Towards a comprehensive understanding of the decomposition of nitrocellulose

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The miracle of nitrocellulose (NC)

NC is an interesting and a complicated substance.

Since decades, it is said it will be out of use soon.

In the 1980s the LOVA (low vulnerability) demand arose.
NC and propellants made of NC were judged - they will not fulfil the demands.

Further on:
> NC and NC-based materials are not stable enough to withstand all the thermal loads.
> On bullet impact, large propellant charges detonated.
> To hot burning – to much barrel erosion.
> ……..

And more arguments against NC have been searched for:
NC is made from a natural product – quality is not constant, or cannot defined properly.
The production is dangerous and environmentally not benign
…….
and what else more

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The miracle of nitrocellulose (NC) – cont'd

Much effort was made to replace NC by other polymers

PolyGlyn, (PGN), PolyNimmo, HTPB, GAP, Poly(AMMO), Poly(BAMO), energetic thermoplastics,…

But NC and NC-based products are still alive !

Reason and conclusion:

NC-based products have properties not easy to realize with other polymeric energetics

One drawback up today: the embrittlement of all these substitutes at lower temperatures

A well-made double base NC-propellant gets brittle at quite low temperatures…
lower than the typical standard temperature of -54°C

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Decomposition of nitrocellulose – a never-ending problem?

NC is probably the best and most investigated substance in military use.

Big efforts have been made to find out its decomposition behavior.

So all should be known and solved.

At least the knowledge should be just on the level that people mean to know enough.

Enough? for what purposes?

The minimum demand is to suffer no ‘big surprises’ during its use.
Tight surveillance programs ensure safety.

New questions and demands?
Ideas on extended modelling – to consider all ingredient in a propellant sample
and the texture of residual fiber arrangements

- could we model heat output of propellant, from the basics, for example ?
- ideally without measurements (this may be somewhat like to reach the stars…)
- assessment of new stabilizers, for this also re-look on the main decomposition ways of NC

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Some ‘basics’ with decomposition of energetic materials

Thermodynamic stability of EM

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EoF of substances and their decomposition behavior without attack of reactants

EoF: the standard enthalpy of formation

substance	EoF [kJ/mol]	thermal decomp. at 20 to 35°C over 10 years
RDX	+ 67	stable
HMX	+ 84	stable
nitroguanidine	- 87	stable
methane	- 75	stable
benzene	+ 49	stable
TNT	- 67	stable
CO_2	- 394	stable
cellulose	- 960	stable
ADN	- 150	slow decompos.
nitroglycerin	- 370	slow decompos.
nitrocellulose N = 14.14 m.-%	- 653	slow decompos.
nitrocellulose N = 13.2 m.-%	- 687	slow decompos.
nitrocellulose N = 12.6 m.-%	- 708	slow decompos.

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EoF of substances and their decomposition behavior without attack of reactants

EoF: the standard enthalpy of formation

substance	EoF [kJ/mol]	thermal decomp. at 20 to 35°C over 10 years	enthalpy of reaction	
			[kJ/mol]	type
RDX	+ 67	stable	1254.32	Q_{Ex}
HMX	+ 84	stable	1667.18	Q_{Ex}
nitroguanidine	- 87	stable	325.90	Q_{Ex}
methane	- 75	stable	175.1 (1 : 4 O_2 by mass)	$-\Delta H_R$
benzene	+ 49	stable	690.2 (1:3.687 O_2 by m.)	$-\Delta H_R$
TNT	- 67	stable	855.5	Q_{Ex}
CO_2	- 394	stable	-	-
cellulose	- 960	stable	257.84	Q_{Ex}
ADN	- 150	slow decompos.	413.95	Q_{Ex}
nitroglycerin	- 370	slow decompos.	1515.8	Q_{Ex}
nitrocellulose N = 14.14 m.-%	- 653	slow decompos.	1432.1	Q_{Ex}
nitrocellulose N = 13.2 m.-%	- 687	slow decompos.	1210.6	Q_{Ex}
nitrocellulose N = 12.6 m.-%	- 708	slow decompos.	1084.9	Q_{Ex}

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Establishment of differences in terms

- Energetic materials tend to decompose in thermodynamically more stable products.
- The decomposition rates are widespread:
  nitrate esters as NC, nitroglycerin decompose already at room temperature;
  RDX, HMX, FOX-7 are stable even at elevated temperatures.
- The reasons for the differences are
  > the chemical structure,
  > the values of bond dissociation enthalpies,
  > the possibility to be attacked by reactants as water, oxygen, acids, bases, …..
- Because decomposition rates are largely different between substance groups:

  A separation based on the decomposition rates has evolved over time into mainly two groups using own terms, instrumentations and reaction kinetic descriptions.
- *Chemical stability* deals with the *assessment of faster* decomposing substances.
- *Thermal analysis* is preferred term in *dealing with the slow* decomposing substances.

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The peculiarity – the weighting of decomposition reactions

Typical decomposition behavior of EM is very complex

- with several parallel reactions
- with several consecutive reactions
- one or more autocatalytic reaction parts

…. and each reaction with its own Arrhenius parameters.

And further on:

Diffusion controlled reactions
Phase changes, crystal phases may react differently, solid-liquid
Induction of radical reactions, post-cure reactions
Humidity influences, compatibility mismatch

…….

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Demonstration of the complex behavior with five parallel reactions

$$\left(\frac{dA(t,T)}{dt}\right)\Bigg|_T = -\left(k_1(T)+k_2(T)+k_3(T)+k_4(T)+k_5(T)\right)\cdot A(t,T)$$

Each reaction follow first order

$$A(t,T) = A(0)\cdot \exp\left[-\left(k_1(T)+k_2(T)+k_3(T)+k_4(T)+k_5(T)\right)\cdot t\right]$$

$$k\text{-all}(T) = k_1(T)+k_2(T)+k_3(T)+k_4(T)+k_5(T)$$

$$k_J(T) = Z_J\cdot \exp\left(\frac{Ea_J}{R\cdot T}\right)$$

	Reaction1	Reaction2	Reaction3	Reaction4	Reaction5
lg(Z_j [1/d])	7.5	11	13.5	19	25
Ea_j [kJ/mol]	70	100	120	160	205
A(0) [conc. unit]	1				
R [J/mol/K]	8.31411				

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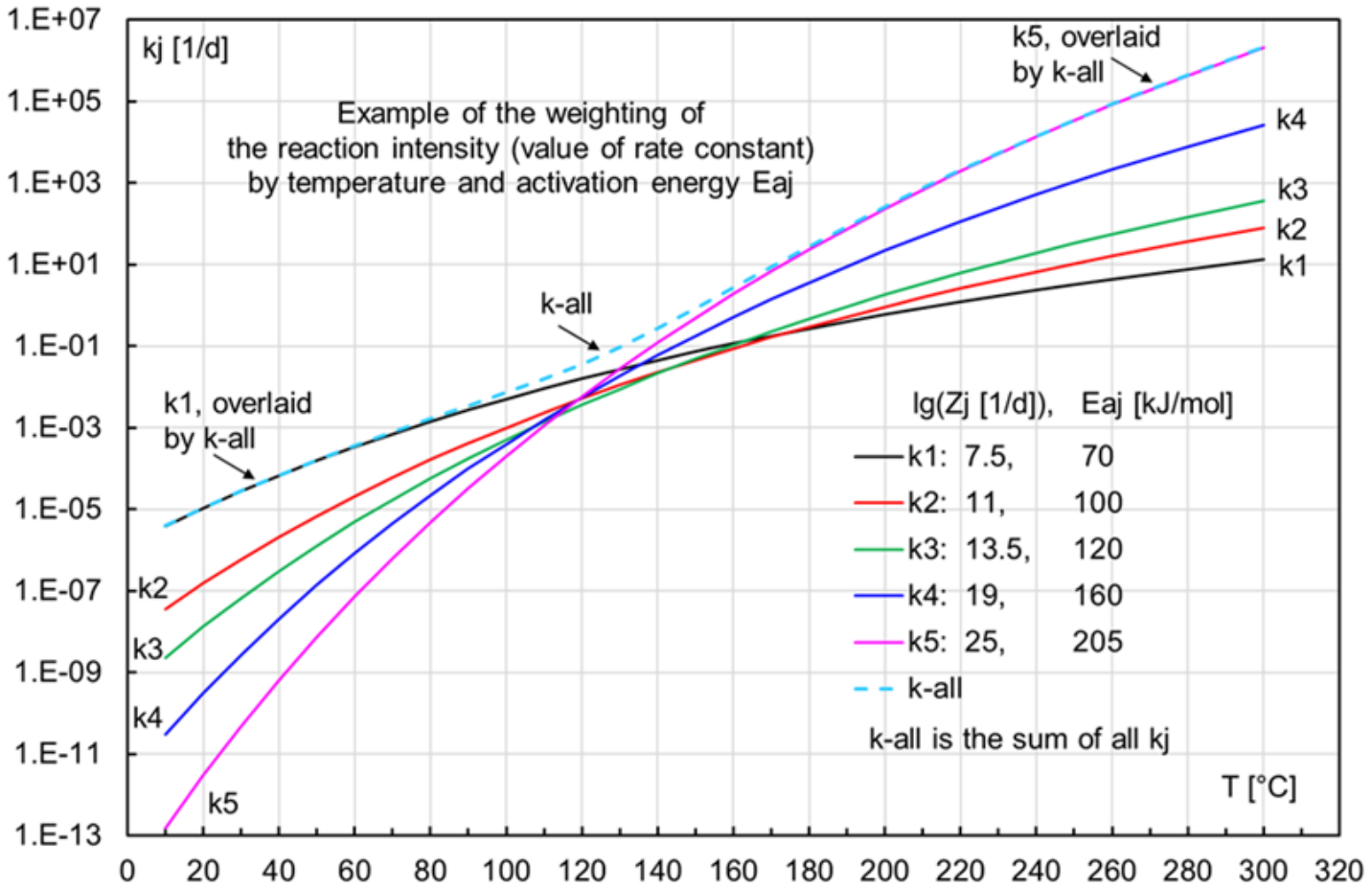
The weighting – temperature and Ea determined discrimination



The broken line in cyan is what is seen by typical summing-up analyses as with DSC, TGA, microcalorimetry.

The **weighting** with activation energy gives advantage for the reaction with **high Ea** at **higher temperatures**.

At **low temperatures** the reaction with **low Ea** is in advantage.

