

Characterization of ageing of NC-based double base rocket propellants by not often used measurement properties

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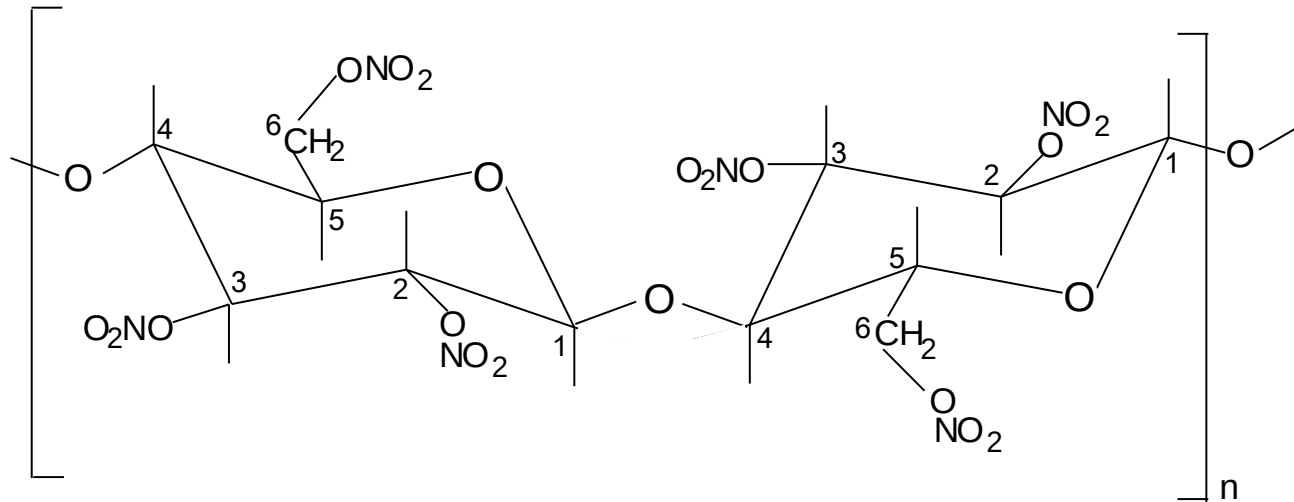
Presentation on the
8th International NC-Symposium
organized by Company MANUCO, Bergerac
June 5-7, 2018
Bergerac, France

Objectives

- NC (nitrocellulose) based double base rocket propellants (db RP) fulfil an important part in propelled systems: tactical, anti structure weapons, emergency eject devices and others.
- Their advantage is minimum (low to zero) signature, adaptable burning rate, mesa burning behaviour with catalysts.
- Relatively cheap ingredients.
- A demand is the necessary ISS (in-service surveillance) primarily because of intrinsic slow decomposition of the NC and secondarily the other nitrate esters used (NG, BTTN, TMETN, DGDN....).
- Short overview on the principles of ageing behaviour, which is mainly determined by NC
Methods here are heat generation rate, molar mass degradation
- Measurement methods rarely applied for ageing characterization:
gas generation, mass loss, dynamic mechanical analysis (DMA).
- Ageing followed by DMA.

Some facts about the stability and reactivity of nitrocellulose (NC)

Chemical structure of nitrocellulose (NC)



Monomer base of nitrocellulose. Shown is as example the formally fully nitrated monomer. The nitration occurs at the ring positions C2 and C3 and at the CH₂ group at position 5, named C6. One ring is named anhydroglucopyranose (AHP)

The monomeric unit is the one of cellobiose.

The connection between two glucosidic units is called: 1→4-O-β-D-glucosidic bond or (generally) 1→4-O-β-D-glycosidic bond.

The β means bonding via equatorial orientation; α means bonding via axial orientation.

Severe complications in stability assessment of NC – decomposition is manifold

A couple of years ago an extensive modelling of decomposition behaviour was performed, via the observed different steps in nitration a dye with aromatic groups.

Results reported on 6th NC Symposium 2014

See also

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.

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

Manfred A. Bohn, Mohammed Moniruzzaman, John Bellerby

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

Paper 107, pages 107-1 to 107-20. CD-Proceed. 45th International Annual Conference of ICT, June 24 to 27, 2014, Karlsruhe, Germany.

ISSN 0722-4087. Fraunhofer-Institut fuer Chemische Technologie (ICT), D-76318 Pfinztal. Germany.

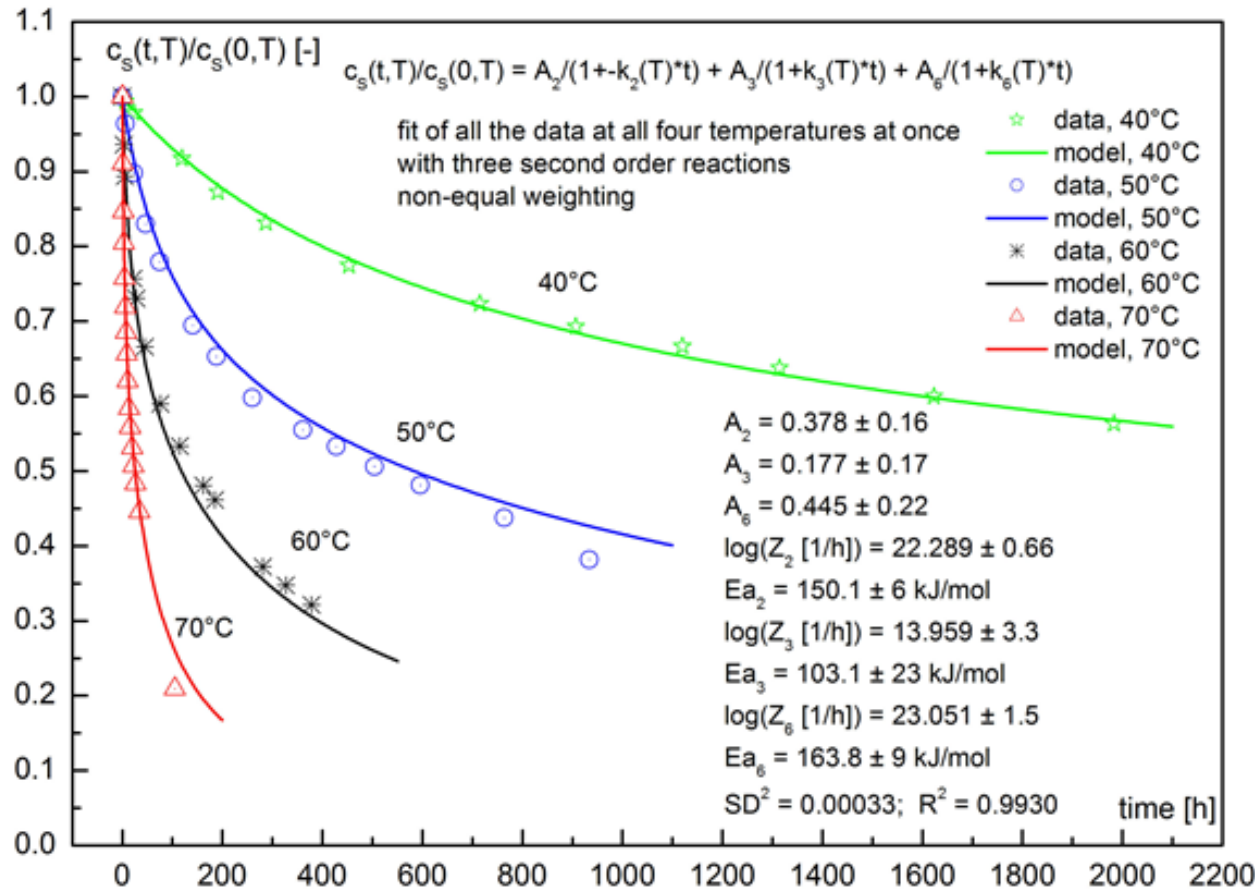
The material presented here is part of a paper given on ICT Conference 2018:

Manfred A. Bohn

Principles of ageing of double base propellants and its assessment by several methods following propellant properties.

Paper 96 pages 96-1 to 96-25. Proceed. of 49th International Annual Conference of ICT on 'Energetic Materials – Synthesis, Processing, Performance', June 26 to 29, **2018**, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut fuer Chemische Technologie (ICT), 76318 Pfinztal. Germany.

Nitration of a aromatic dye by decomposing NC – indication of three reaction ranges



Modelling of the concentration courses of the aromatic dye with three second order reactions occurring in parallel. Followed is the un-nitrated dye concentration

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

Compilation of the results of the modelling

Comparison of the activation energies for each nitration site on AHP ring with QM calculated bond dissociation enthalpies

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
BDEnth [kJ/mol]	160.8	133.0	174.4	QM calculation [see reference below]

Note: the average value of the activation energy is with 148 kJ/mol in the range of the found activation energies of the stabilizer decrease resulting from thermolytic ester decomposition.

The order of stability of the three AHP ring sites is now twofold

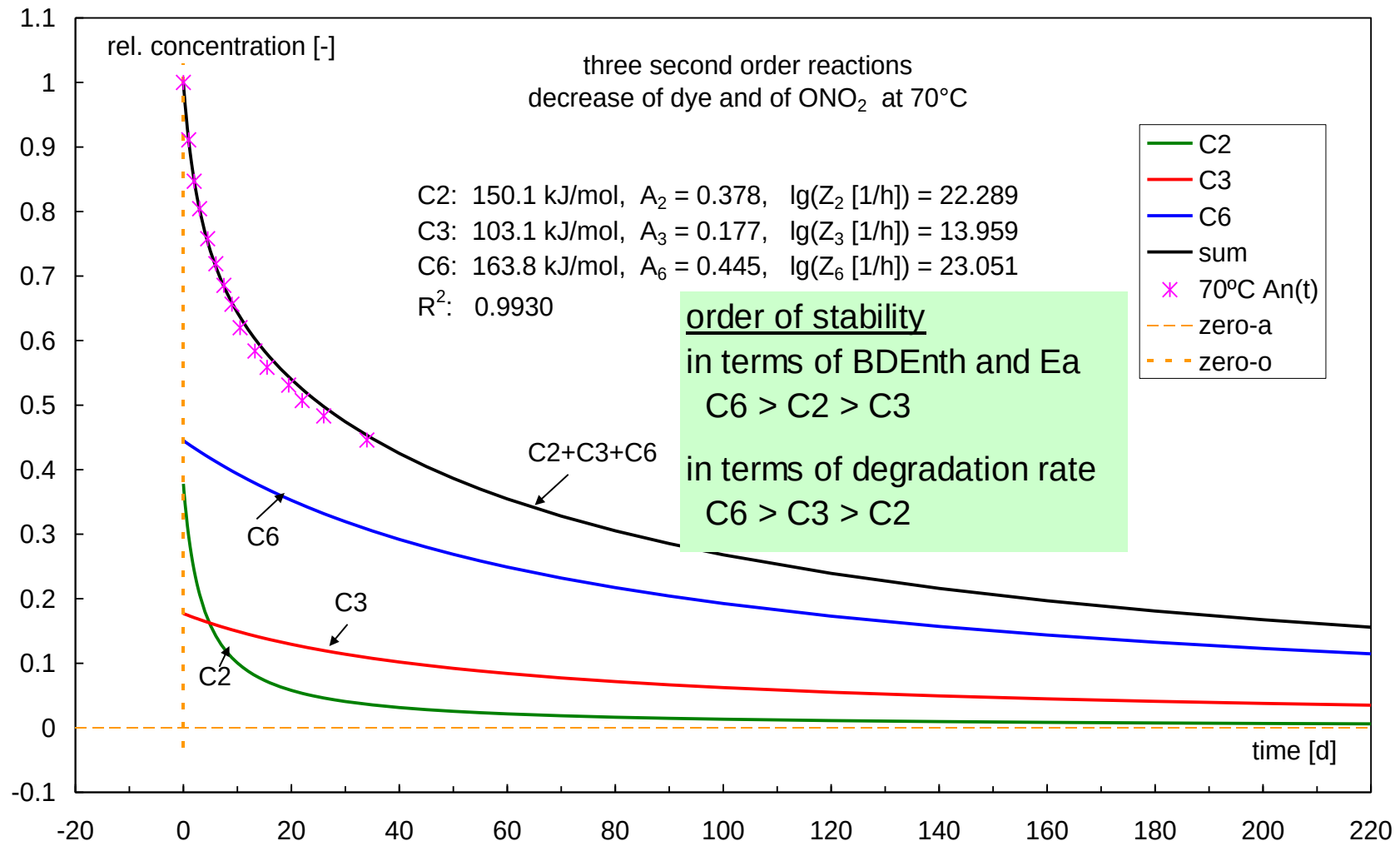
> with regard to activation energy and bond dissociation enthalpy: C6 > C2 > C3

