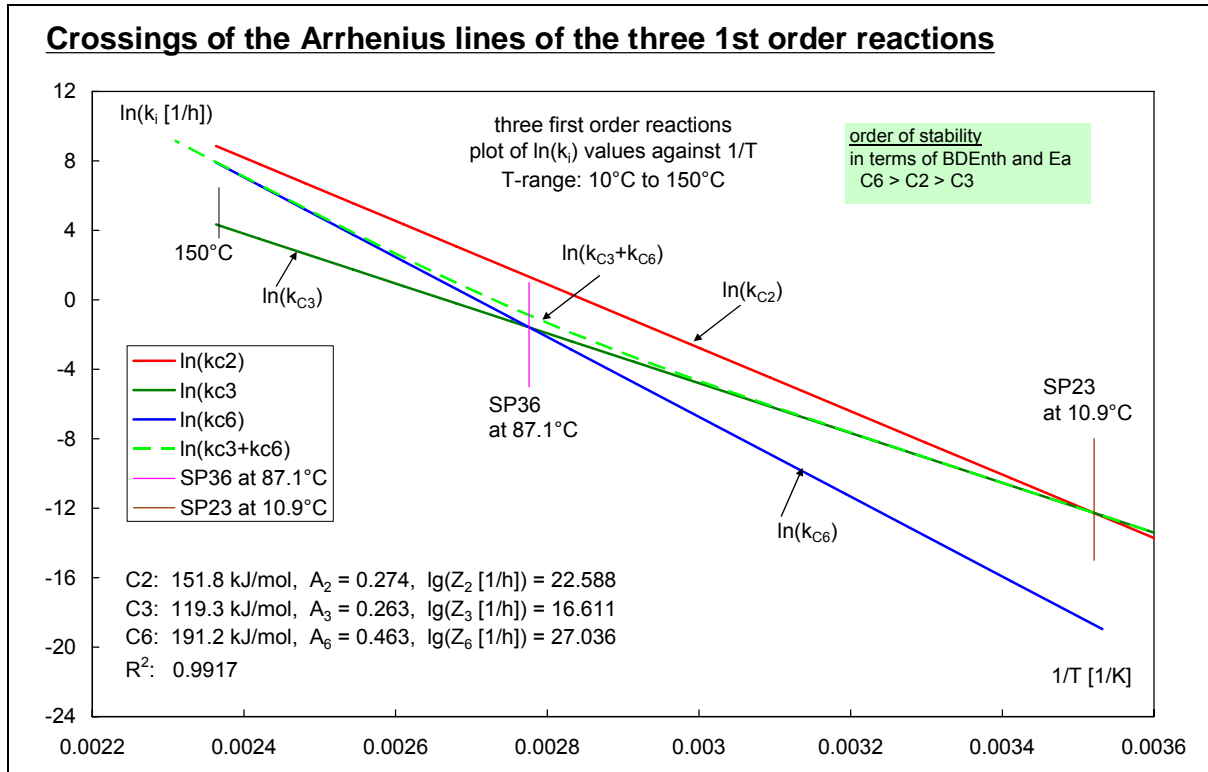
Besides a mechanistic change, thermolysis against hydrolysis, there is a further cause of change in apparent activation energies, namely the effect of the decomposition of the three AHP nitrate ester sites, but with the same mechanism, here always a homolytic or thermolytic bond cleavage producing radicals.