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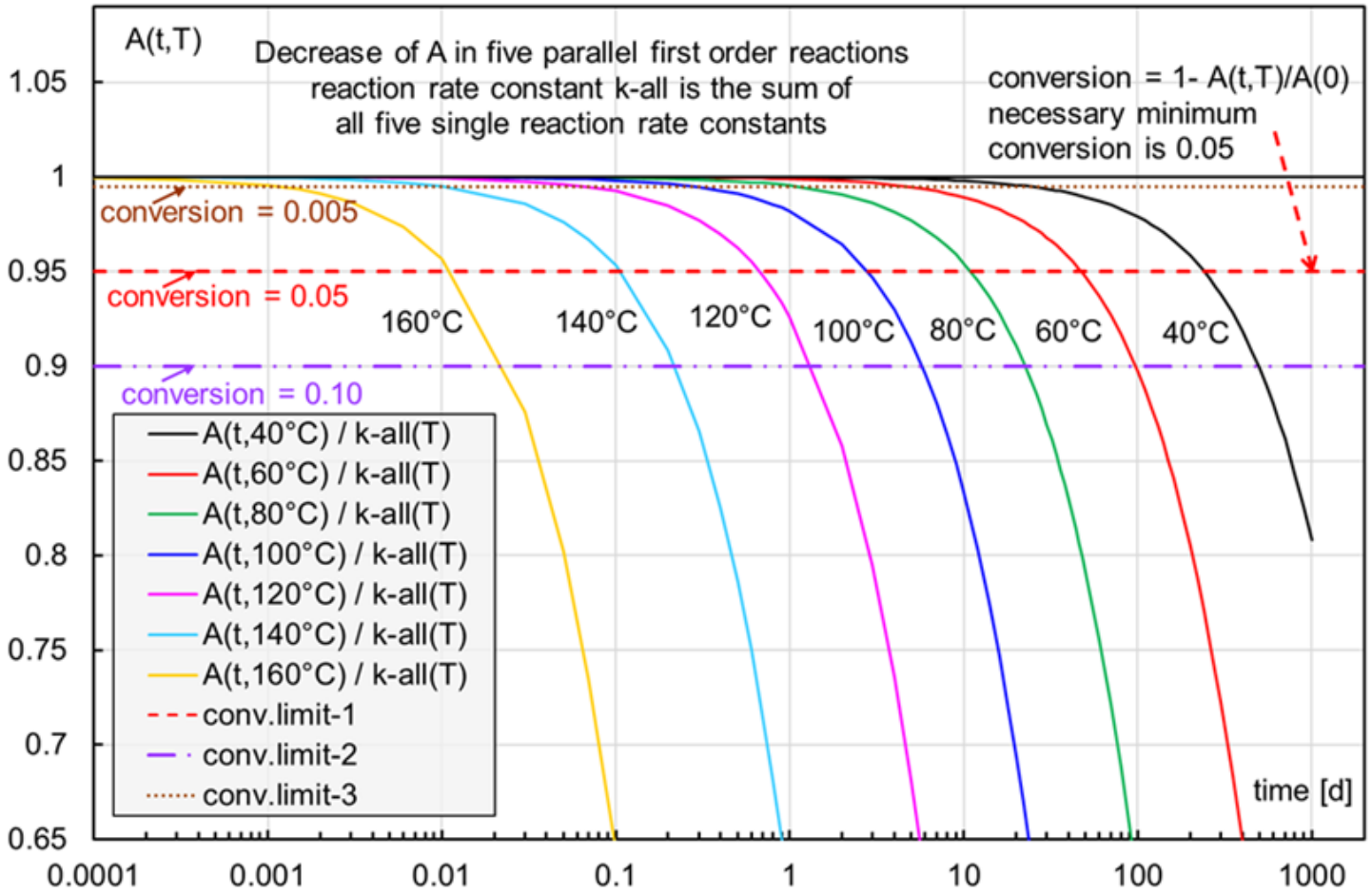
Times to reach certain levels of conversion

$$ty(T) = \frac{1}{k_j(T)} \cdot \ln\left(\frac{1}{y}\right) = \frac{1}{k_j(T)} \cdot \ln\left(\frac{A(0)}{A(ty(T))}\right)$$



To recognize the decomposition analytically with low error and in an amount to be handled with models, a **certain conversion** is necessary.

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Example – comparison of low and high temperature measured data

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Single base NC propellant P2N

Heat generation of a single base NC propellant with about 2 mass-% acardite II as stabilizer.

This propellant is used in so-called belt restraint systems in automotive cars.

Such propellants are called gas generants (GG).

They operate any device by formation of gas pressure.

The P2N was thoroughly investigated with:

- isothermal microcalorimetric measurements;
- non-isothermal DSC measurements.

The task is to make predictions of use-time.

Both data set results are compared.

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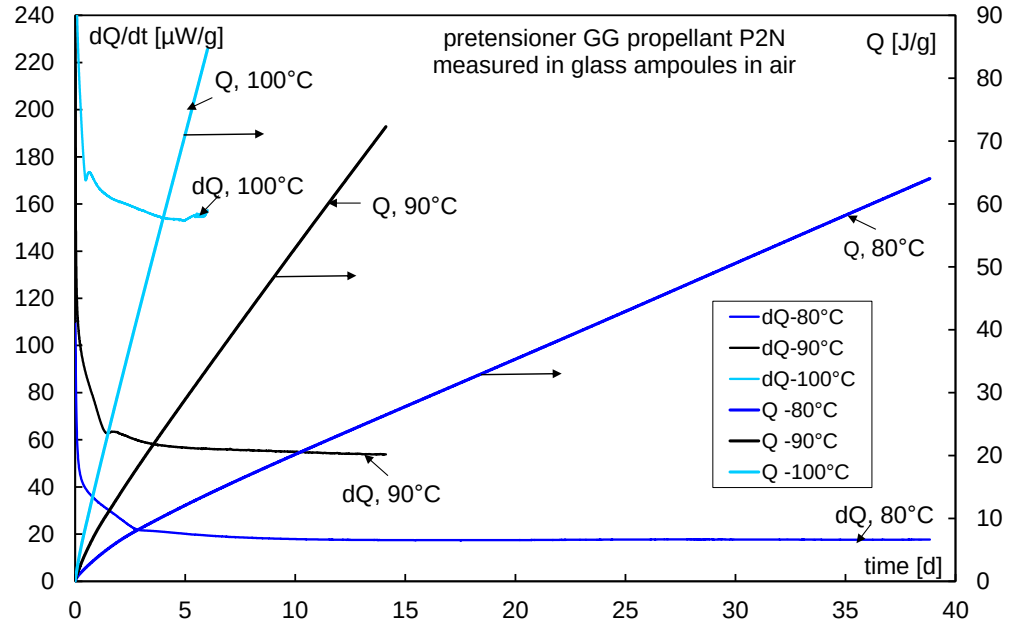
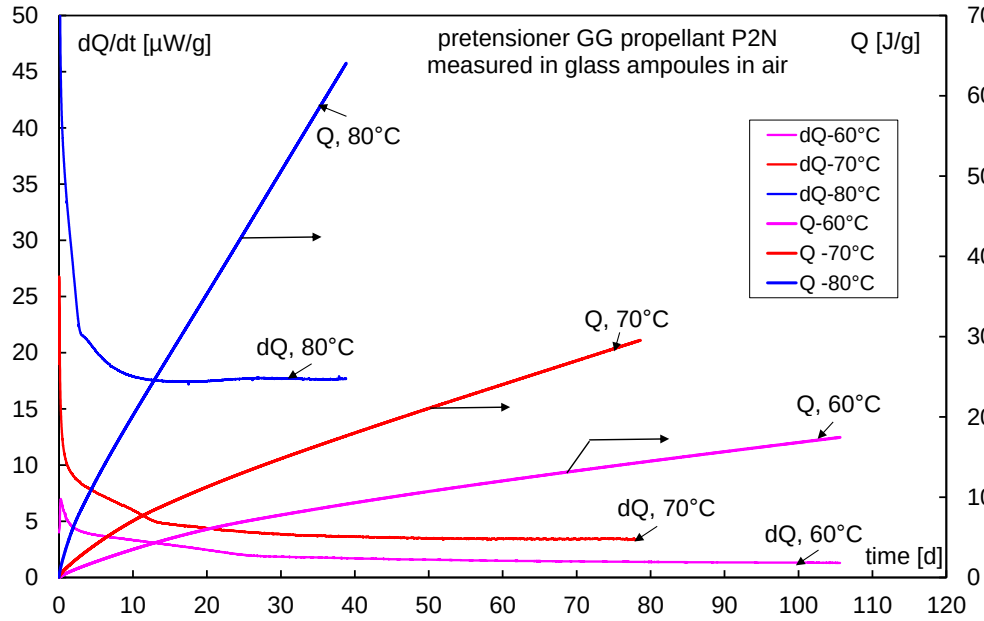
Measured data at lower isothermal temperature range by microcalorimetry



Heat generation rate HGR (dQ/dt) and heat generation HG (Q) of propellant P2N as function of time and temperature, 80°C, 90°C, 100°C.

Heat generation rate HGR (dQ/dt) and heat generation HG (Q) of propellant P2N as function of time and temperature, 60°C, 70°C, 80°C.



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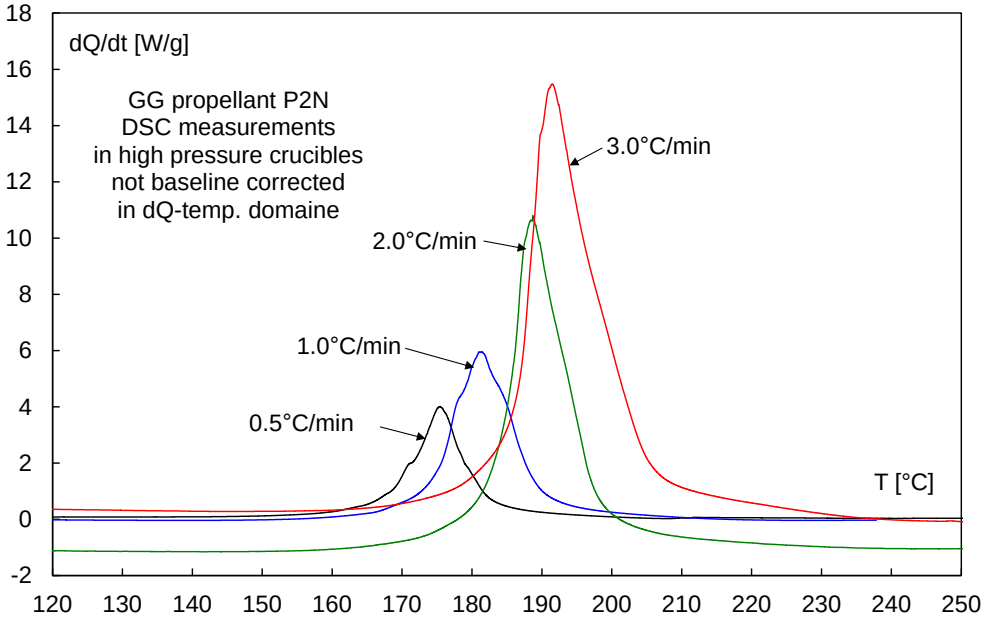
Measured data at higher non-isothermal temperature range by DSC