M.A. Bohn

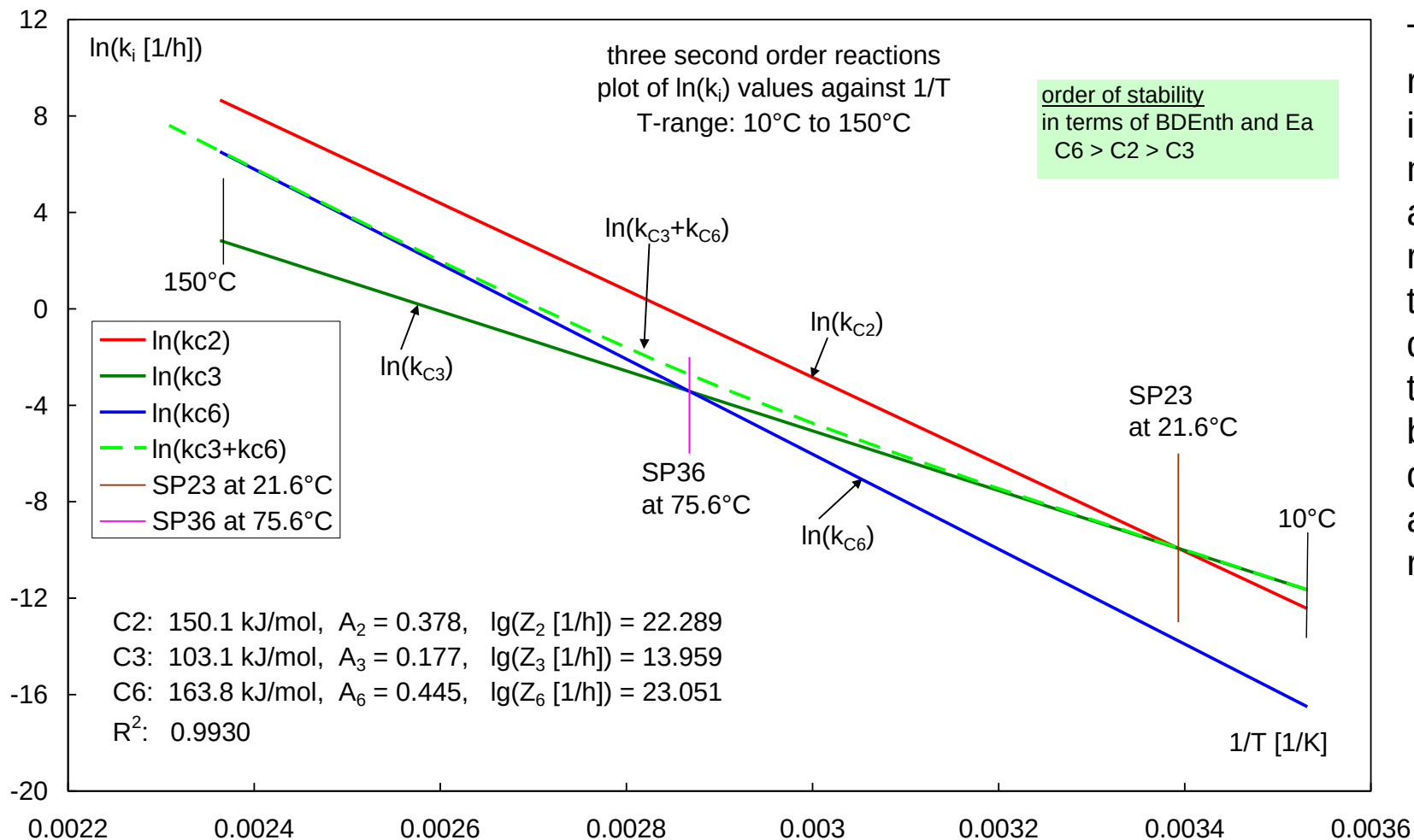
Bond dissociation enthalpies of the CO-NO₂ bonds in nitric acid ester groups and in peroxy-nitrite and peroxy-nitrate groups determined by DFT calculations.

Paper 71, pages 71-1 to 71-12 in Proc. 39th International Annual Conference of ICT on Energetic Materials; June 24 to 27, **2008**. Karlsruhe, Germany. ISSN: 0722-4087. Fraunhofer Institut fuer Chemische Technologie (ICT), 76318 Pfinztal, Germany.

Decrease of NE groups at the three positions on the AHP ring of NC

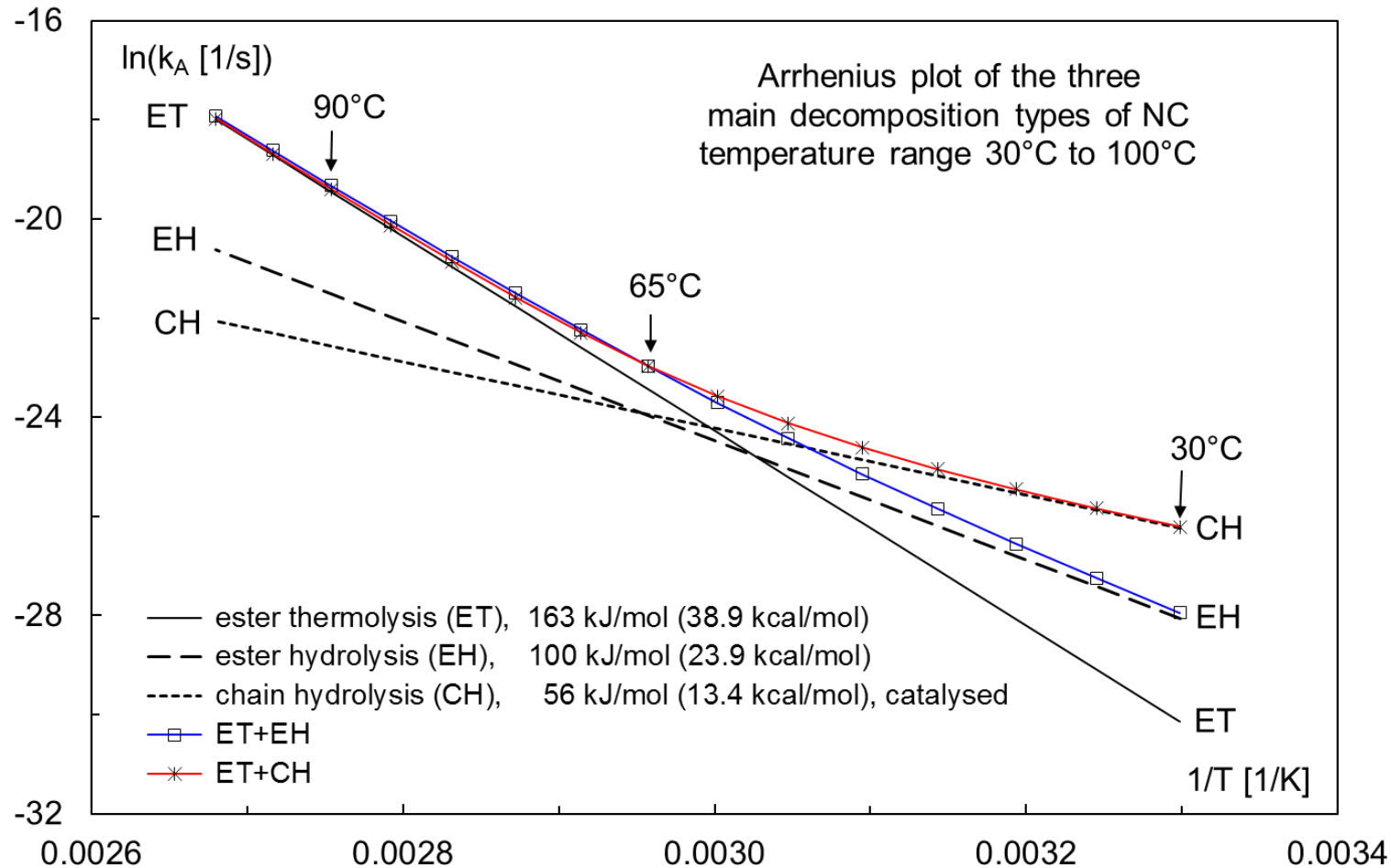


Arrhenius plots of the reaction rate constants



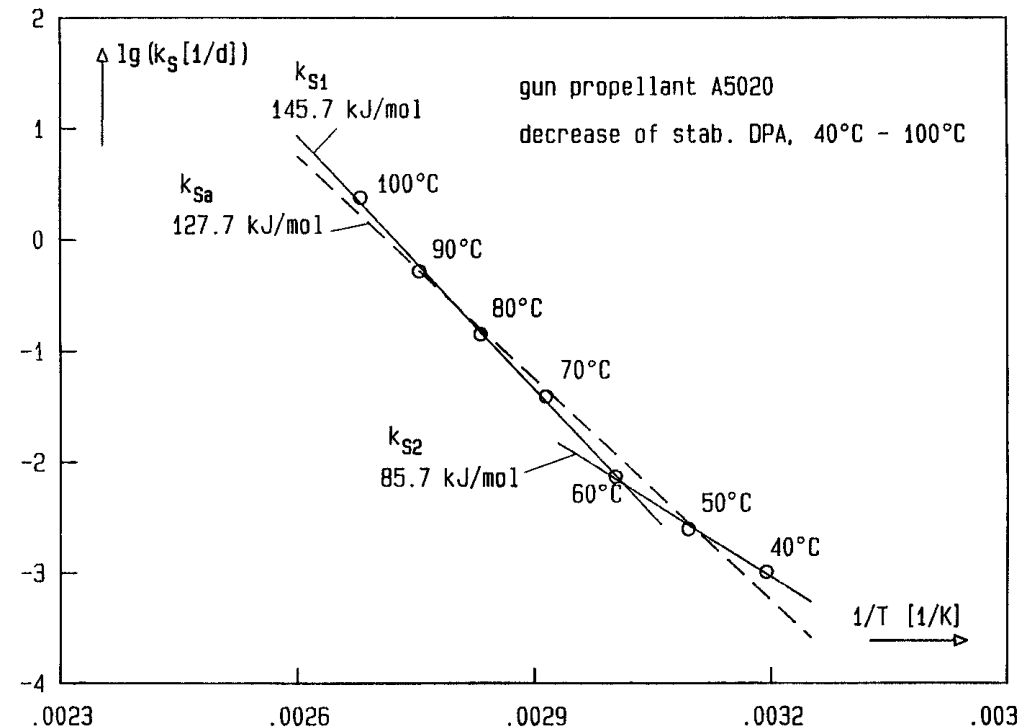
The three nitration reactions of the indicator molecule, the aromatic dye, are representative to the thermal decomposition of the used NC, because the NC decomposition is assumed to be rate determining.