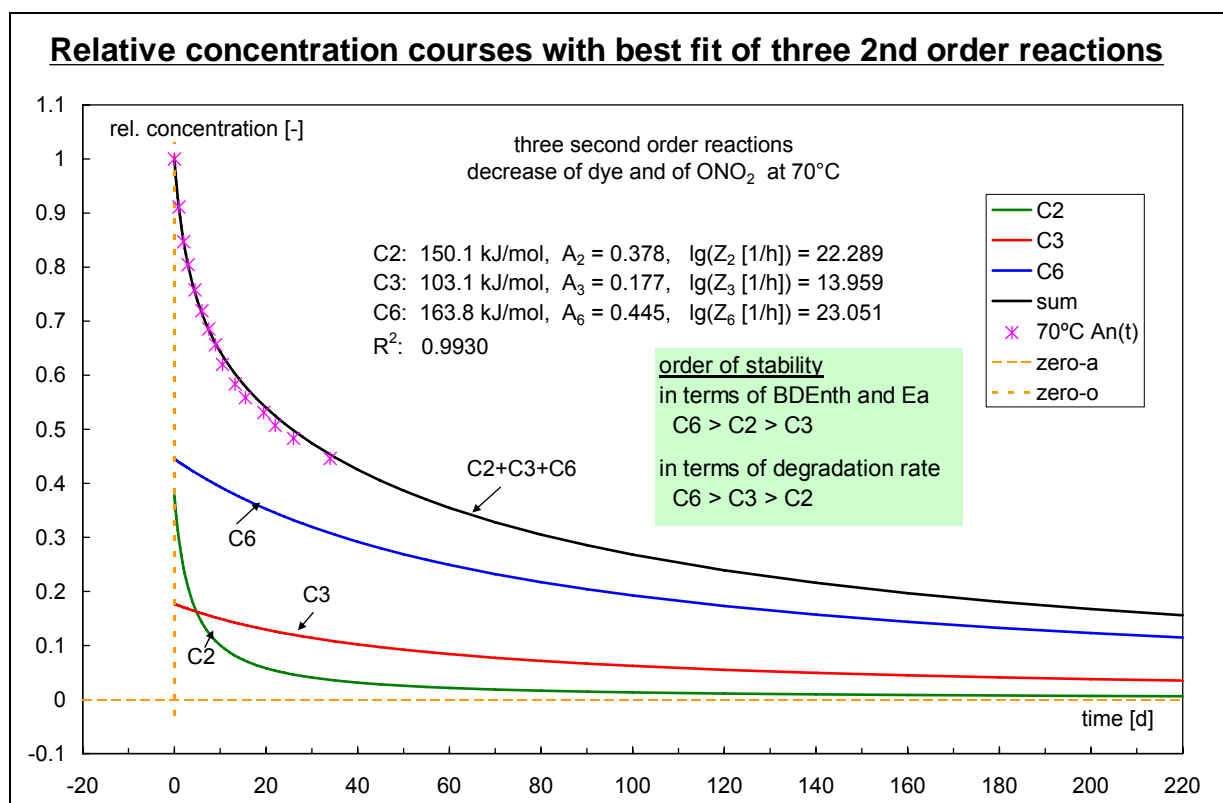
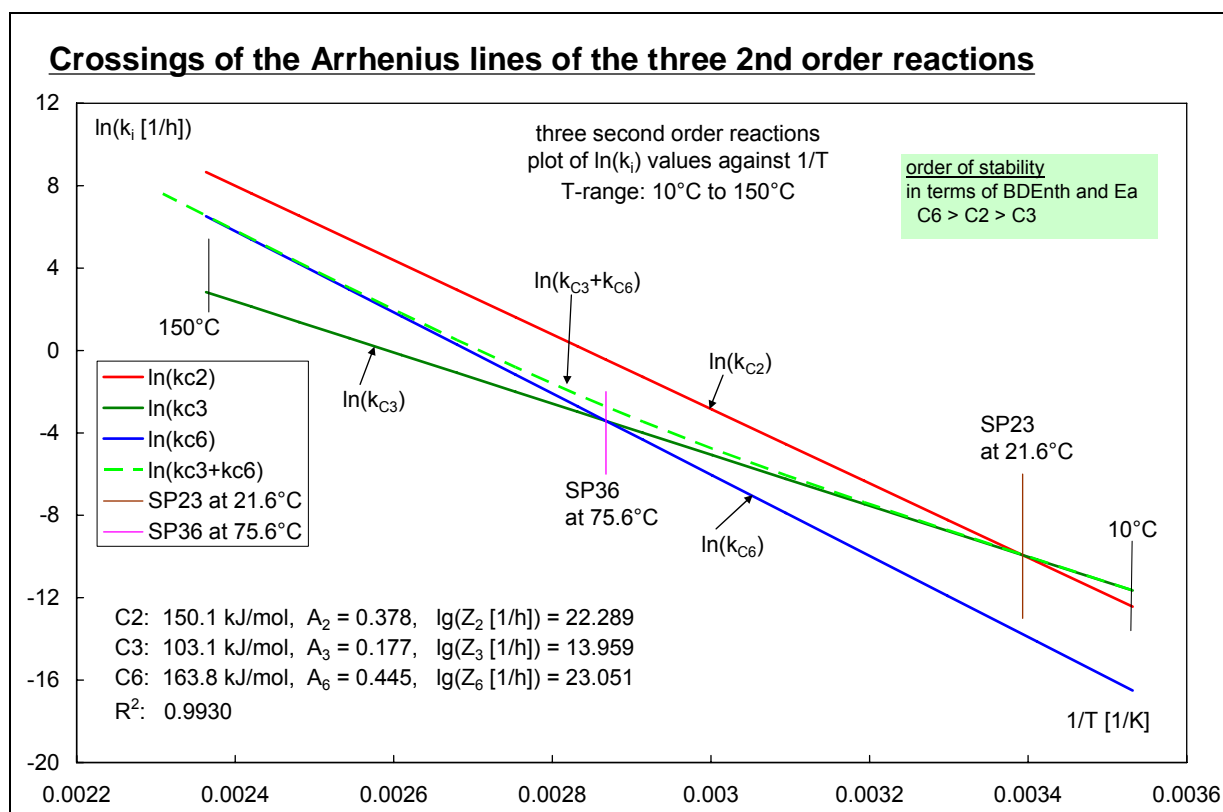
In the following two viewgraphs the Arrhenius lines of the first order modelling and the decrease of the relative, normalized concentrations of the three AHP sites are shown. Further on this is followed by the same presentations of the second order modelling. With both each modellings two crossing points are found in the temperature range 0 to 100°C, see following table.