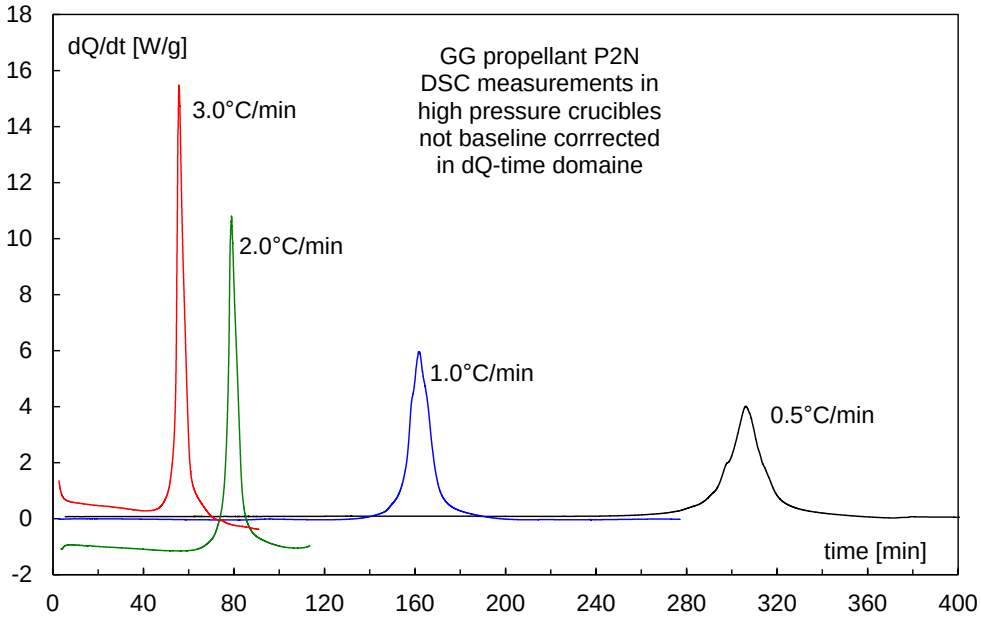
DSC-measurements on GG P2N in high-pressure stainless steel crucibles at constant heat rates.

Curves show a congruent shape and shift development to higher temperatures.

Curves not delimited and not base-line corrected.

Same DSC-thermograms as on the left but here as function of measurement times.

Note the quite low heat rates!
This is a necessary demand.



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Model for kinetic description of microcalorimetric data

$$Q(t,T) = Qe \cdot \left((1-a) \cdot k_0(T) \cdot t + a \cdot (1 - \exp(-k_V(T) \cdot t))\right)$$

model name 'Q: main: zero order + initial: first order'

Qe is the problematic quantity, because it is mostly not directly measurable.
Qe can be temperature range sensitive, means Qe = f(T).

Q	heat generation (HG) [J/g];
t	aging time;
T	aging temperature;
Qe	HG **after completion** of the decomposition reactions of the propellant at investigation temperature mostly used is Qex obtained by thermochemical calculation of decomposition; here Qe = 3712 J/g
a	partitioning factor between the two parts of the equation [-];
k_0	reaction rate constant of the zero order decomposition; $k_0(T) = Z_0 \exp(-Ea_0/RT)$; [1/time]
k_V	reaction rate constant of the initial part, $k_V(T) = Z_V \exp(-Ea_V/RT)$; [1/time], k_V is the reaction rate constant of a small part fast decomposing material;
Qa	= a Qe. Qa is the maximum value in HG of the initial decomposition.

$$\alpha(t,T) = (1-a) \cdot k_0(T) \cdot t + a \cdot (1 - \exp(-k_V(T) \cdot t))$$

α degree of conversion, α = Q/Qe.

Qe influences the time to reach a certain conversion
People tend to use to high Qe values

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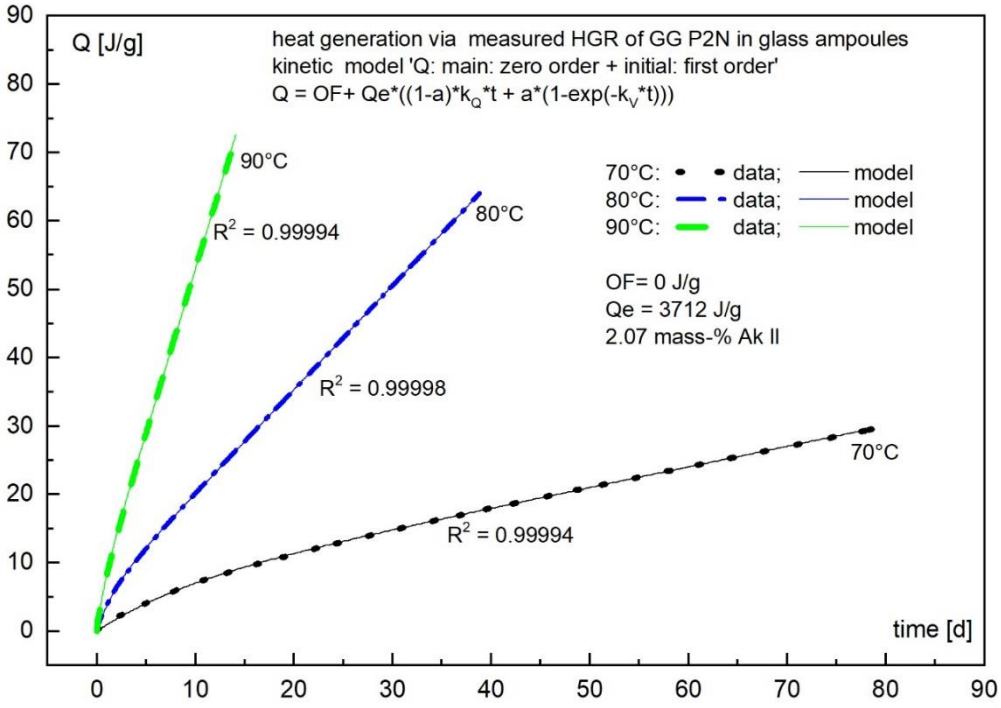
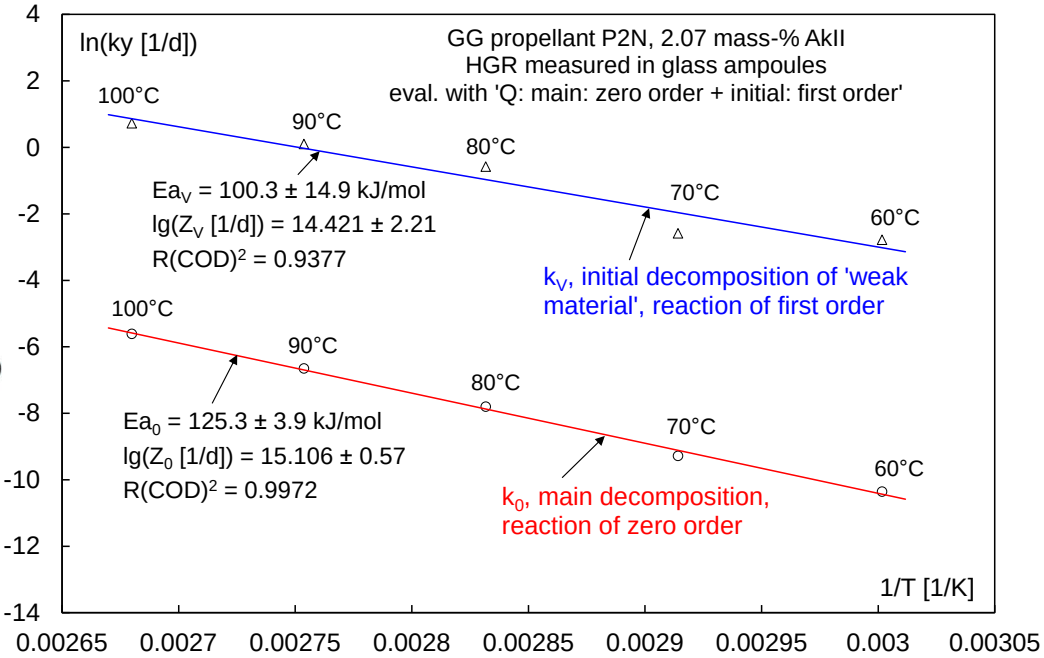
Kinetic description of microcalorimetric data – result 1



Combined kinetic modelling of initial (with k_V) and main linear part (with k_0) of heat generation at 70 to 90°C for GG propellant P2N. Broken lines indicate measured data.

Arrhenius plot of the temperature dependence of the two reaction rate constants of heat generation increase of GG propellant P2N, initial part (minor) and linear part (main).