Illustration of the overlay of two main low temperature decompositions with the high temperature thermolysis of NE-groups (means homolytical cleavage of CO-NO₂)



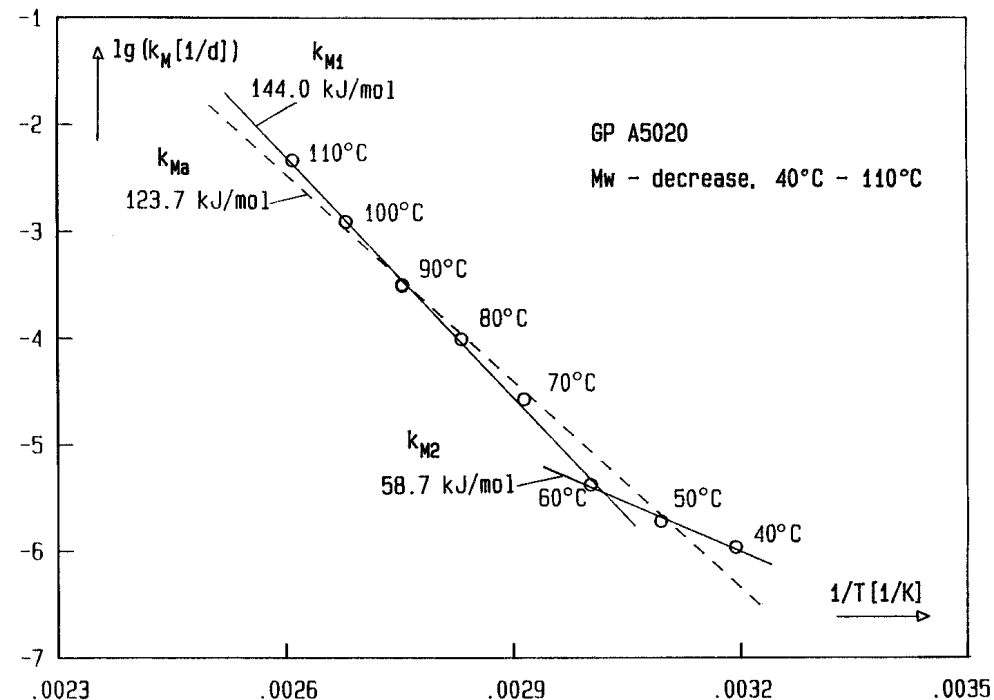
Applied in
STANAG 4582
(HFC-STANAG)
and
AOP-48

Experimental examples for the bend in Arrhenius plot



Example of a bend in Arrhenius plot of the reaction rate constants for the decrease of mean molar mass Mw of the NC in single base gun propellant A5020. The higher temperature mechanism shows an activation energy of 144 kJ/mol, the lower temperature mechanism (below 60°C) has 59 kJ/mol.

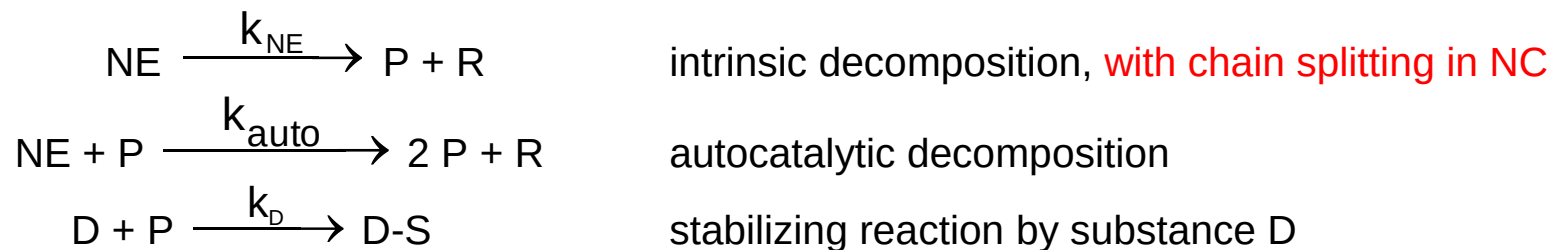
Example of a bend in Arrhenius plot of the reaction rate constants for the DPA stabilizer decrease in single base gun propellant A5020. The higher temperature mechanism shows an activation energy of 146 kJ/mol, the lower temperature mechanism (below 60°C) has 86 kJ/mol.



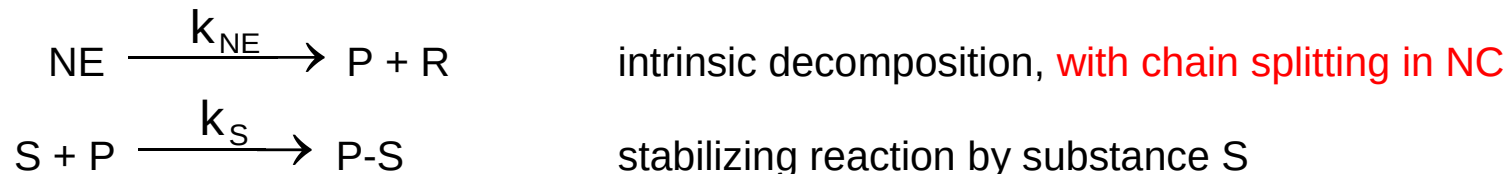
Decomposition kinetics of NC

Decomposition of NC (here generally named NE) is quite complicated. One main feature is the autocatalytic decomposition, which must be suppressed. This is achieved by stabilizers. *Here substance S is more effective than substance D.*

Note: in spite of active and effective stabilizer S present in the material, one has the intrinsic degradation of NC (NE) and which causes stabilizer consumption and NC chain scission.



With an effective (mean good) stabilizer S the autocatalytic feedback reaction is sufficiently suppressed and the above reaction scheme reduces to the following one.



Description or modelling the data sets of chosen properties

For good predictions of in-service times (life prediction) four points have to be fulfilled

- > Establish reliable data with low experimental scattering
here the accuracy of temperature is important
- > Description of the data with reaction kinetically based models
- > Use of the adequate temperature parameterization of the rate constants of property change
(with chemical processes this means reaction rate constants)
- > Quality of data description
Important for reliable extrapolation to get good predictions of in-service times
- > Use several models to test the description quality
- > Use so-called information criteria to find out the model, which describes the data best

For assessment of description quality and modelling of data see:

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Five kinetic models for stabilizer consumption and two for molar mass decrease

Eq.	kinetic rate equation	kinetic type	name of model, type suitability, how to handle
1	$\frac{dS(t)}{dt} = -k_1 \cdot S(t) - k_0$	first + zero order, two reactions	'S: exponential + linear', parametric very suitable, easy to handle
2	$\frac{dS(t)}{dt} = -k_1 \cdot S(t)$	first order, one reaction	'S: exponential', parametric limited suitable, easy to handle
3	$\frac{dS(t)}{dt} = -k_0$	zero order, one reaction	'S: linear' or 'S: zero order' parametric , very limited suitable easy to handle
4	$\frac{dS(t)}{dt} = -k^I \cdot S(t)^n$	nth order, one reaction	'S: nth order', parametric suitable, easy to handle
5	$\frac{dS(t)}{dt} = -k_{SP} \cdot S(t) \cdot (S(t) + NE(0) \cdot k_{NE} \cdot t)$	two reactions, model describes NE decomposition and consumption of S; this is the correct reaction kinetic base	'S: extended', with reaction kinetic base suitable, to handle with advanced fit codes (for example Origin™, Origin Lab Corp.)
6	$\frac{d\left(\frac{Mn(t,T)}{m}\right)}{dt} = -k_{Mn}(T) \cdot \left(\left(\frac{Mn(t,T)}{m}\right) + \left(\frac{Mn(t,T)}{m}\right)^2\right)$	chain splitting by random chain element decomposition	'Mn: chain splitting', reaction kinetic base suitable, easy to handle
	$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -\left(k_{M1} + k_{M2} \cdot \exp(+k_{M1} \cdot t) \cdot \frac{m}{Mn(0)}\right) \cdot \left(\frac{Mn(t)}{m}\right)^2 - (k_{M1} - k_{M2}) \cdot \left(\frac{Mn(t)}{m}\right)$	chain splitting (CS) by random chain element decomposition (ED) and chain recombination (CR)	'Mn: CS by ED and CR', reaction kinetic base suitable, easy to handle

Integrated forms of five stabilizer and two molar mass decrease models shown before

Eq.	equation	time t_0 to $y_s = S(t)/S(0) = 0$	$ty_s(T)$ to reach, $y_s = S(t,T) / S(0)$
1	$S(t,T) = \left(S(0) + \frac{k_0(T)}{k_1(T)} \right) \cdot \exp(-k_1(T) \cdot t) - \frac{k_0(T)}{k_1(T)}$	$t_0(T) = \frac{1}{k_1(T)} \cdot \ln \left(\frac{S(0) \cdot k_1(T)}{k_0(T)} + 1 \right)$	$ty_s(T) = \frac{1}{k_1(T)} \cdot \ln \left(\frac{1 + \frac{k_0(T)}{S(0) \cdot k_1(T)}}{y_s + \frac{k_0(T)}{S(0) \cdot k_1(T)}} \right)$
2	$S(t,T) = S(0) \cdot \exp(-k_1(T) \cdot t)$	$t_0(T) \rightarrow \infty$	$ty_s(T) = \frac{1}{k_1(T)} \cdot \ln \left(\frac{1}{y_s} \right)$
3	$S(t,T) = S(0) - k_0(T) \cdot t$	$t_0(T) = \frac{S(0)}{k_0(T)}$	$ty_s(T) = \frac{S(0)}{k_0(T)} \cdot (1 - y_s)$
4	$S(t,T) = S(0) \cdot [1 - (1-n) \cdot k(T) \cdot t]^{\frac{1}{1-n}}$ with $k(T) = \frac{k^l(T)}{S(0)^{1-n}}$	$t_0(T) = \frac{1}{k(T)} \left(\frac{1}{1-n} \right)$ only for $n < 1$	$ty_s(T) = \frac{1}{k(T)} \cdot \frac{1 - (y_s)^{1-n}}{1-n}$ only for $n < 1$
5	$S(t) = \frac{\sqrt{\exp(-NE(0) \cdot k_{NE} \cdot k_{SP} \cdot t^2)}}{\frac{1}{S(0)} + \sqrt{\frac{\pi}{2} \cdot \frac{k_{SP}}{NE(0) \cdot k_{NE}} \cdot \operatorname{erf} \left(\sqrt{\frac{NE(0) \cdot k_{NE} \cdot k_{SP}}{2}} \cdot t \right)}}$	$t_0(T) \rightarrow \infty$	no closed form for $ty_s(T)$
6	$Mn(t,T) = \frac{m}{\left(1 + \frac{m}{Mn(0)} \right) \cdot \exp(+k_{Mn}(T) \cdot t) - 1}$	$t_0(T) \rightarrow \infty$	$ty_{Mn}(T) = \frac{1}{k_{Mn}(T)} \cdot \ln \left(\frac{1 + \frac{Mn(0)}{m}}{\frac{y_{Mn}}{1 + \frac{Mn(0)}{m}}} \right)$
7	$\frac{Mn(t)}{m} = \frac{\exp(-k_{M1} \cdot t)}{\frac{m}{Mn(0)} + \frac{k_{M1}}{k_{M1} - k_{M2}} \cdot (\exp(-k_{M2} \cdot t) - \exp(-k_{M1} \cdot t))}$	$t_0(T) \rightarrow \infty$	no closed form for $ty_{Mn}(T)$

