Characterization of the ageing of HTPB bonded HMX based insensitive high explosive charge

by Heat Flow Microcalorimetry (HFC), Chemiluminescence, Gap test and Dynamic Mechanical Analysis (DMA)

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Fraunhofer Institut Chemische Technologie

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Chemiluminescence in air between 100°C and 140°C

Summary and conclusions

What is HEC of type KS 32

KS32 is a polymer bonded high explosive charge (HEC),
manufactured by EADS-TDW, Schrobenhausen, Bayern, Germany (now part of MBDA)

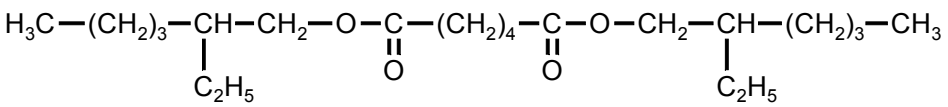
Typical composition

Energetic material	HMX	85.0 mass-%
Binder	HTPB cured with IPDI	13.7 mass-%
Plasticizer	DOA	1.0 mass-%
Antioxidant	protected phenol type	0.1 mass-%
Curing catalyst	DBTL	0.001 mass-%
Additionals		0.199 mass-%

HTPB hydroxy terminated polybutadiene

IPDI ísophorone diisocyanate

DOA di-(iso-octyl) adipate (DiOA)



DBTL di-(n-butyl) tin dilaureate (DnBTDL) $(CH_3CH_2CH_2CH_2)_2\ Sn\ [OCO(CH_2)_{10}CH_3]_2$

Objectives

- To age the material accelerated up to the equivalent loads with regard to in-service loads
- To age at the two extremes
  under air and under oxygen-free atmosphere (here under argon)
- To get information about the Arrhenius parameters valid at accelerated and in-service temperatures.
  The minus centigrade region was not included because the chemical and diffusion processes are very slow there and are expected of minor to no influence.
- To look at some properties if they can be used as ageing monitor

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Basic stability data of HEC of type KS32

Autoignition temperature determined in Wood metal bath

5°C/min heat rate	244°C
20°C/min heat rate	243°C

Holland Mass Loss test at 110°C

0-8 h	0.02 %
0-72 h	0.01 %
8-72 h	-0.01 % (limit value: 2 %)

Vacuum Stability Test, 100°C, 40h

2.5g	0.03 ml/g (limit value: 1.2 ml/g)

Time-temperature or ageing program for KS 32

Accelerated ageing at thermal equivalent loads

The best way to perform accelerated ageing on a material for prediction purpose is to do it in such a way that the thermal load at in-service will be covered.

This is named equivalent load ageing.

The equivalent load must be calculated from given or demanded in-service loads for the test conditions at elevated temperatures.
The in-service loads can be assumes as isothermal over a set usetime as 20 years or stored at time-temperature profile as experienced during missions

For this one needs a temperature parameterization of properties of the material

What to do if you do not known them at the beginning?

Recommended procedure

Assume a ageing at low activation energies in a two step mechanism.

Such a two-step mechanistic ageing can be simulated quite reasonably with the generalized van'T Hoff rule

Equivalent load relation between ‘test time - test temperature’ and ‘in-service time - in-service temperature

For chemically caused ageing processes the following formula has proven by experience as suitable (Ea about 80 to 120 kJ/mol, temperature range 30°C to 90°C)

Generalized formulated van’T Hoff rule

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

- t_E time in years at temperature T_E
- t_T test time in days at test temperature T_T
- F reaction rate change factor per 10°C temperature change
  rate decreases with temp. decrease / rate increases with temp. Increase
- T_T test temperature in °C
- T_E in-service (environmental) temperature in °C
- ΔT_F temperature interval for actual value of F, here ΔT_F is always 10°C

For details and worked out examples with two mechanisms see
Manfred A. Bohn
Prediction of equivalent time-temperature loads for accelerated ageing to simulate preset in-storage ageing and time-temperature profile loads.
Paper 78, 40th Conference of ICT, 2009.