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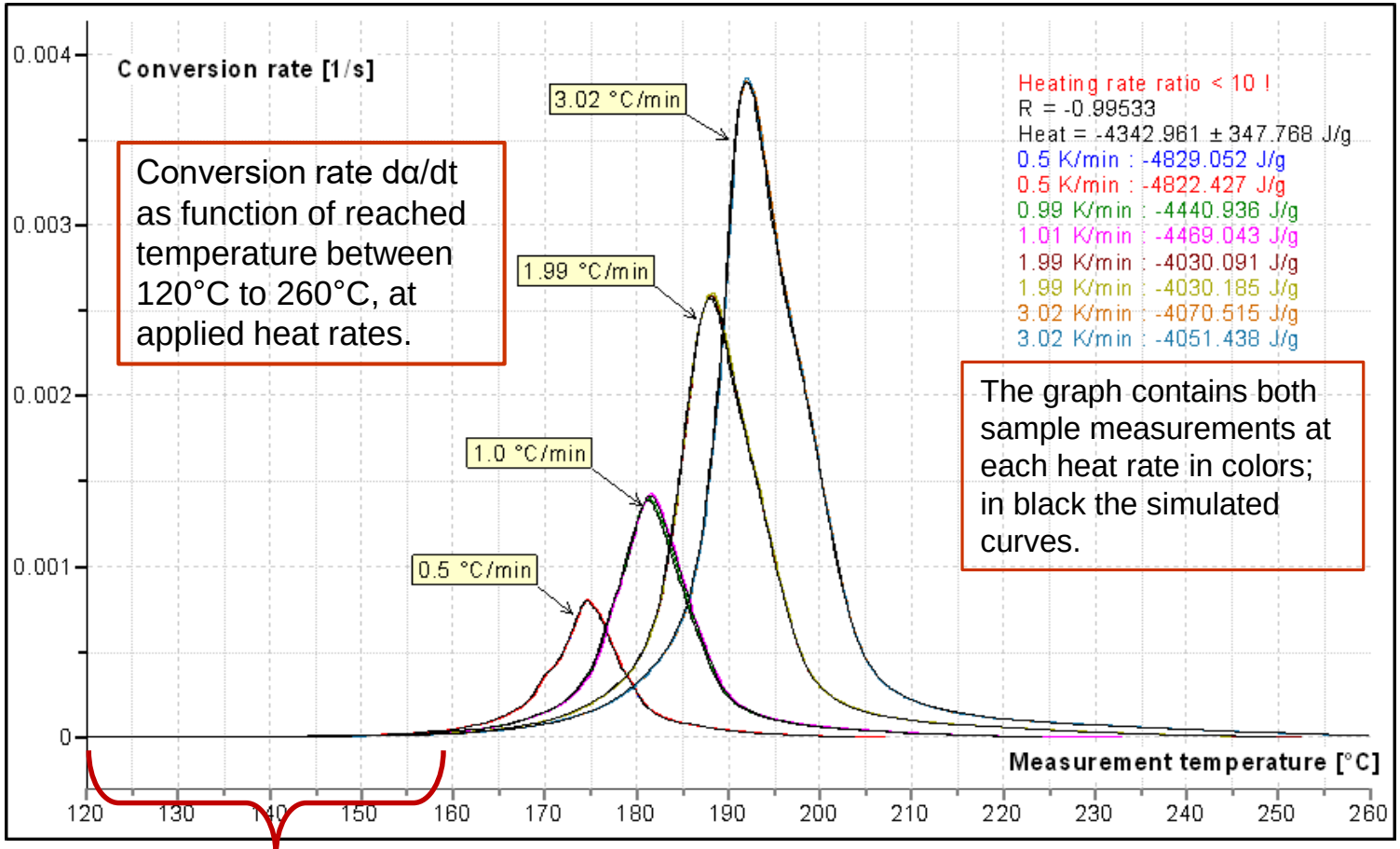
Evaluation of DSC data with Friedman-type analysis

Baseline corrected and delimited DSC HGR data (dQ/dt).

With scanning methods one covers the full temperature range, so we have full information of decomposition behaviour.

No ! **False conclusion**
There is not enough conversion at lower temperatures, means no information.



Conversion rate dα/dt as function of reached temperature between 120°C to 260°C, at applied heat rates.

The graph contains both sample measurements at each heat rate in colors; in black the simulated curves.

With the usual sample amount used in DSC the limited sensitivity of the instruments cannot detect any conversion below <120 to 150°C. Means no information on substance decomposition is obtained and any evaluation below these temperatures is a (popular) fallacy.

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Friedman analysis of non-isothermal data (also called model-free analysis)

Iso-conversional methods rely on the iso-conversional principle with two basic assumptions:

(1) the reaction rate (conversion rate) $d\alpha/dt$ at a chosen reaction progress (degree of conversion) α is only a function of temperature;

This assumes no phase changes in the considered temperature range and no mechanistic changes;

Means the reaction model f may not change in its basic characteristic.

(2) the temperature dependence at the iso-conversional state can be expressed by the Arrhenius equation.

Friedman method is a parametric method.
It is not a true kinetic evaluation of the data.

The iso-conversional procedure gives the two Arrhenius parameters at fixed conversions α, the activation energy $Ea(\alpha)$ and a composed pre-exponential factor $Z^*(\alpha)$.

Note: the reaction model $f(\alpha)$ is part of the composed pre-exponential factor Z^*, it is not deconvolutable.

$$\left(\frac{d\alpha(T(t))}{dt}\right)\Bigg|_{\alpha} = f(\alpha)\cdot k(\alpha,T(t)) \qquad = f(\alpha)\cdot Z(\alpha)\cdot \exp\left(-\frac{Ea(\alpha)}{R\cdot T(t)}\right) \qquad = Z^*(\alpha)\cdot \exp\left(-\frac{Ea(\alpha)}{R\cdot T(t)}\right)$$

Further problem: The kinetic expression (of all thermal analysis) considers only one formal reaction rate constant.

<u>Reduced iso-conversional method:</u>
Kissinger or Ozawa and related ones, all are also only para-metric methods

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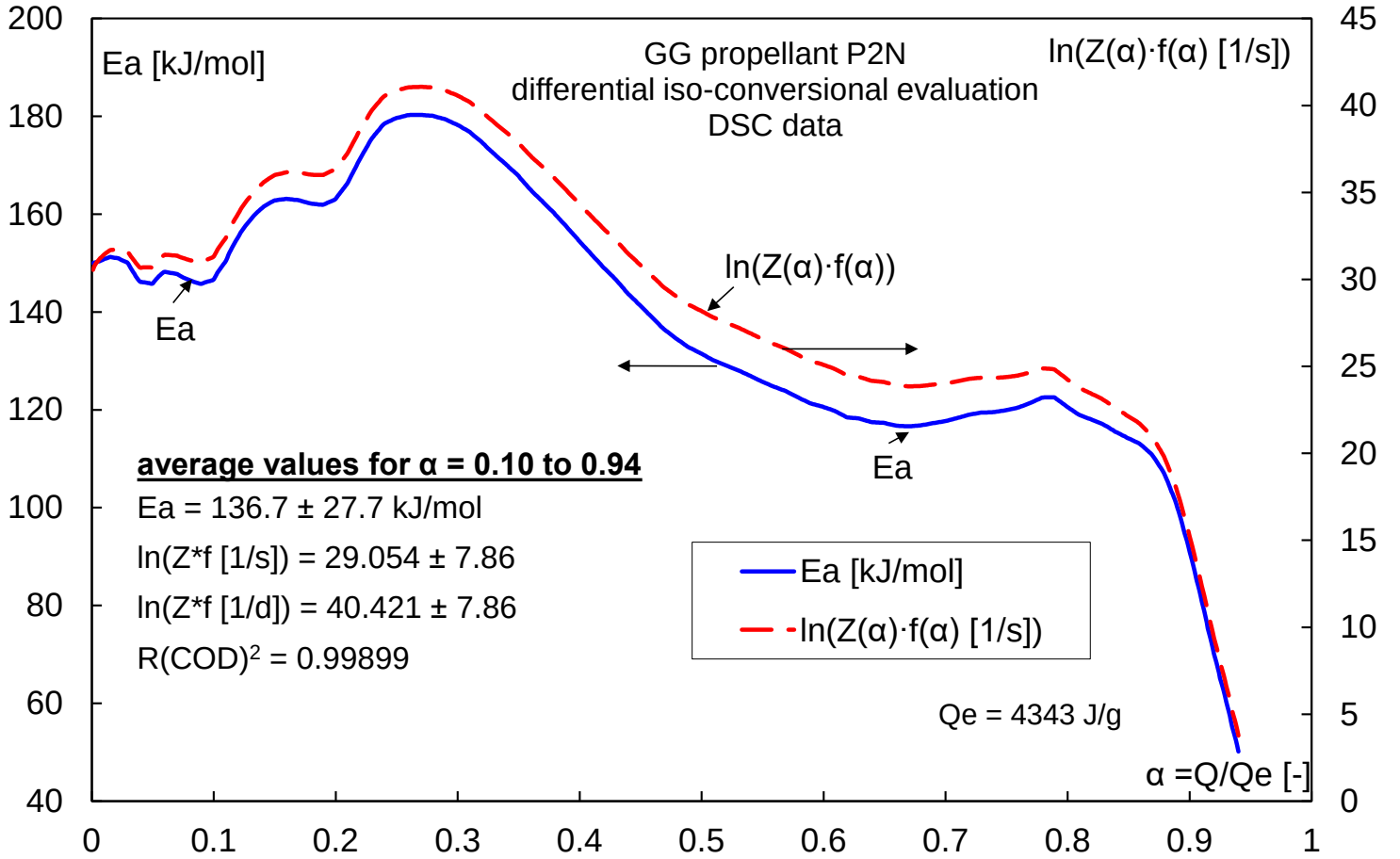
Result of Friedman evaluation – Arrhenius parameters as function of conversion

Result of Friedman evaluation (differential iso-conversional evaluation) of the DSC data of GG P2N.

Activation energy and pre-exponential factor are obtained as function of conversion.

The so-called reaction model f(α) is included in effective pre-factor.

The normalization quantity Qe is part of f(α). Qe is taken from the DSC data itself. - It can be to high in application cases.



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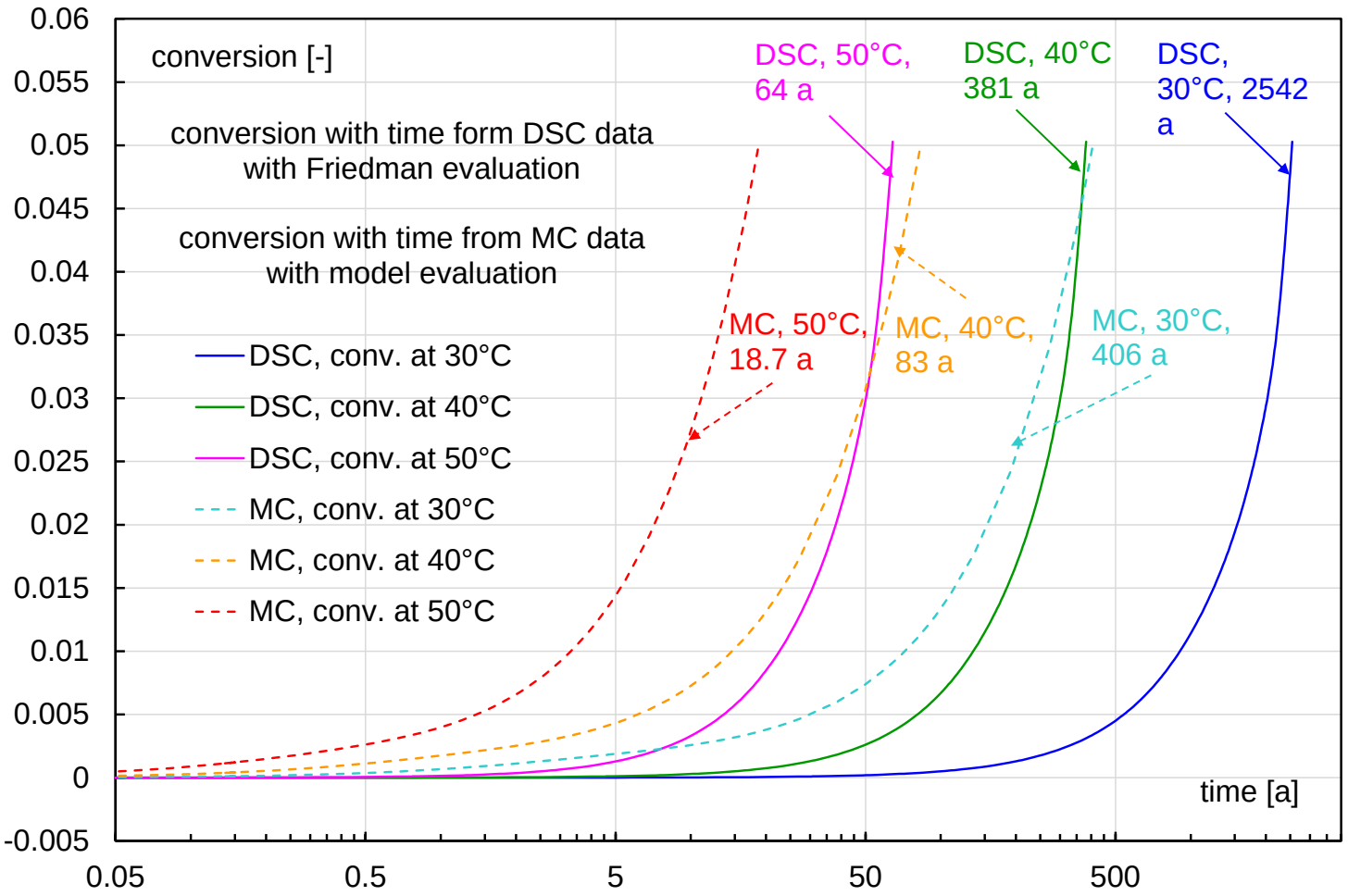
Comparison: microcalorimetric versus DSC data - times to chosen conversion