Modelling type	Crossing temp. of $k_2 - k_3$ [°C]	Crossing temp. of $k_3 - k_6$ [°C]
Three first order reactions in parallel	10.9	87.1
Activation energies below / above [kJ/mol]	119.3 / 151.8	119.3 / 191.2
Three second order reactions in parallel	21.6	75.6
Activation energies below / above [kJ/mol]	103.1 / 150.1	103.1 / 163.8
Results from Volltrauer-Fontjin /9/	-	85 (77-97)
Activation energies below / above [kJ/mol]	-	106.4 / 178.8

Volltrauer and Fontjin have found also a change in activation energy in dependence of investigation temperature, which was 22°C to 147°C. The analytical method was chemiluminescence analysis of the species NO and NO₂ /9/. They were determined quantitatively in real time, means during decomposition of nitrocellulose. A crossover temperature around 85°C was identified. Below 77°C the activation energy was 106.4 kJ/mol and above the value was 178.8 kJ/mol. These values indicate also homolytical decomposition of the nitrate ester groups. Moreover the crossover temperature of 85°C is in the range found with the presented modelling. In conclusion the activation energies in the upper and in the

lower temperature range seem to originate by the different decomposition rates of the nitrate ester groups in NC, which is assumed to be the homolytical bond scission of CO-NO_2 in the first step. The lower crossover temperature found with the modellings may interfere with the apparent E_a values between these two crossing points. This interference may be not noticed after a period of ageing, because the nitrate ester groups at C2 are already decomposed to a great extent. On the other hand with very fresh material there could be found a relative high activation energy between 20°C and 90°C , which will disappear in later times.





4. Conclusions

The stabilization of a NC film with an aromatic dye molecule, which has activated benzene rings, revealed a step-wise reaction behaviour via the concentration decrease of the

dye. The reaction of stabilizer or dye with NO or NO₂ is of second order. During the initial period of decomposition, the approximation of first order for the stabilizer decrease is possible, assuming a constant concentration of NO₂. In order to get the correct activation energies for the degradation of the nitrate esters at the three anhydroglucopyranose (AHP) ring sites of NC, the modelling of the decrease of dye concentration has to consider the different partial degrees of substitution at the three sites C2, C3 and C6. For the modelling it is best to use all data at all temperatures at once. This technique provides immediately with the Arrhenius parameters and the normalized partial degrees of substitution.

One can have the situation of a second order reaction for the formal NC decrease via the formation of N₂O₄. In this case two NO₂ radicals form the radically neutral dinitrogen dioxide, which spatially coordinates the two NO₂ radicals. N₂O₄ attacks the stabilizer and one NO₂ exerts the radical substitution at the benzene rings. Therefore the stabilizer reaction is still bimolecular. The remaining radical NO₂ of N₂O₄ species combines with the given-off radical species from the stabilizer, mostly an H radical, and facilitates the substitution at the stabilizer benzene rings.

The order of stability of the three AHP ring sites is indeed 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

In this way the discrepancy between the two opinions in the literature is solved.

A further feature of the degradation with three different Arrhenius parameters is the crossing of the Arrhenius lines. This means one has a change in apparent activation energy with investigation temperature because of the different Arrhenius parameters. This supports the practical application using two mechanistic behaviours of NC-based material, as it is expressed in STANAG 4582 /11/ and in AOP 48 /12/. Further on it supports the findings of Volltrauer and Fontjin gained by chemiluminescence analysis. They reported a crossover temperature around 85°C (77°C to 97°C) with activation energy values of 106.4 and 178.6 kJ/mol below and above this crossover temperature, respectively. The modellings give a temperature range of 75°C to 88 °C and 103 to 119 kJ/mol below and 163 to 191 kJ/mol above this temperature crossover range.

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