Heat generation rate of db RP and safe storage time

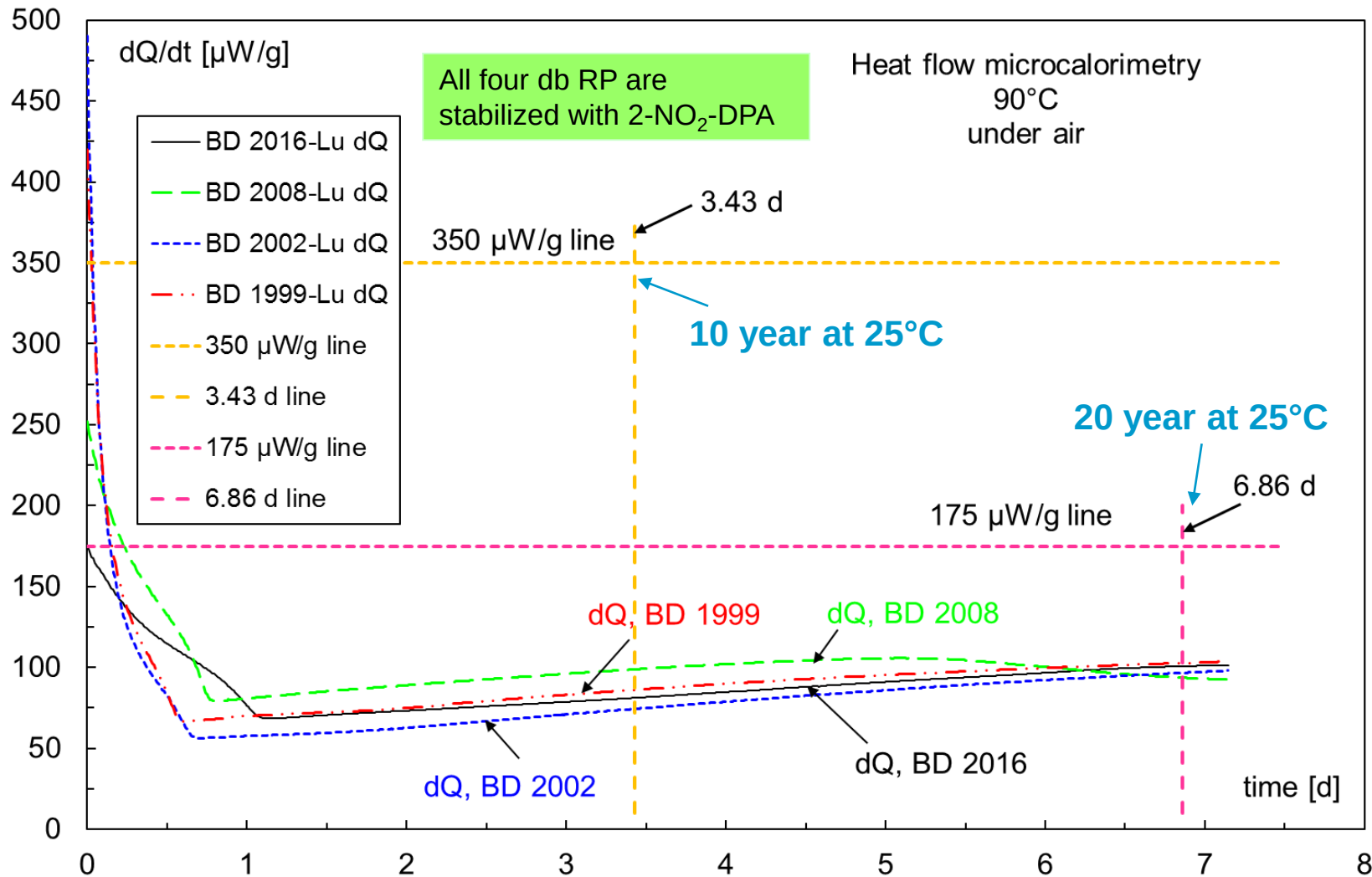
Is safe storage time extendable beyond 10 years at 25°C ?
Yes, but one has to follow the rules set by 'HFC-STANAG'
(STANAG 4582)

See also

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Heat generation rate as indicator for chemical stability



Extension of time:

1. Measure to longer times
2. Reduce correspondingly the dQ/dt-limit at chosen test temperature (limit, which is given for 10 years, 25°C)

Double test time and half of dQ/dt-limit gives double assessment time, when measured heat flow does not exceed the new dQ/dt-limit

Any smaller ratio possible.

Environmental time-temperature relations based on STANAG and AOP

	STANAG 4582, AOP-48		vant' Hoff	
	Ea ₁ = 120 kJ/mol		F = 2.9	
	Ea ₂ = 80 kJ/mol			
T _E [°C]	t _E [d]	t _E [a]	t _E [d]	t _E [a]
12	15905.8	43.5	14578.3	39.9
15	11194.0	30.6	10592.3	29.0
18	7935.2	21.7	7696.1	21.1
20	6333.4	17.3	6220.0	17.0
22	5070.5	13.9	5027.0	13.8
25	3652.5	10.0	3652.5	10.0
30	2145.0	5.9	2144.8	5.9
35	1281.6	3.5	1259.5	3.5
40	778.5	2.1	739.6	2.0
45	480.3	1.3	434.3	1.2

van't Hoff with F = 2.9 represents very well the two mechanistic scheme of STANAG 4582 ('HFC STANAG') and AOP-48

van't Hoff based relations

$$t_T [d] = t_E [a] \cdot F_{\Delta T}^{-(T_T - T_E) / \Delta T_F} \cdot 365.25$$

$$t_E [a] = t_T [d] \cdot F_{\Delta T}^{+(T_T - T_E) / \Delta T_F} / 365.25$$

Van't Hoff method represents the two-mechanistic procedure very well.

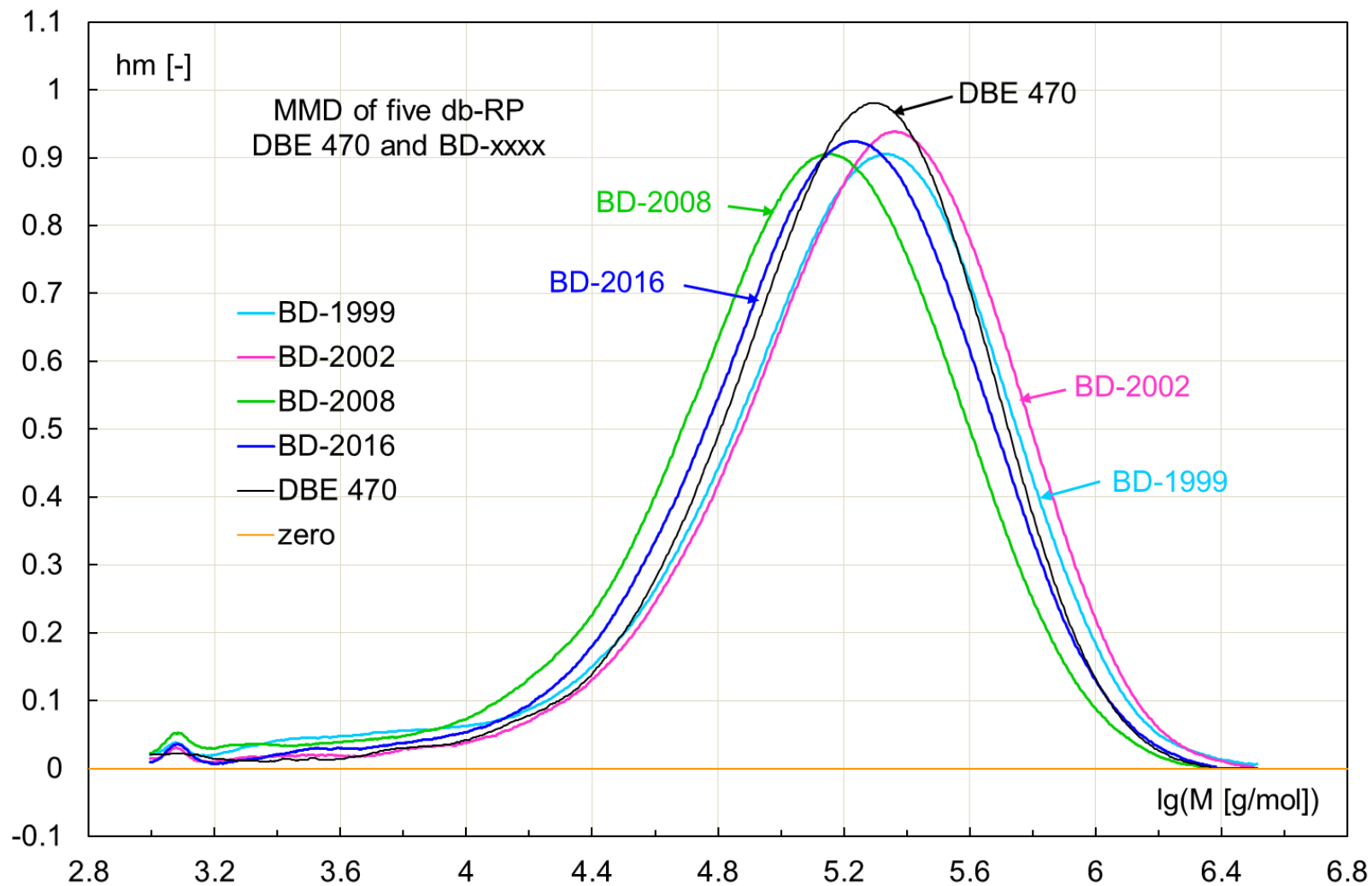
Gel Permeation Chromatography (GPC) on double base rocket propellants

Determination of molar mass distributions(MMD) of NC
by gel permeation chromatography (GPC)
Calibration of column set by narrowly distributed PS standards
THF as solvent and eluent.