Times to conversion α = 0.05 of GG P2N at isothermal temperatures.

Comparison of data obtained with

> modelled microcalorimetric data (broken lines),

> Friedman evaluation of DSC data in the range 140 to 260°C (full lines).



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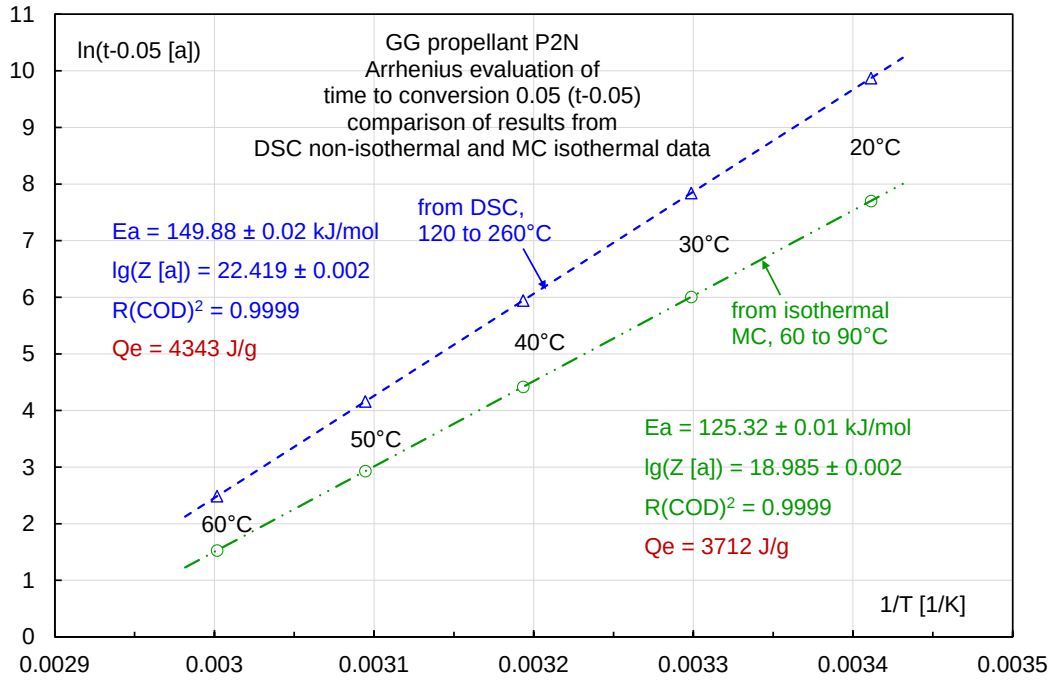
Arrhenius parameters



T [°C]	DSC t-0.05 [a]	MC t-0.05 [a]	Ratio
20	19336.1	2212.3	8.7
30	2542.1	405.8	6.3
40	380.58	82.96	4.6
50	64.11	18.71	3.4
60	12.022	4.61	2.6
70	2.486	1.235	2.0
Ea [kJ/mol]	149.9 ± 0.02	125.3 ± 0.01	1.19
lg(Z [a])	22.419 ± 0.002	18.985 ± 0.002	1.18
$R(COD)^2$	0.9999	0.9999	1
meas. T-range [°C]	120 – 260	60 – 90	-
eval. T-range [°C] for t-0.05	20 – 100	20 – 60	-
Qe [J/g]	4343	3712	1.17
T-course	non-isothermal	isothermal	-

Arrhenius plots of the times to reach α = 0.05 conversion of GG P2N. Comparison of results from DSC and microcalorimetric data, Qe values different.

Because of the different slopes of the Arrhenius lines they intersect here at 95 to 100°C, for Ak II stabilized propellant

Data from DSC are sensitive for reactions with higher activation energies, the extrapolation gives smaller reaction rates and in turn longer times.

Conclusion: with typical DSC data no reliable prediction can be made of use times at in-service temperatures of 20 to 60°C.

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Use of quantum chemistry

Calculation of transition states (TS) for the possible reactions
TS activation enthalpies ($\Delta H^{\ddagger}_{R}$) and TS free enthalpies ($\Delta G^{\ddagger}_{R}$)
molecular configuration of the transition state

Calculation of reaction enthalpies ΔH_R and reaction free enthalpies ΔG_R
also as function of temperature

Calculation of standard enthalpies of formation ΔH^0_f
(in part very calculation intensive)
eventually also as function of temperature, $\Delta H^0_f(T)$

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What are the pre-requisites at time to get more realistic results

Molecules in vacuum, as it was in former times, is not enough

Necessary: construction of realistic surroundings for the molecules under consideration

To use ‘fast’ basic methods, with good accuracy
DFT (electronic) **D**ensity **F**unctional **T**heory
In contrast to the very calculation intensive Hartree-Fock method

Realistic surroundings
> continuum with an averaged dielectric constant
dispersion interactions are possible
> specific environment built up by the same molecule as the target molecule
or solvent type surrounding with solvent molecules
dispersion and also polar interaction between target and environment

Fast computers in every aspect (clock rate, multi-kernel processors, fast memory chips,….)

Quantum chemical programs with extended possibilities **and**
from companies, which have competent and permanent developer crews **and**
will exist in future to get updates and bug-fixing

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QM-programs at ICT – Dmol^3 in Materials Studio

BIOVIA Materials Studio Version 2021, 2023

Developed by Accelrys Inc., San Diego, CA, USA

Now belonging to Dassault Systèmes SE, Velizy Villacoublay, France

It is a program system for QM and MM (molecular modelling)

QM-Part: is called Dmol^3

- Energy - performs a single-point energy calculation.
- Geometry Optimization - searches for a minimum energy structure.
- Dynamics - performs a molecular dynamics calculation.
- TS Search - search for TS by linear synchronous transit (LST), quadratic synchronous transit (QST).
- TS Optimization - searches for a transition state using eigenvector-following methods.
- TS Confirmation - produces a refined reaction path based on an LST or QST search.
- Reaction Kinetics - calculates rate coefficients for a reaction whose transition state is known.
- Minimum Energy Path - computes energy barriers and reaction pathways.

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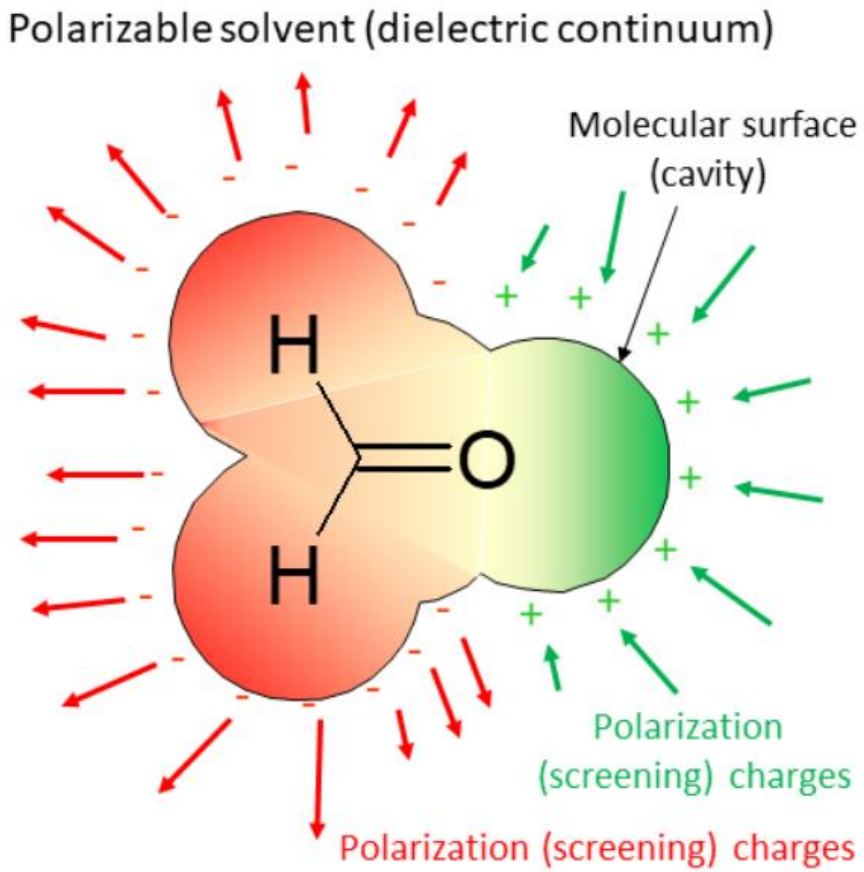
COSMO to consider a polarizable environment (in Dmol^3)



COSMO: COnductor-like Screening Model
It is a continuum solvation model (CSM)

Simplified interaction between target and dielectric surrounding;
The calculation extent is largely reduced by simplified boundary condition.
The induced charges in the 'solvent' are balancing the polarization by the target molecule.
No SCF calculation to calculate the 'exact' polar interaction.