Ageing scheme for KS32

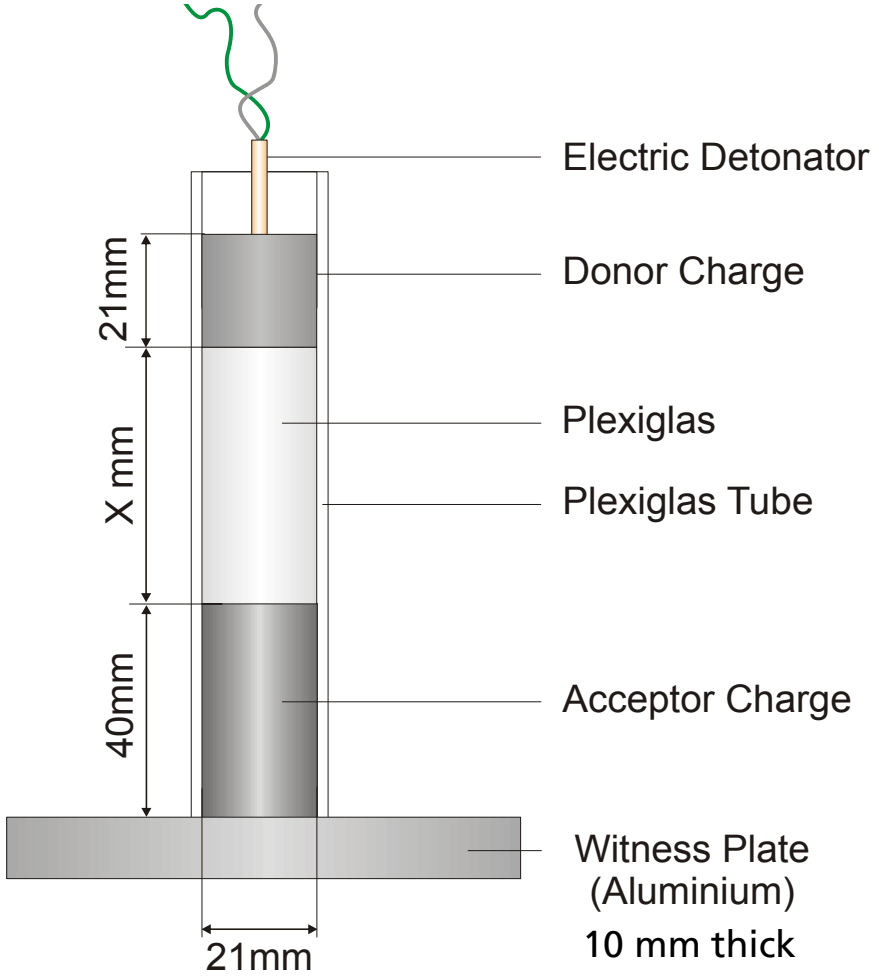
one month: 365/12 = 30.4 days; ageing equivalent of 20 years at 25°C is 24.3 months at 50°C

years at 25°C ->		5	10	15	20	25	30	35
ageing temp. [°C]								
40	in days	462	924	1386	1848	2310	2772	3234
	in mo	15.2	30.4	45.6	60.8	76.0	91.2	106.4
50	in days	185	370	554	739	924	1109	1294
	in mo	6.1	12.2	18.2	24.3	30.4	36.5	42.6
60	in days	74	148	222	296	370	444	518
	in mo	2.4	4.9	7.3	9.7	12.2	14.6	17.0
70	in days	30	59	89	118	148	177	207
	in mo		1.9	2.9	3.9	4.9	5.8	6.8
80	in days	12	24	36	47	59	71	83
	in mo			1.2	1.5	1.9	2.3	2.7
90	in days	4.7	9.5	14	19	24	28	33

The factor of 2.5 is assumed for KS32, this gives a conservative estimate of storage times to reach preset ageing times at 25°C; means longer storage times than with factor 3.