Important

The evaluation of the elugrams is a step, which needs care in order to get good MMD and useful calculated mean molar masses M_n , M_w , M_z .
Evaluation of elugrams should / must be done according to the procedure given in the 'NC-STANAG' (STANAG 4178, Ed 2 or/and AOP 4178, Ed 3 at time in ratification)

Molar mass distribution (MMD) of NC in double base propellants



Db RP from
three
manufacturer
US
Brazil
Germany

All propellants
behave very
similar

Ageing effect on MMD of NC with DBE 470

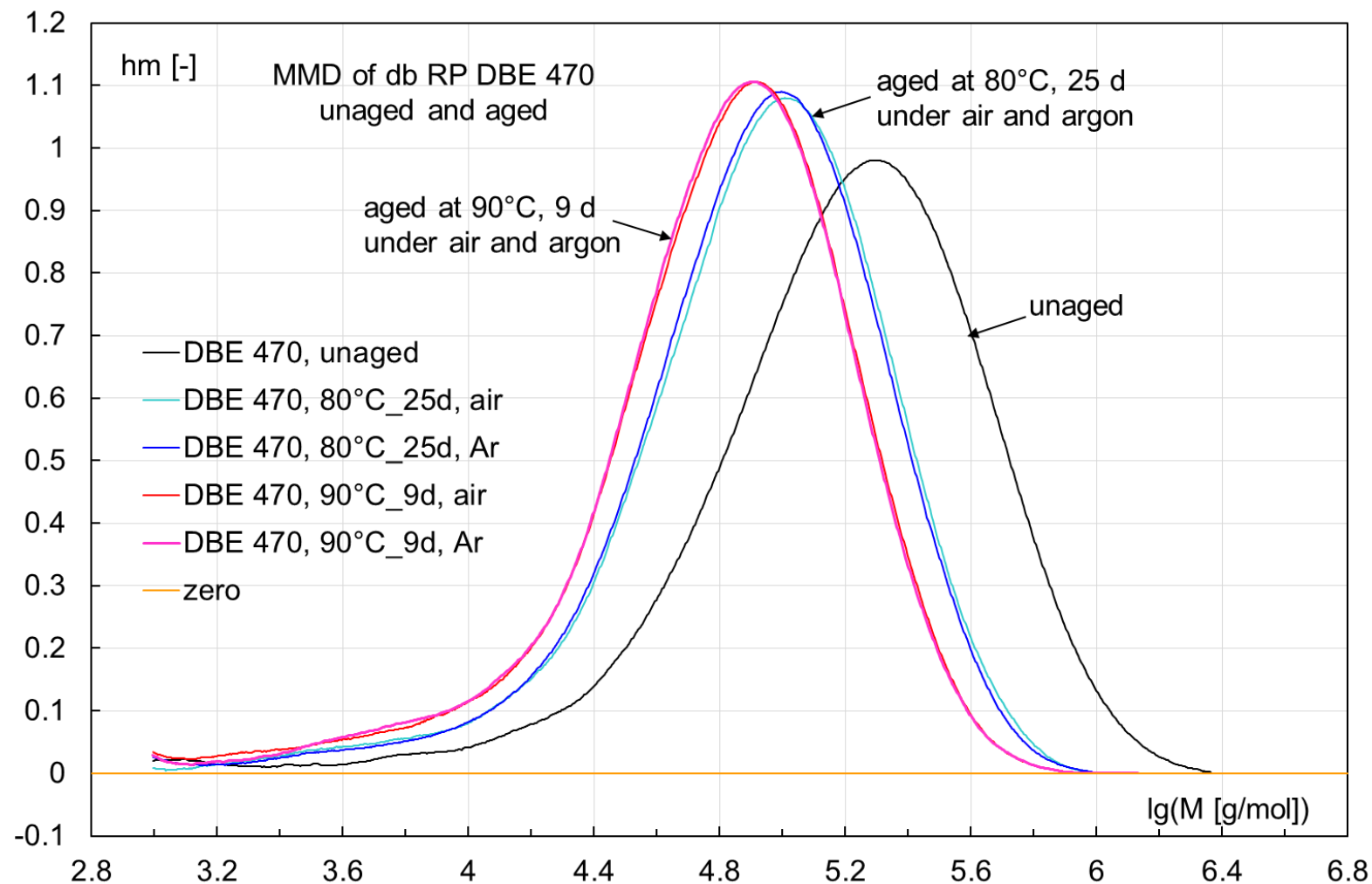
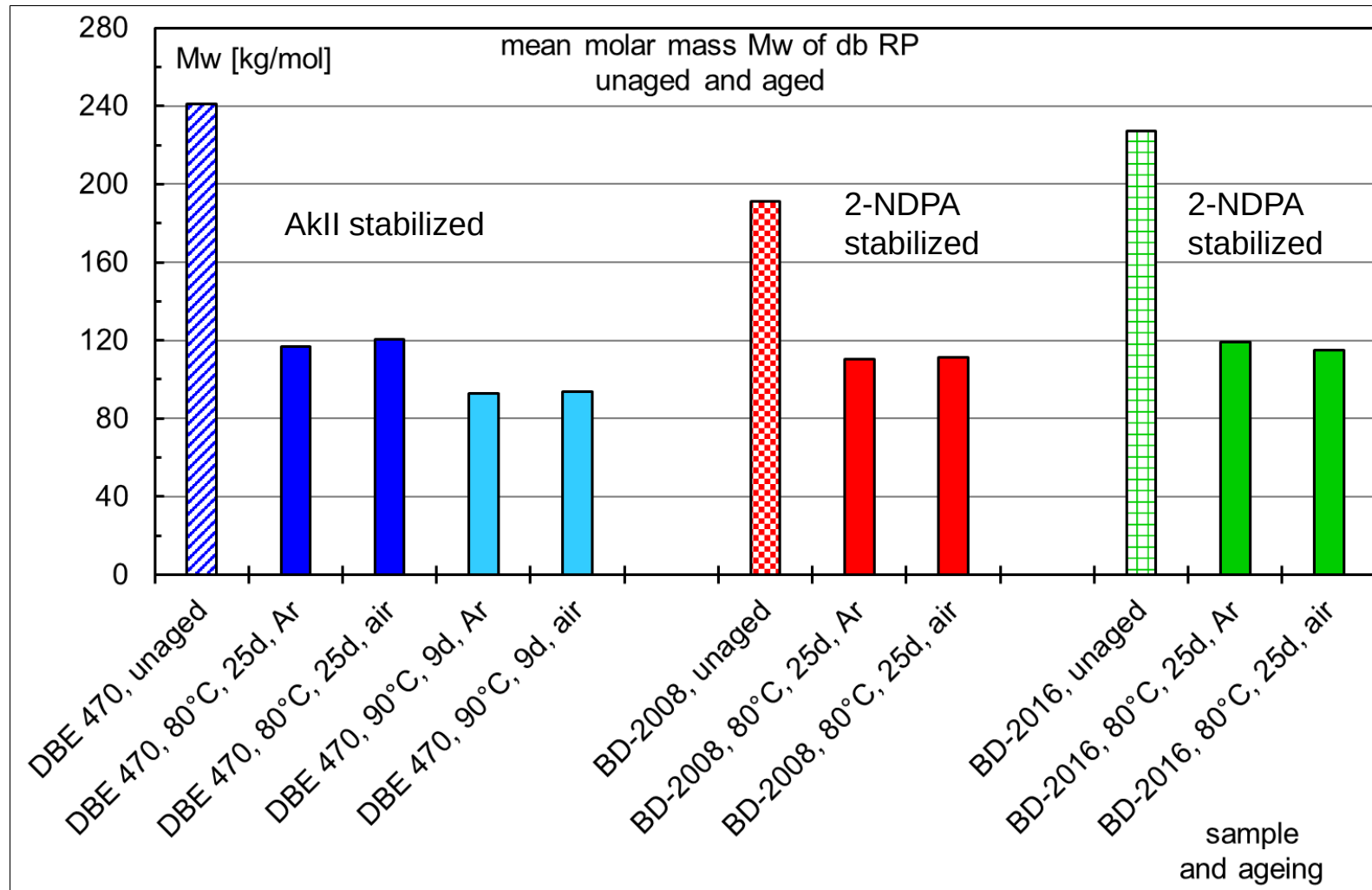


Illustration of decrease of Mw (the mass weighted mean molar mass)

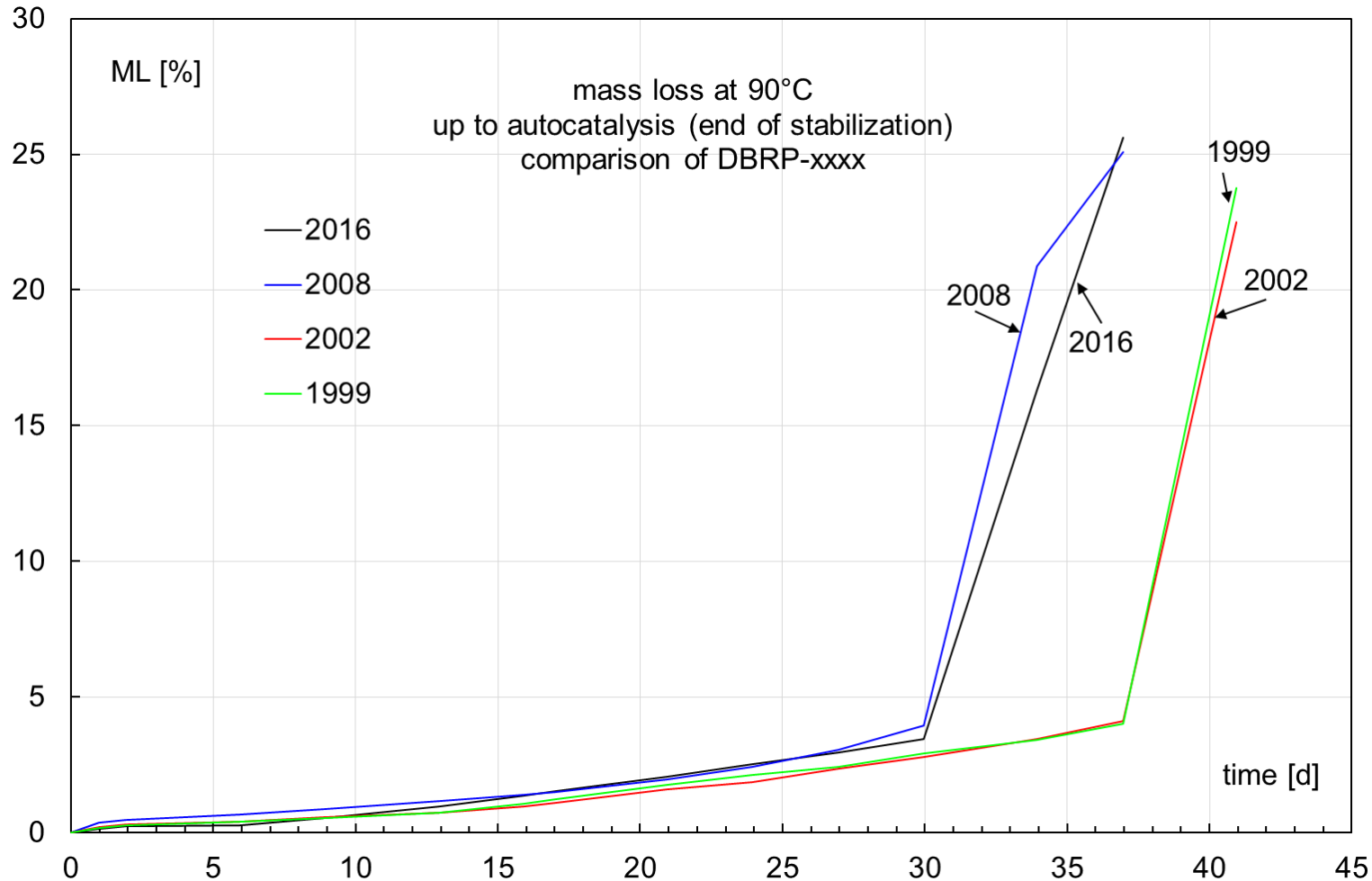


Determined via the GPC from MMD after ageing in HFMC ampoules under air and under argon