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QM-programs at ICT – Gaussian G16W Revision C.01

Gaussian Inc.
Wallingford, CT 06492, USA

Gaussian 16 is the latest in the Gaussian series of programs
16 means 2016, it started with G70 in 1970

GaussView 6 is the latest graphical interface used with Gaussian

Possibilities with the Gaussian program are manifold

https://gaussian.com/g16main/

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PCM – methods, to consider the polarizable environment (in Gaussian)

PCM: polarizable continuum model
target molecule in the cavity of the continuum environment

Sounds at first similar to COSMO, but with PCM no conductor-like behavior to simplify the boundary condition

Gaussian uses the SCRF method to calculate the interaction between target and environment

SCRF: Self consistent reaction field

Calculations go forth and back between target and environment until the interaction energy has settled
Similar to SCF (self consistent field) for finding the ground state energy of a molecule

IEFPCM: integral equation formalism for PCM (IEF-PCM)

The continuum environment is characterized by a dielectric constant.

Water:	ε=78.3553
Acetonitrile:	ε=35.688
Methanol:	ε=32.613
Ethanol:	ε=24.852
IsoQuinoline:	ε=11.00
o-NitroToluene:	ε=25.669
Chloroform:	ε=4.7113

Also any DC can be set to simulate the surrounding

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Non-continuum environment: the ONIOM methods (Morokuma methods)

ONIOM: Our own **N**-layered **I**ntegrated molecular **O**rbital and molecular **M**echanics.

This method handles large molecules by defining two or three layers within the structure that are treated at different levels of accuracy.
means lower than the target area inside a large molecule
or the target molecule in a defined molecular environment

Keiji Morokuma developed the (extrapolative) ONIOM method around 1993 to 1995.
It integrates molecular orbital and molecular mechanics methods at several levels and can be used to calculate large molecules. (But before this idea already exists).

ONIOM calculations can use a Molecular Mechanics (MM) method for the system as a whole and an QM or Molecular Orbital (MO) one for the site of interest.

These are then MO:MM calculations or QM:MM

Alternatively, two ab initio methods can be combined; in this case, the calculation type is called MO:MO

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Non-continuum environment: the ONIOM methods (Morokuma methods)

ONIOM: Our own **N**-layered **I**ntegrated molecular **O**rbital and molecular **M**echanics.

Japanese Chemist; Fukui Institute for Fundamental Chemistry, Kyoto University; *1934 - †2017

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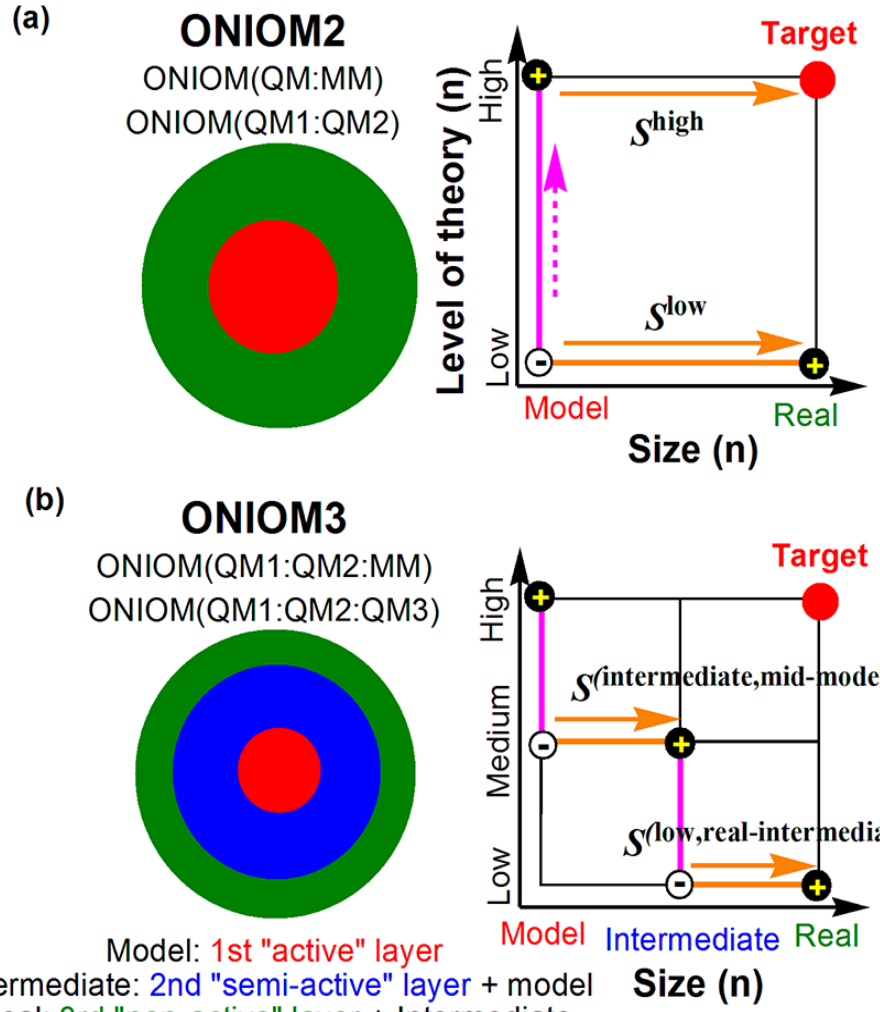
Illustration of ONIOM method



2 layers

model = target
real = the whole molecular arrangement
MM and QM2 are the 'cheap' methods
QM1 is the expensive (accurate) method

$$E_{ONIOM}(QM1:MM) = E_{QM1,model} + E_{MM,real} - E_{MM,model}.$$

$$E_{ONIOM}(QM1:QM2) = E_{QM1,model} + E_{QM2,real} - E_{QM2,model}.$$

3 layers

The ONIOM Method and Its Applications
Keiji Morokuma ua
Chemical Reviews 115 (**2015**), 5678−5796
DOI: 10.1021/cr5004419

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DFT (Electron Density Functional Theorem) - calculations

With DFT calculations one has to specify the so-called functional and the applied basis set

A functional is the system of equations to handle the connection between electron density distribution (this is what is searched for) in a molecule by using the positions of the electrons in the orbitals of the molecule

The basis set describes the orbitals in the molecule

We have used in the following:
functional: ‘ωB97X-D’ and the basis set: ‘aug-cc-pvtz’.

The ωB97X-D functional has improvements to the Becke 97 (B97) functional:

a long-range correction of electron interaction
an empirical Grimme type dispersion interaction

It provides low errors for the calculation of reaction enthalpies and noncovalent interactions.

Prof. Axel Dieter Becke, theoretical Chemist, born in Germany, now in Halifax, Dalhousie Univ., Canada

Prof. Stefan Grimme, theoretical Chemist, University of Bonn, Germany

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Basis set

The basis set describes the orbitals in the molecule

aug-cc-pvtz: augmented correlation consistent polarized valence triple zeta

augmented: addition of diffuse functions to better describe weakly interacting molecules
valence: t he outer orbitals are described
triple zeta: three basis sets for each atomic orbital (AO)

The aug-cc-pvtz basis set is a large basis set with

23 basis functions (4 s-type, 3 x 3 p-type and 2 x 5 d-type basis functions)
for every hydrogen atom

and

46 basis functions (5 s-type, 4 x 3 p-type, 3 x 5 d-type and 2 x 7 f-type basis functions)
for every C, N and O atom.

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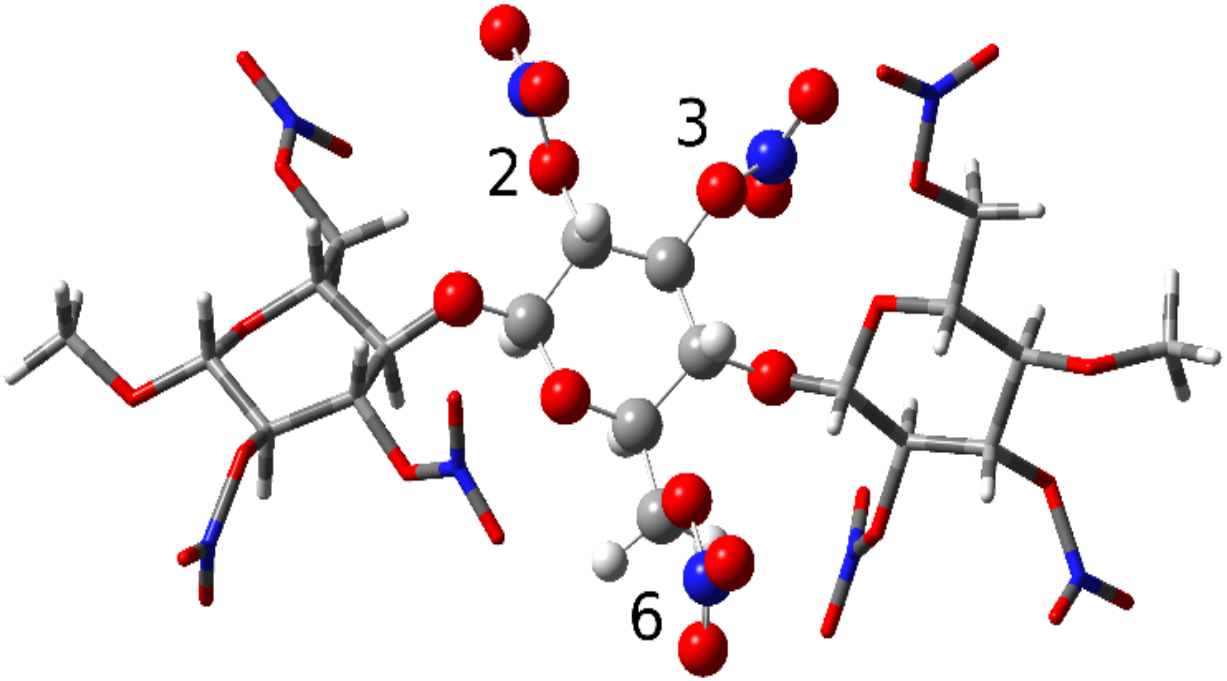
ONIOM - application with nitrocellulose



The O-NO_2 positions on the central ring are indicated as 2, 3 and 6.

Color code: oxygen in red, nitrogen in blue, carbon in gray and hydrogen in white.

Geometry optimized minimum structure of the NC trimer in ONIOM configuration and in IEFPCM solvation.
The central ring (ball-and-stick representation) is computed with ωB97X-D / aug-cc-pvtz, the outer rings (tube type representation) are treated with BLYP / 6-31++G(d,p).