Test on sensitiveness by gap-test

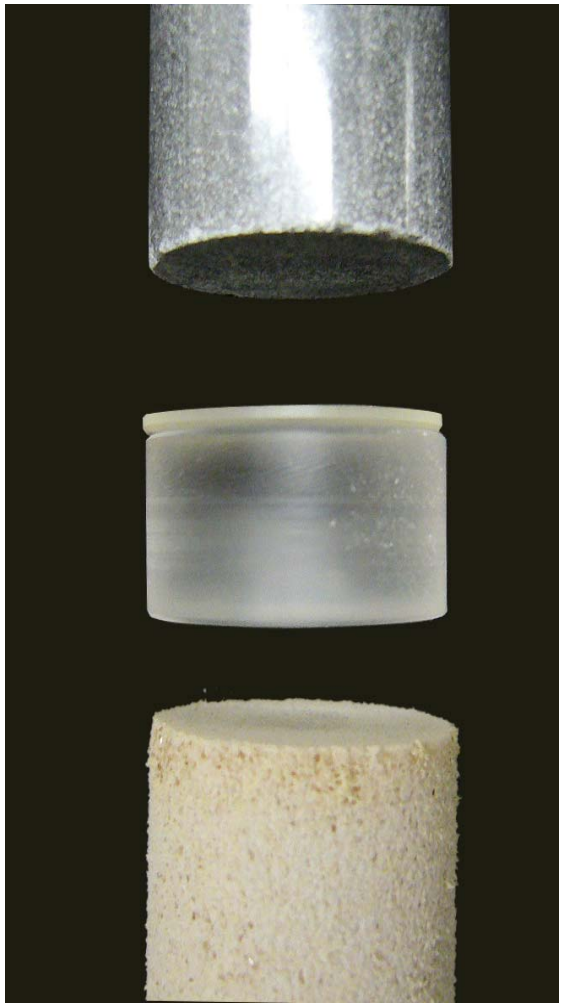
Scheme of ICT-Gap-test, 21mm



Donor with one booster
HX charge:
diam. 21 mm, length 21 mm
RDX / wax / graphite (94.5 % / 4.5 % / 1 %)
pressing force 50 kN
detonator in central bore: T-CU-30-T11U

Actual length of KS32 samples were 42 mm

Assembly of charges in 21 mm ICT-gap-test



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Ageing of gap-test samples

Left:

Ageing in air.

Full air access by removing of the not sealed stopper two to three times per week.