The pattern is very similar for mean molar masses Mn, Mz and peak Mp of MMD

Mass loss (ML) with double base rocket propellants

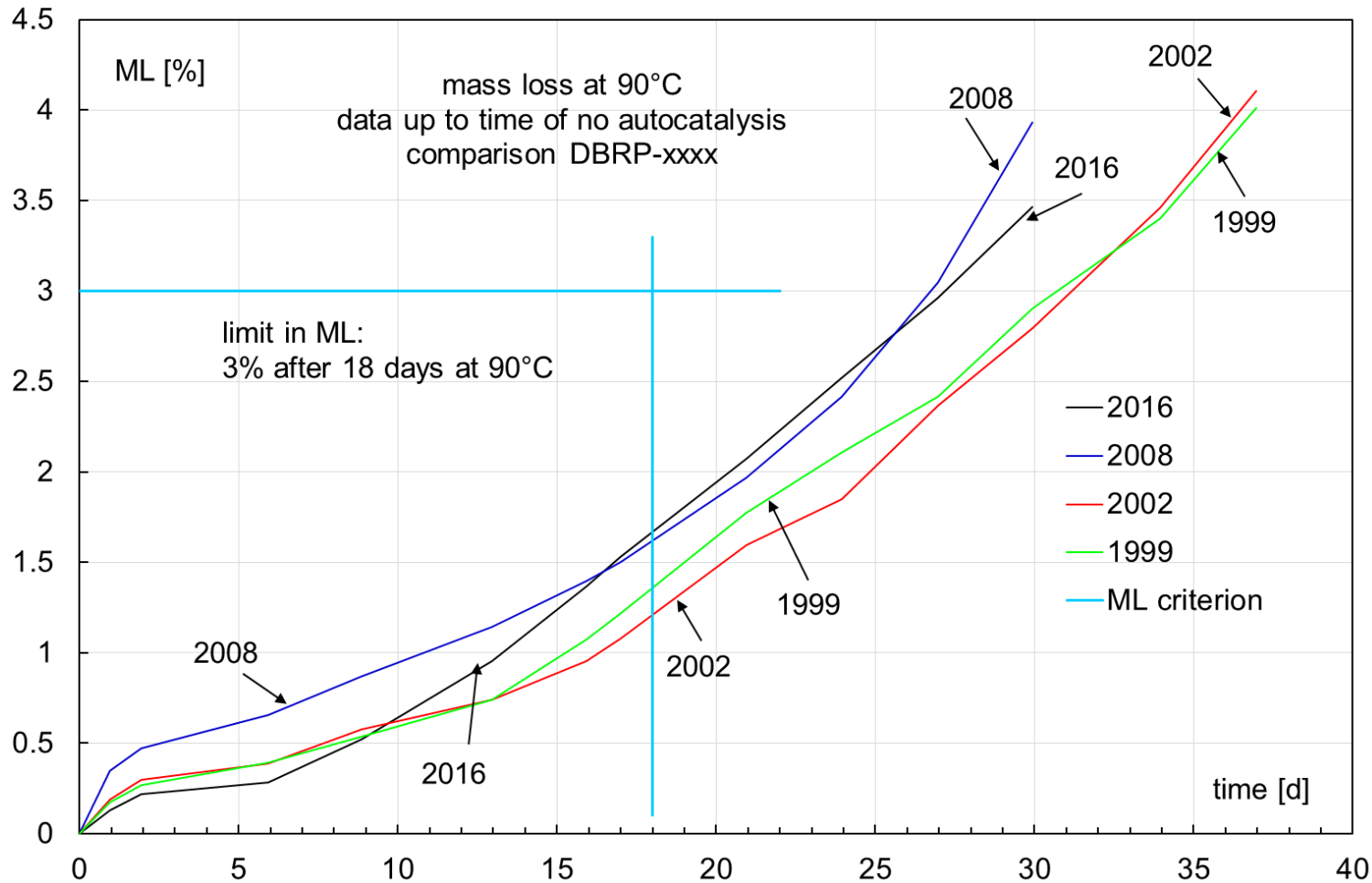
Mass loss as indicator for the very end of stabilisation



The strong increase in ML indicates the end of any stabiliser action, mean all stabilizer (including consecutive ones) are consumed.

The strong increase is caused twofold: autocatalysis and thermal runaway (caused by selfheating of the sample) acting together.

Mass loss as stability criterion



The stability criterion $\leq 3\%$ ML after 18d at 90°C corresponds to about 50 years at 25°C isothermal load.

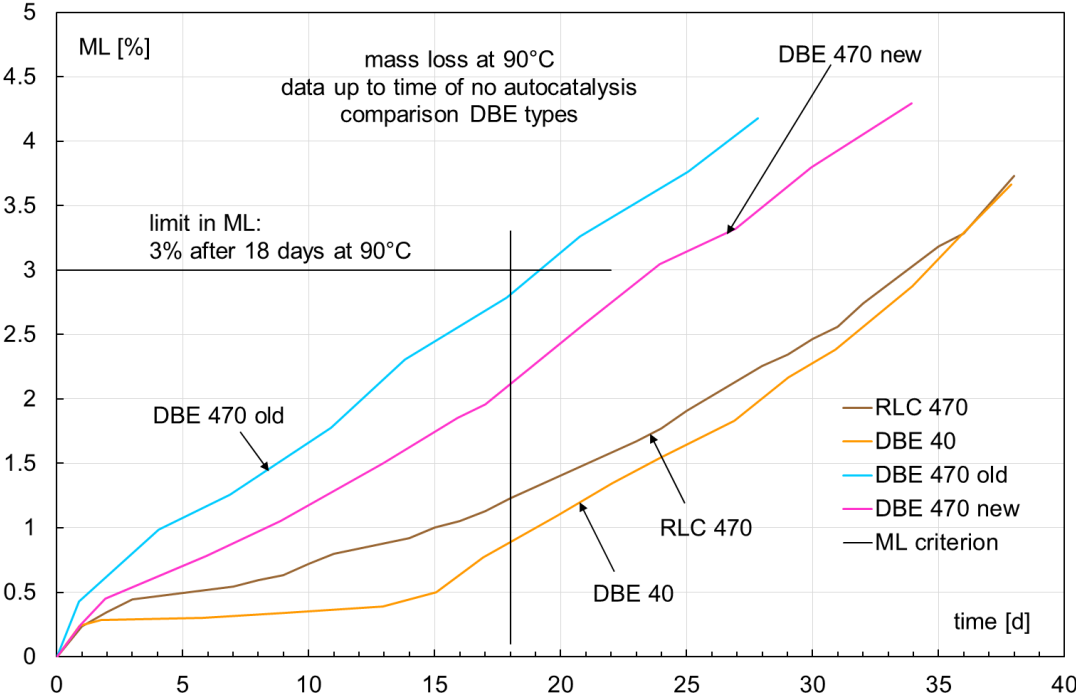
Remarkable:
Two manufactures (USA and Brazil) with this four RP give good agreement and consistency.

Characteristics of propellant formulation

Revealed by mass loss (ML) as function of time:

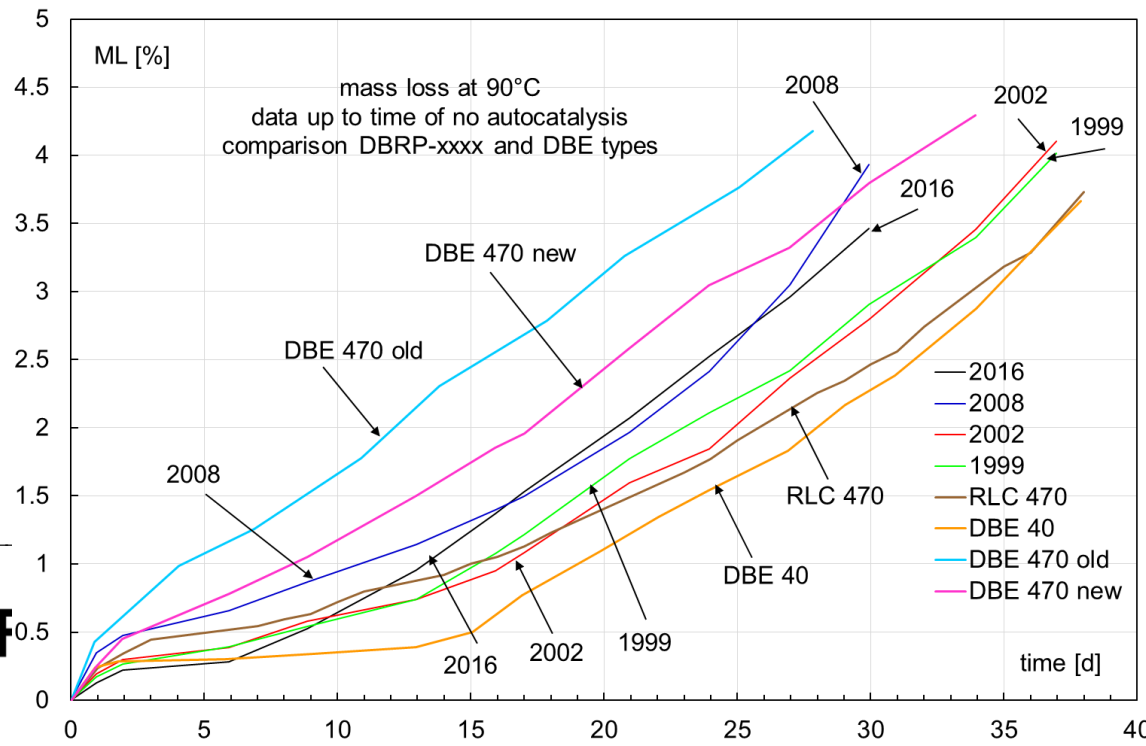
Influence of stabilizer type on ML course.

It seems that 2-NO₂-DPA is a better stabilizer than Akardite II in order to keep the course at lower ML level.