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Bond dissociation in NC and NG (nitroglycerin) - homolytic CO-NO_2 bond cleavage

Computed O-NO_2 bond dissociation enthalpies and bond dissociation Gibbs free energies for relaxed (geometry optimized) and unrelaxed (geometry fixed after bond split) alkoxy radicals in kJ/mol **at 80ºC** computed with the ONIOM trimer.
Calculation with IEFPCM: NC trimer in NC-continuum,
NG in NG-continuum and NG in NC-continuum.

all in kJ/mol	After NO_2 split-off, the alkoxy radicals are			
	unrelaxed		relaxed	
NC in NC, ε_r = 7.0				
Position	$\Delta_{bond}H$	$\Delta_{bond}G$	$\Delta_{bond}H$	$\Delta_{bond}G$
2	161.7	123.1	150.2	87.6
3	164.9	115.0	157.8	96.3
6	160.7	107.1	153.9	87.2
NG in NG, ε_r = 19.3				
1, 3	-	-	164.0	90.5
2	-	-	158.7	83.6
NG in NC, ε_r = 7.0				
1, 3	-	-	164.0	91.8
2	-	-	159.0	86.3

thermally induced homolytic split of the relatively weak RO-NO_2 bond, thereby producing two radicals:

$R{-}O{-}NO_2 \rightarrow R{-}O^{\bullet} + {}^{\bullet}NO_2$

Bond splitting is endothermal (positive ΔH_{bR}) and endergonic (positive ΔG_{bR})

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Bond dissociation in NC - elimination of nitrous acid

Instead of the formation of NO_2 it is stated that nitrous acid, HNO_2, can be produced directly:

$$RH{-}O{-}NO_2 \rightarrow TS \rightarrow R{=}O + HNO_2$$

This reaction is a type of monomolecular elimination and involves a five membered transition state (TS) and leaves behind an aldehyde or a ketone group

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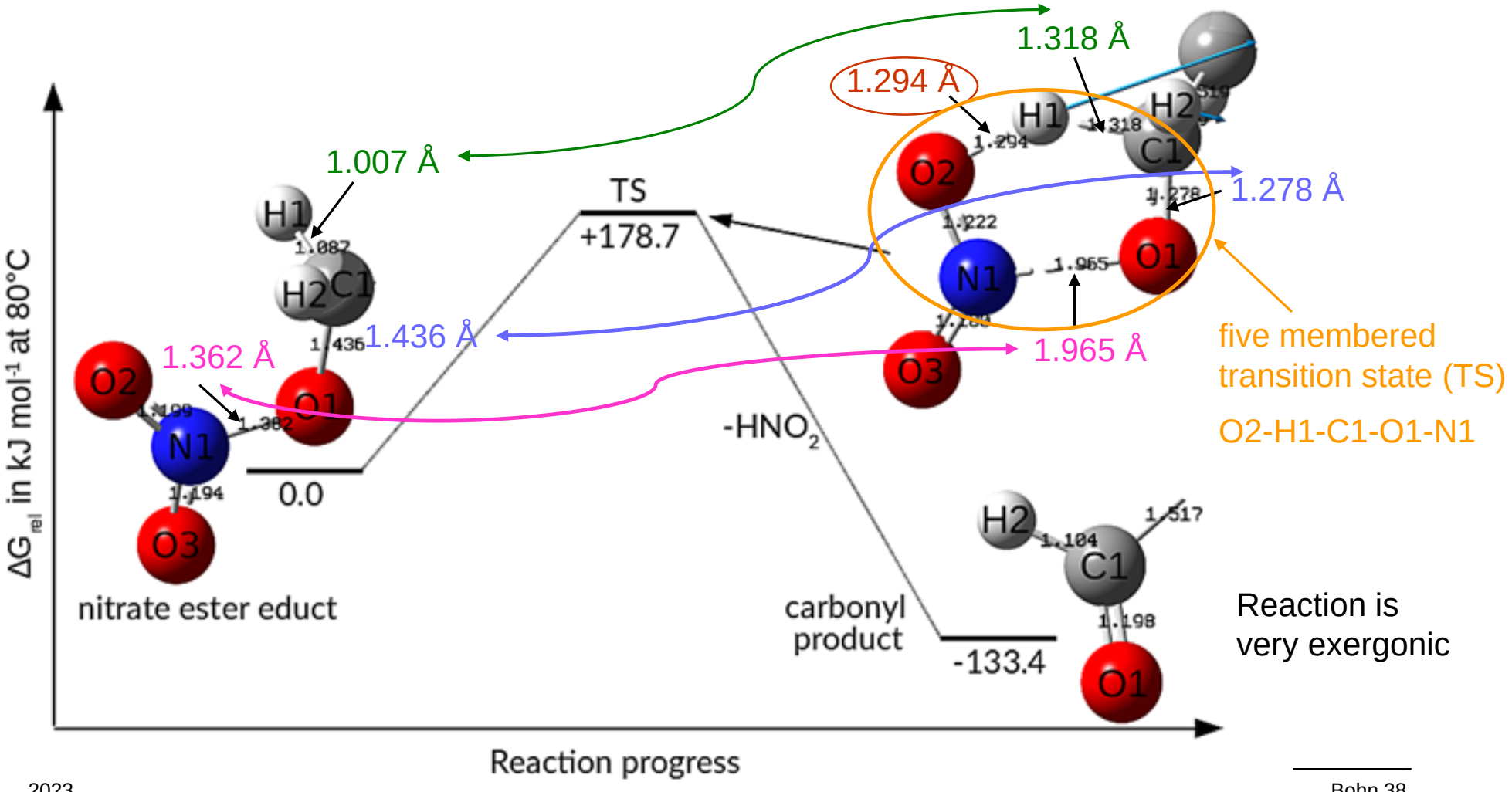
Elimination of HONO from RH-O-NO_2 via transition state (TS)

Educt, TS and product are shown. The ordinate is the Gibbs free energy at 80°C relative to the educt



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Bond dissociation in NC - elimination of nitrous acid - results

Computed TS activation and reaction enthalpies and Gibbs free energies for HNO_2 elimination in kJ/mol at 80°C computed with the ONIOM trimer. NC in NC, ε_r = 7.0. Always relaxed species.

all in kJ/mol	TS		Products	
Position	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	ΔH_R	ΔG_R
2	177.9	173.8	-77.5	-145.3
3	181.9	186.9	-93.7	-158.6
6	183.7	178.7	-69.5	-133.4

all in kJ/mol	NO_2 split-off	
Position	$\Delta_{bond}H$	$\Delta_{bond}G$
2	150.2	87.6
3	157.8	96.3
6	153.9	87.2

Formation of HNO_2 is irreversible, it should be captured quickly before converted into HNO_3

Formation of $^{\bullet}NO_2$ is reversible, eventually HNO_2 is formed by $^{\bullet}H$ abstraction leaving radical function on ring, and it starts decomposition

Formation of NNO-DPA	ΔH_R	ΔG_R
DPA + $^{\bullet}NO_2$ + $^{\bullet}NO$ ⟶ ON-N-DPA + HNO_2	-87.3	-27.8
DPA + HNO_2 ⟶ ON-N-DPA + H_2O	-50.8	-43.1

This reaction is in favour because of ΔG_R it is more exergonic.

Is N-NO formation a helpful reaction in stabilizing NC ?

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Future objectives

Simulation of heat generation and heat generation rates of NC-based gun propellants

Screening of the efficiency of stabilizer action

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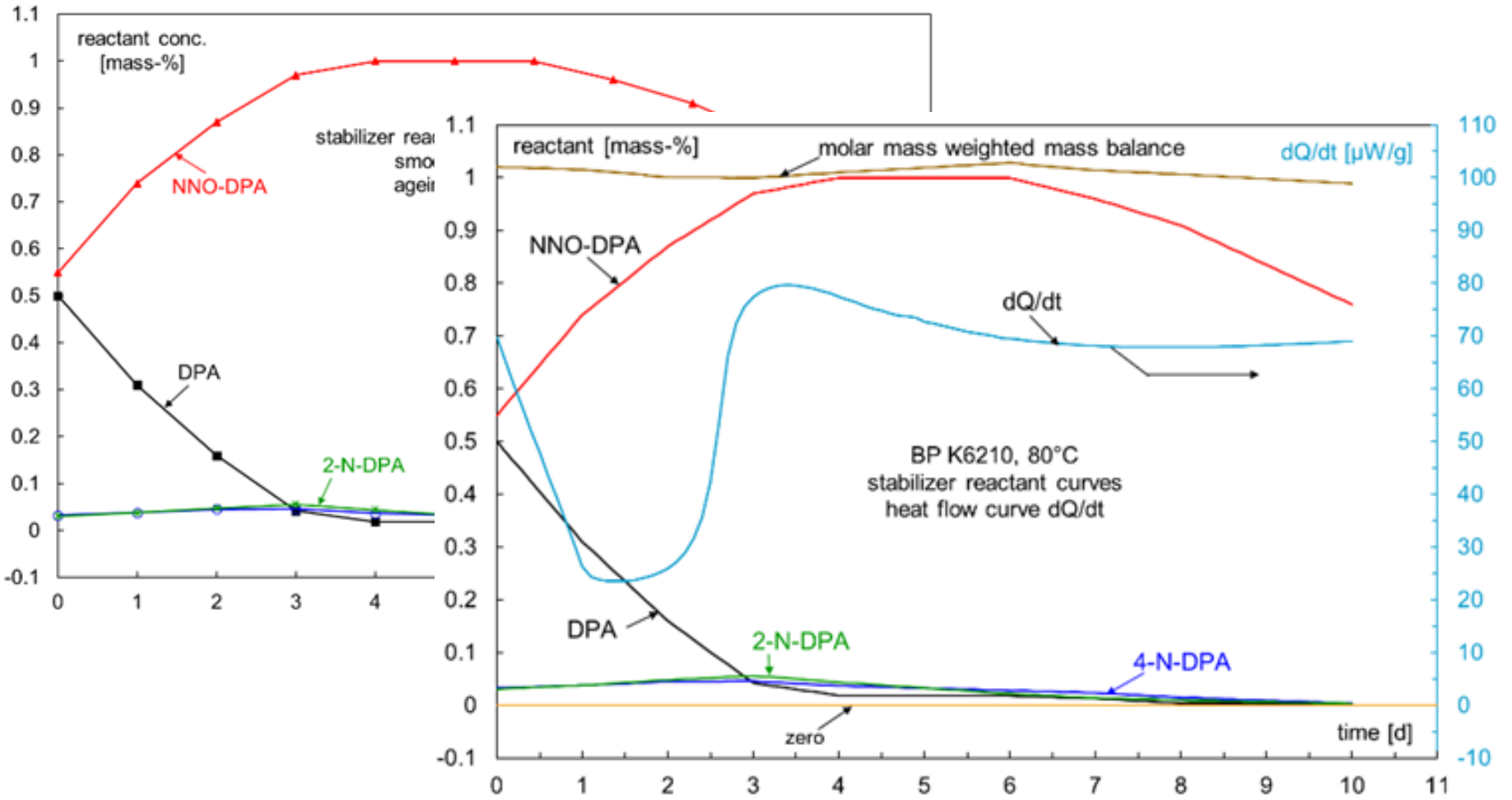
Stabilizer reactions and the heat balance of their action