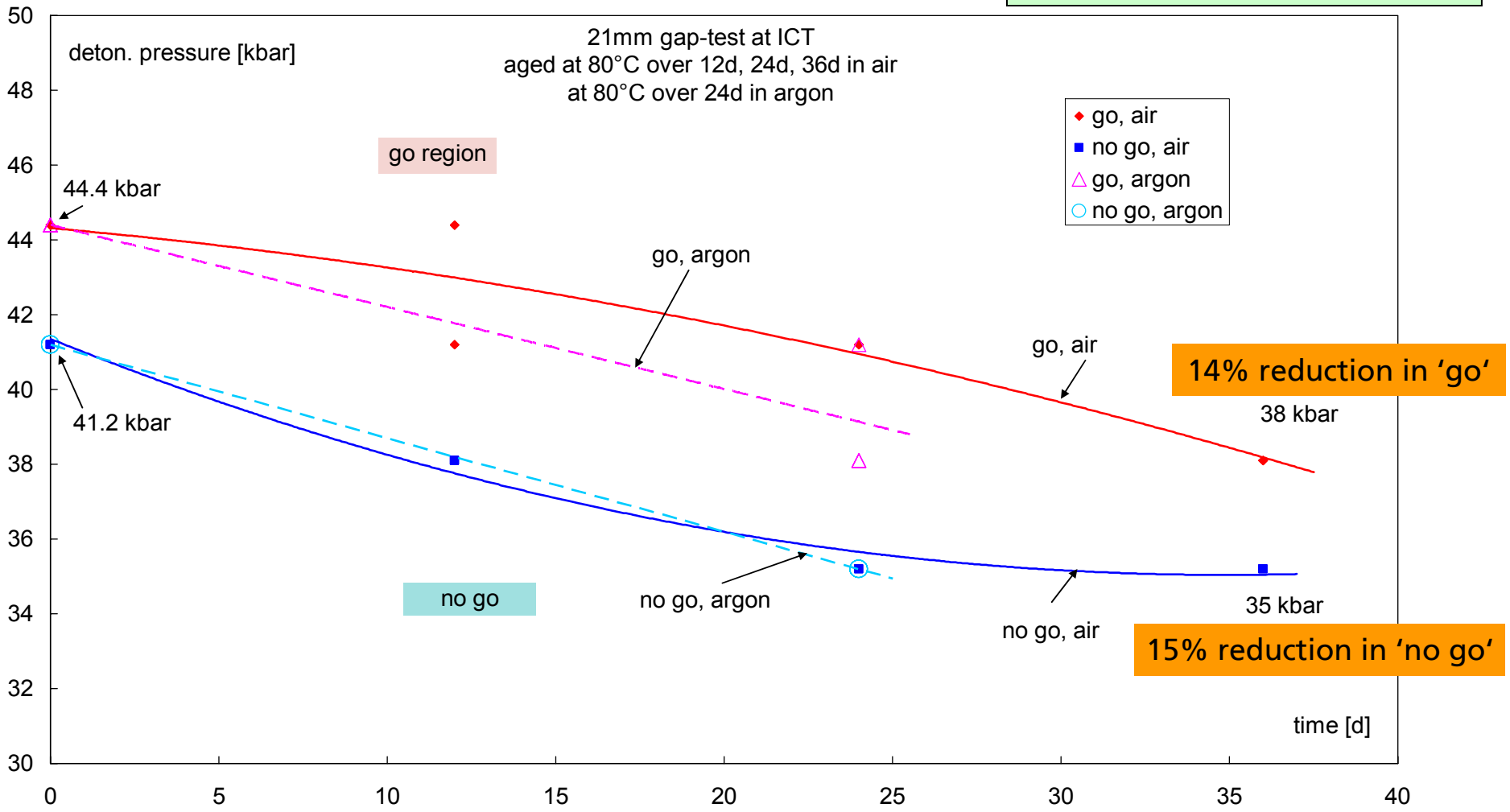
Right:

Ageing in argon, applied with a glove box.

Full sealing (grease in ground surfaces) and securing the stopper.

Results of 21mm gap-test in detonation pressure

36 days at 80°C correspond to 15 years at 25°C



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Glass transition temperature determined by torsion DMA

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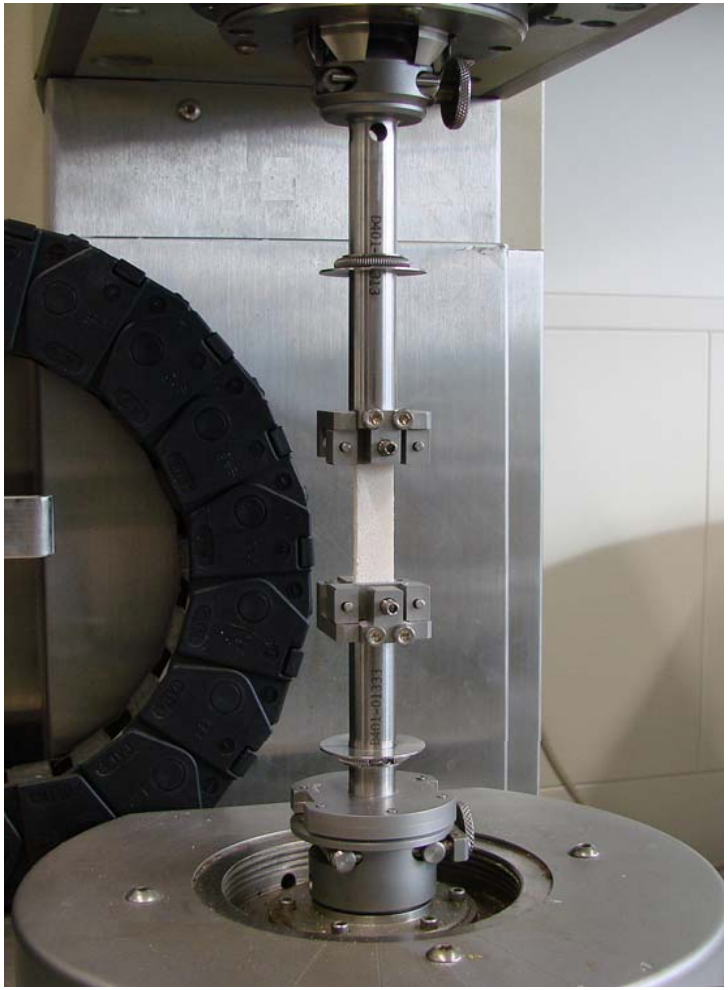
DMA instrument ARES™ – sample mounting, measurement in torsion mode