The DBE and the RLC types are from a German manufacturer

2018

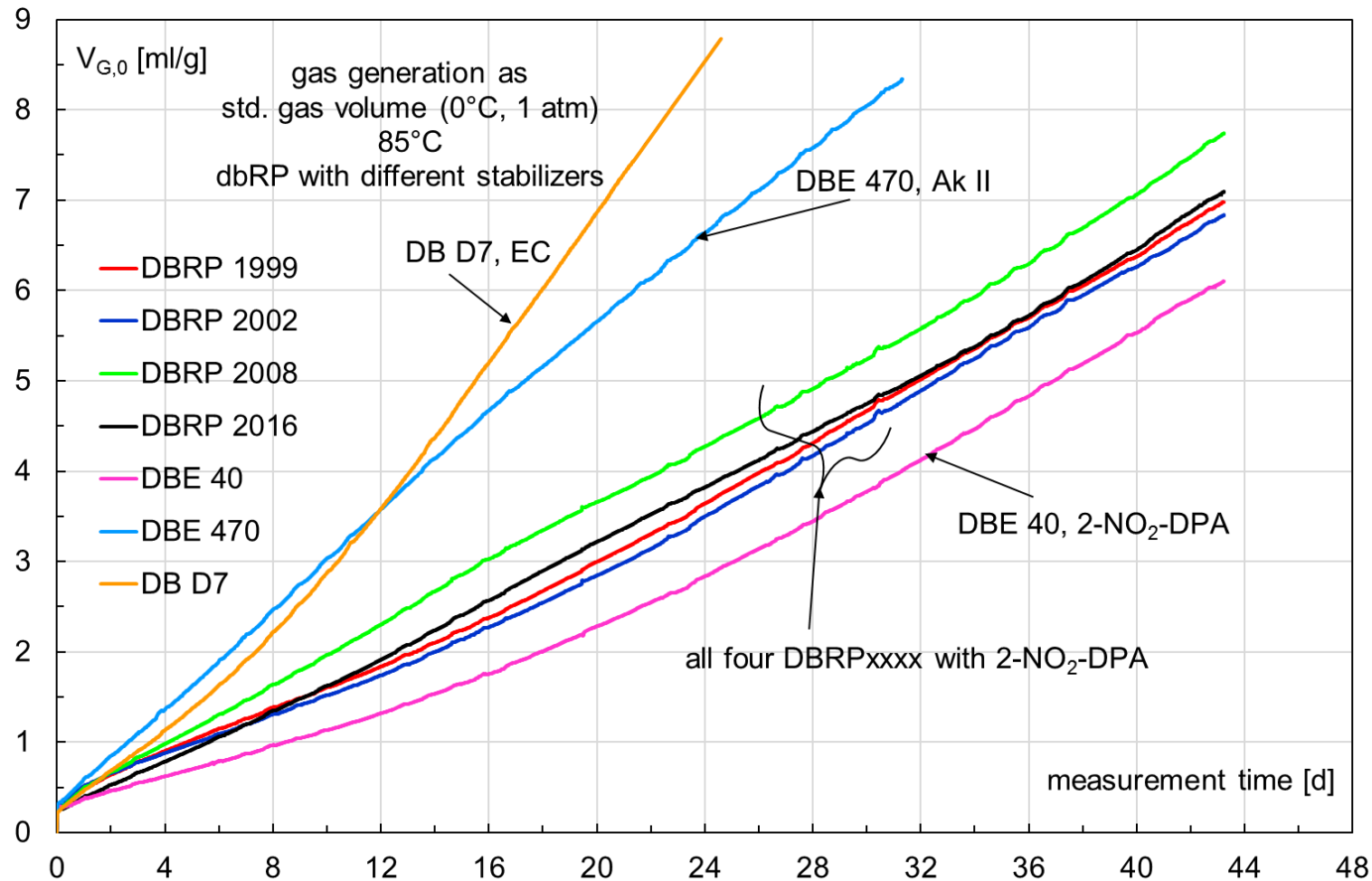


Gas generation (GG) with double base rocket propellants

The apparatus used was the p-VST (pressure Vacuum Stability Tester) of company OZM Research, Czech Republic, called STABIL VI®.

The pressure data of the gas generation were transformed to gas volume data at standard condition (0°C, 1 atm).

Influence of stabilizer in db RP on gas generation (GG) as std. gas volume



The db-RP stabilized with 2-NDPA have least GG and gas generation rate (GGR).

Least good is stabilizer EC (ethylcentralite, Centralite I)

Also with AkII high GG and GGR, already from begin of ageing

Dynamic mechanical analysis (DMA) on double base rocket propellants

DMA in torsion mode

Instrument

ARES™ (**A**dvanced **R**heometric **E**xpansion **S**ystem)

manufactured by former Rheometric Group of Rheometric Scientific Inc., Piscataway, NJ, USA (now TA Instruments, Newcastle, DE, USA)

Deformation frequencies 0.1 Hz, 1 Hz, 10 Hz, 30 Hz Hz

Measurement temperature -110°C to +80°C

Temperature step: 1°C, soak time 28 sec, total stay time at one level is about 65 sec

DMA in torsion determines the complex shear modulus $G^* = G' + iG''$;

G' storage shear modulus, represents the elastic part in the material (energy storage)

G'' loss shear modulus, represents the dissipative part in the material (energy loss)

loss factor $\tan(\delta) = G''/G'$, the ratio of loss shear modulus to storage shear modulus

Advantages

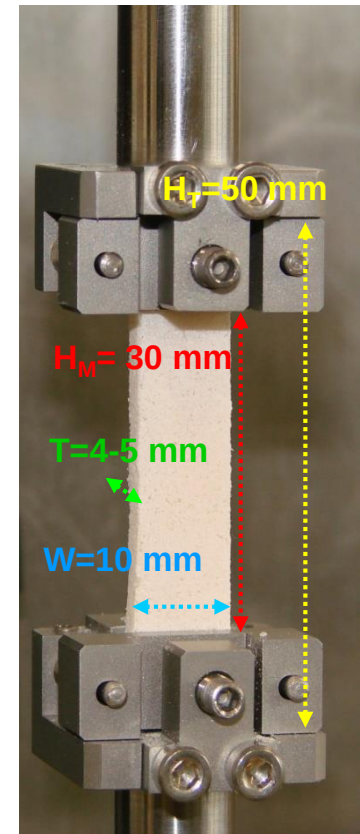
avoiding forced contact between solid filler particles as possible with compressive deformation;

no pre-straining necessary as in tensile deformation;

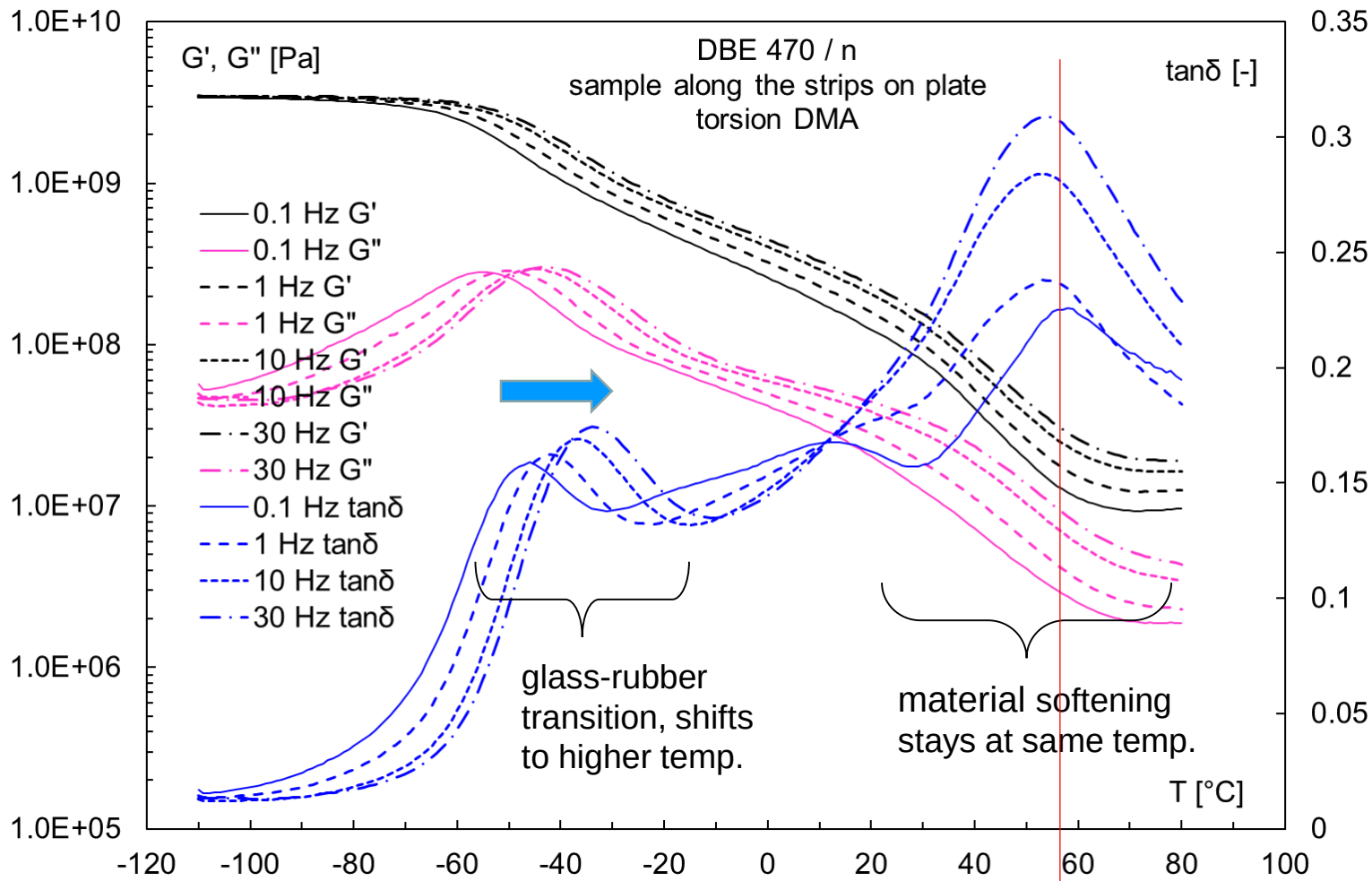
no sample slipping (as may happen in tensile type deformation), sample is well fixed;

no gluing necessary to fix the sample;;

DMA in torsion



Dynamic mechanical analysis of double base RP – DBE 470/n (AkII stabil.)



Glass-rubber transition
in the range -60 to -30°C

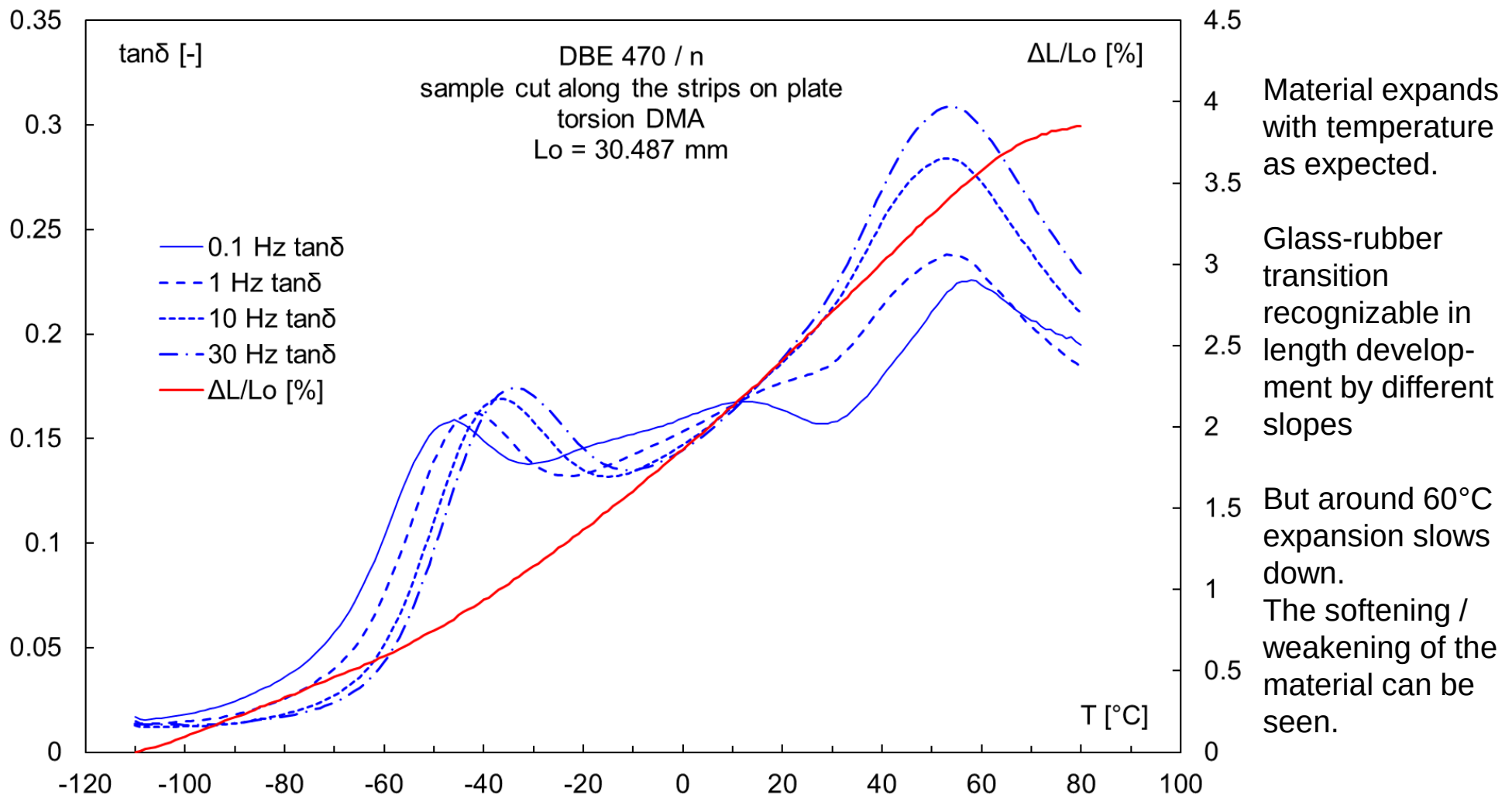
It shifts to higher temperatures with increasing deform. frequency – strain rate hardening;