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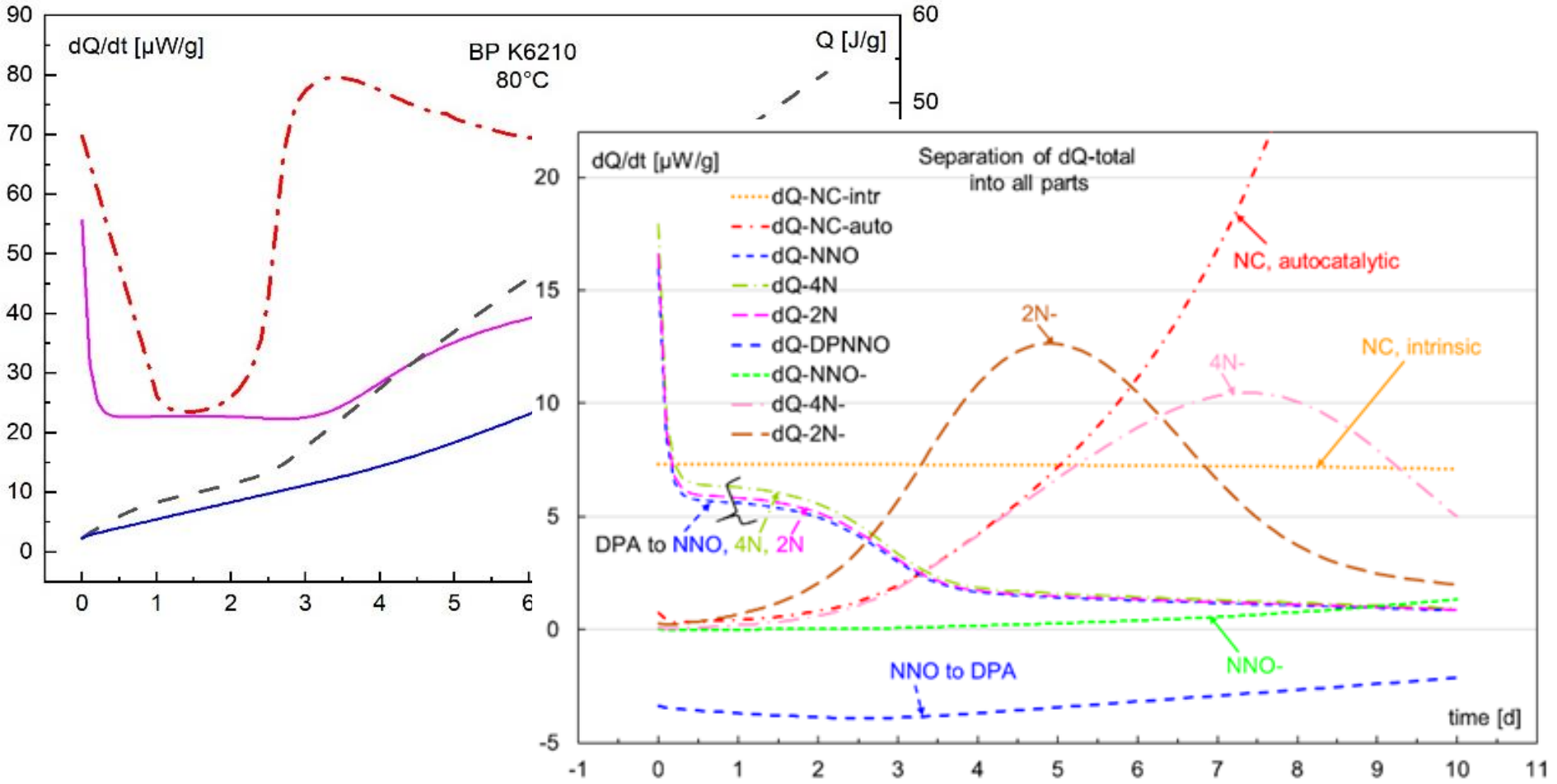
Simulation of heat flow curve of ball powder K6210



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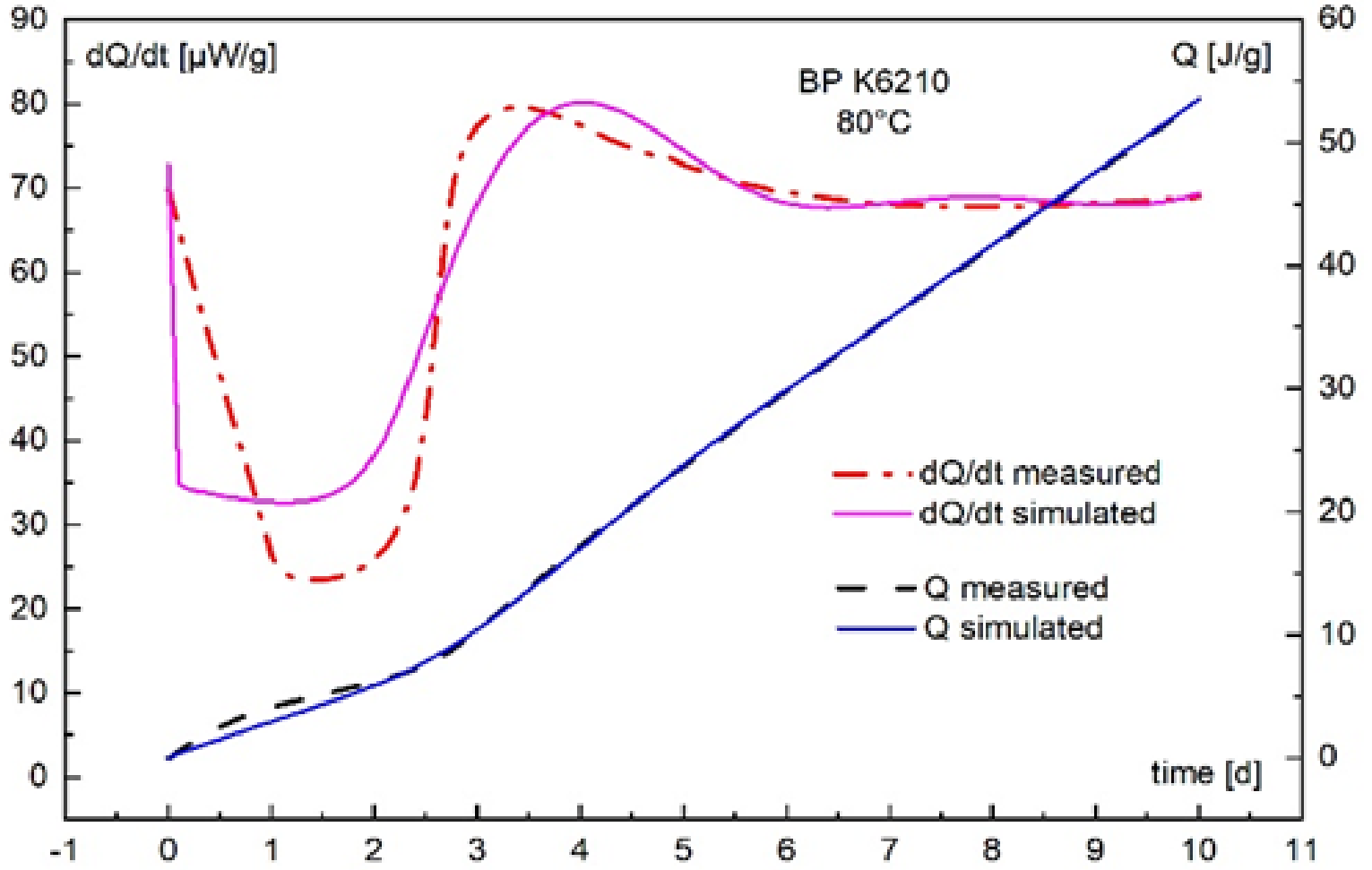
Improved simulation of the heat flow curve of BP 6210



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Conclusions – messages to be taken with you

Experimental

Distinguish ìn terms between

high temperature measurements with DSC and TGA (120 to 350°C)
thermal analysis methods

low temperature measurements as with microcalorimeters (60 to 100°C) and mass loss
chemical stability methods

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Conclusions – messages to be taken with you (cont'd)

Experimental

Keep in mind

the weighting of the reaction rates with temperature (increase with increasing temperature) and
with the activation energies

the larger the activation energy the higher the weight of the corresponding reaction with increasing temperature

At low temperatures reactions with small activation energies dominate

At high temperatures reactions with large activation energies dominate

Extrapolations with high temperature measurements to in-service temperatures (20 to 50°C) result in **massively wrong** assessments

To assess high temperature phenomena as cook-off, high temperature data are useful and even necessary

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Conclusions – messages to be taken with you (cont'd)

NC is already well investigated.

What we need more?

The detailed decomposition mechanism are not in full known.

Help to get more knowledge is now provided by quantum chemical calculations

Define possible reaction and test them with transition state methods.

Determine the TS data $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ as well as reaction parameters ΔH_R and ΔG_R

Calculate bond dissociation enthalpies $\Delta_{bond}H$ and bond dissoc. free energies $\Delta_{bond}G$

What computational methods should be chosen:

DFT method
with good functionals to define the possible electron density distribution in the molecule and relatively large basis sets to describe the orbitals including influences by neighboring atoms: dispersion effects and distortion of the orbitals.

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Conclusions – messages to be taken with you (cont'd)

Calculation of bond dissociation <u>enthalpies</u> $\Delta_{bond}H$ and bond dissoc. free energies $\Delta_{bond}G$

Not just bond energies or bond dissociation energies

What computational methods should be chosen:

DFT method
with good functionals to define the possible electron density distribution in the molecule
and
relatively large basis sets to describe the orbitals, including influences by neighboring atoms:
dispersion effects and distortion of the orbitals.

Use non-vacuum environment for the target molecule:

- first step could be the COSMO technique, has relatively small computational costs.
- Better methods are PCM methods in SCRF treatment
- Best would be ONIOM techniques (Morokuma methods),
  building realistic environment for the target molecule

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The end

Thank you for your attention

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