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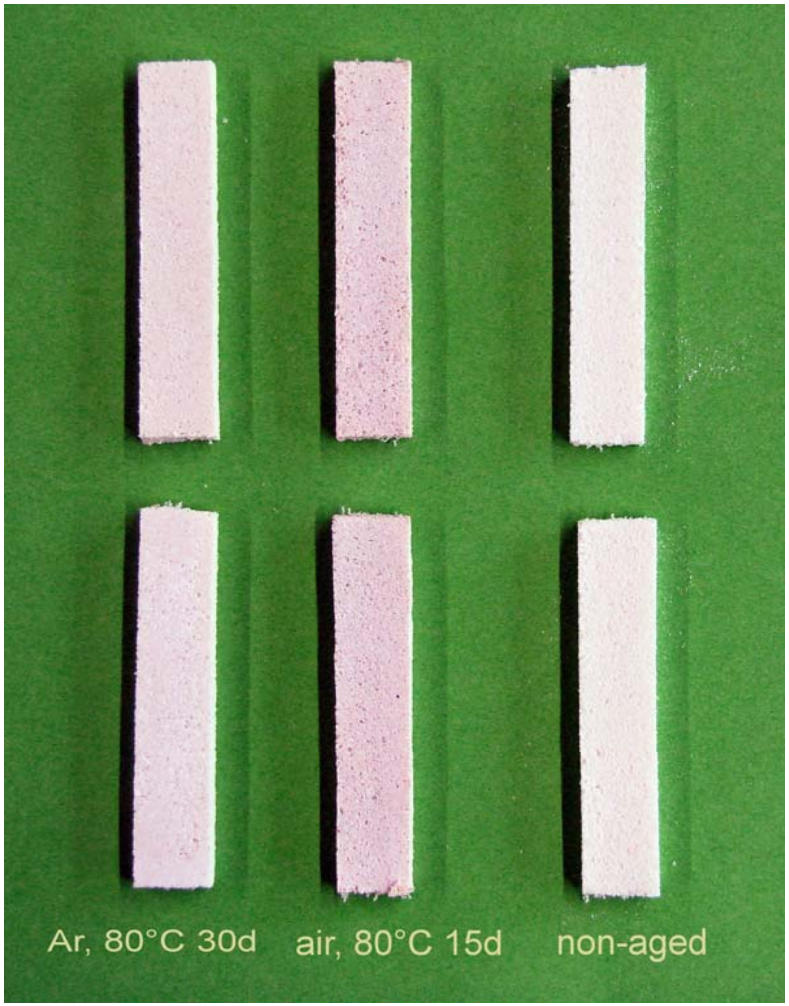
Samples for DMA measurements – ageing procedure – visible influence on samples