Softening / weakening
In range +40 to +70°C

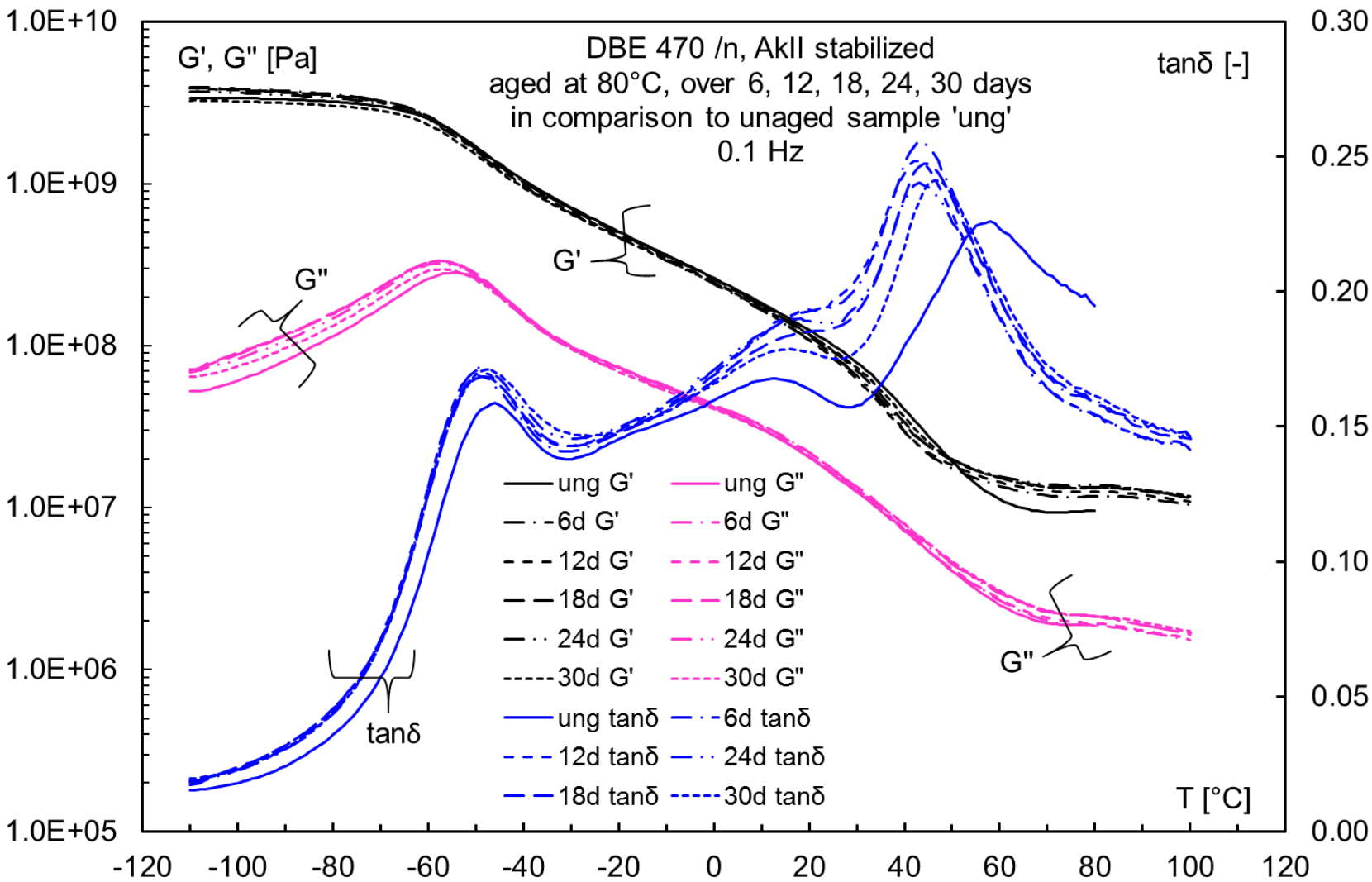
Caused by temperature is not susceptible to strain rate hardening;

DBE 470/n is stabilized with AkII.

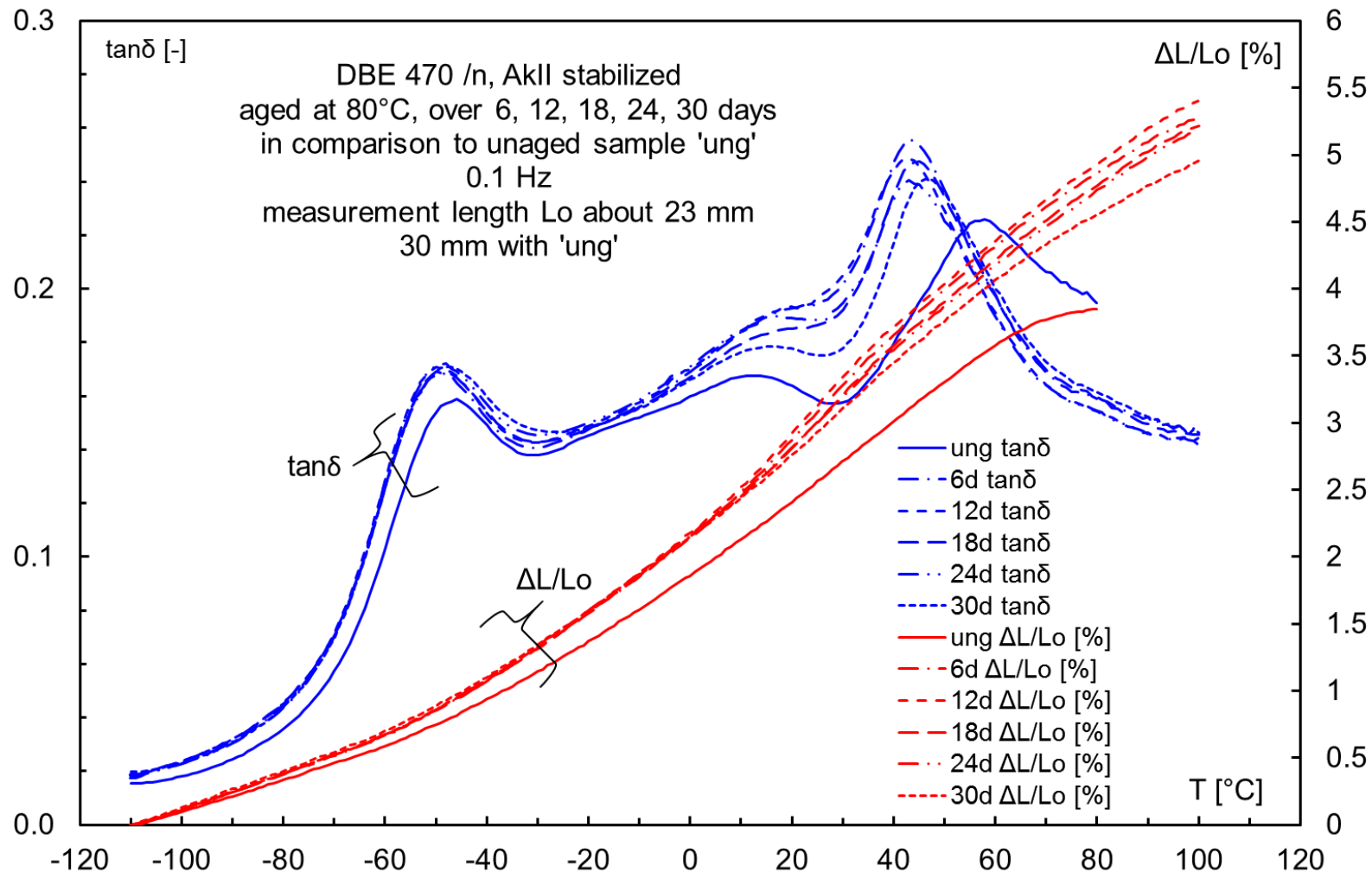
Loss factor $\tan\delta$ and the change in measurement length



Ageing of db-RP DBE 470/n - effect on the DMA results



Effect of ageing on loss factor - change in measurement length



More thermal
expansion
after ageing

To be noted:
The material
softening /
weakening
corresponds
with the
change in
mechanistic
in ageing

Conclusions

NC-based material have a **complicated ageing and decomposition behaviour**.

The individual NE-groups at the anhydroglucopyranose ring have different dissociation enthalpies and they decompose at different rates.

This complicates the investigation of decomposition and ageing.

The application of **torsion DMA** revealed interesting features of db RP:

There is a type of **glass-rubber transition around -60°C to -40°C**.

The loss factor peak ($\tan\delta$) and the loss modulus peak (G'') are shifted to higher temperatures with increasing deformation frequency (strain rate hardening of the material).

Between +50°C and +70°C a softening / weakening of the material happens. The loss factor shows a peak, which is not shifted to higher temperatures with increasing frequency.

This softening may be **involved in the mechanistic changes** found with stabilizer and molar mass decrease.

With **ageing** the **glass-rubber transition is shifted somewhat to lower temperatures**, as well as the softening range.

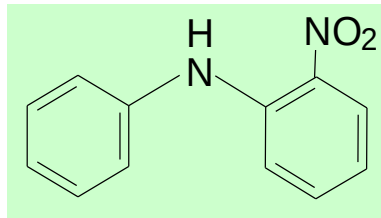
Conclusions – cont.d

Mass loss and gas generation (in vacuum) revealed the difference in stabilizer quality. The samples containing 2-NO₂-DPA are best stabilized with regard to mass loss and gas generation.

Next best is Akardite II (AkII).

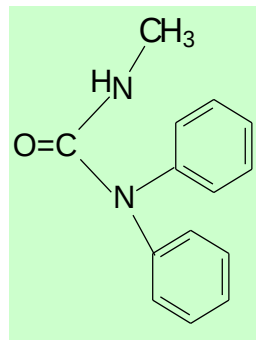
The least best is Ethyl-Centralite (EC, Centralite I).

To mitigate gas generation is important to avoid cracks in the material (Cube Crack Test).



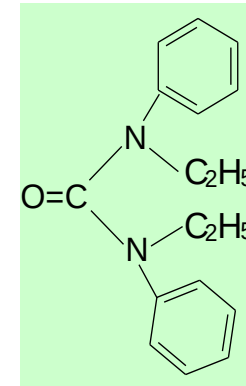
2-Nitro-diphenylamine
(2-NO₂-DPA, 2-NDPA)

first



Akardite II (AkII)

second



Ethyl-Centralite (EC)
Centralite I

last

choice

NC-based materials show a very complex ageing and decomposition behaviour