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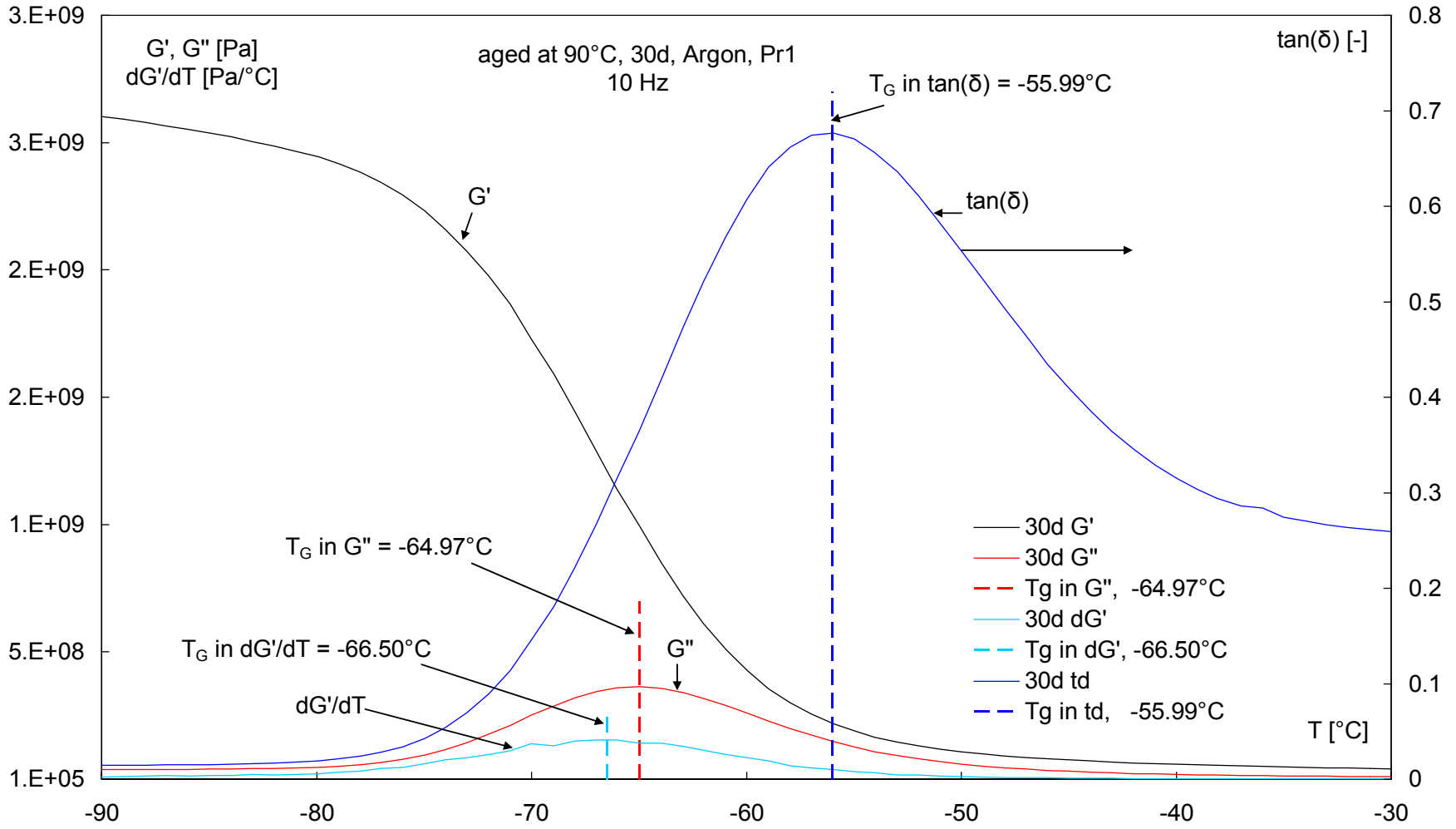
Shear modulus and tan(δ) – different definitions of glass transition temperature T_G

Temperature sweep with measurement at 3 frequencies: 0.1 Hz, 1 Hz and 10 Hz



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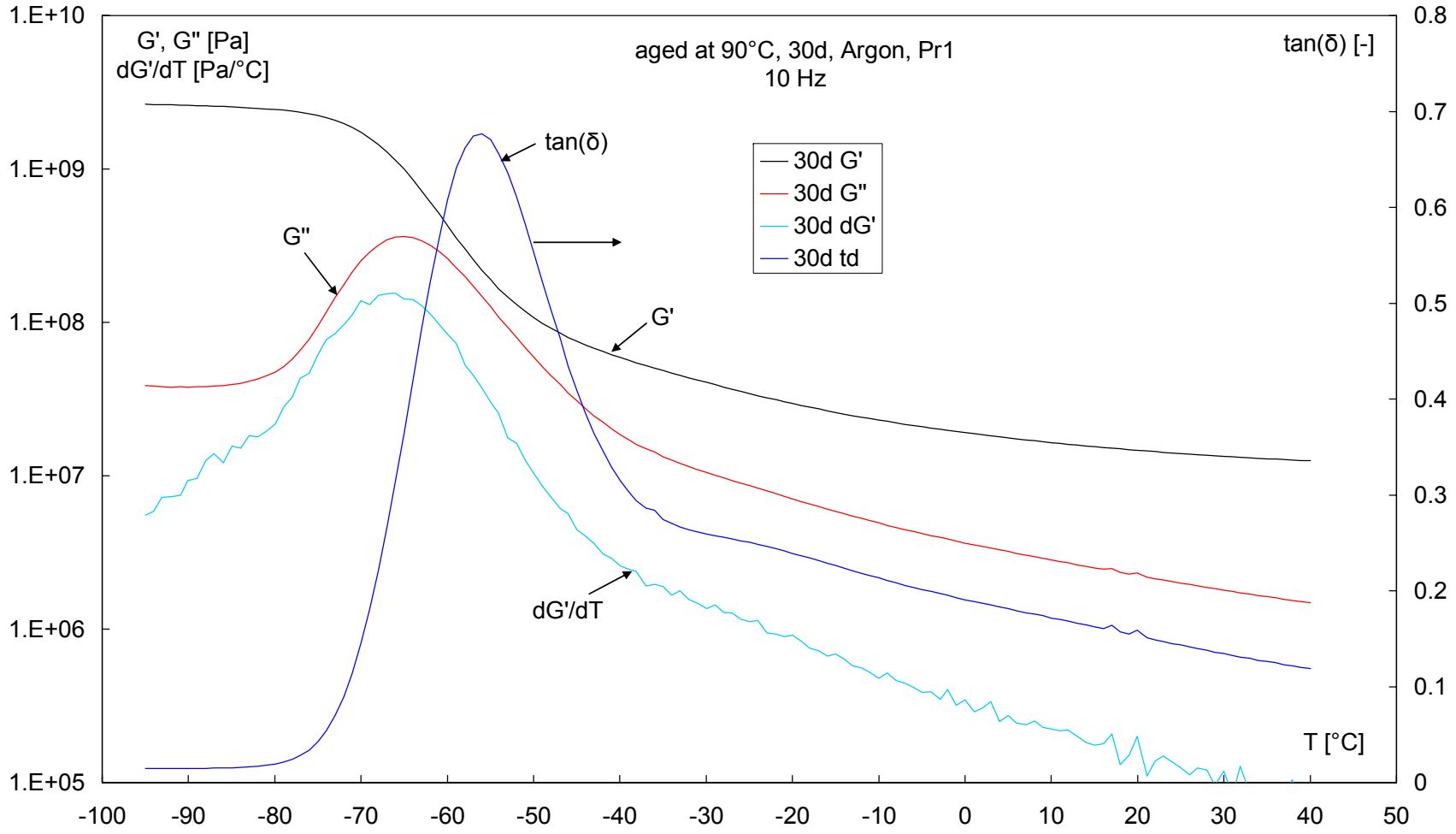
Shear modulus and loss factor tan(δ) – aged sample, 90°C over 30 days



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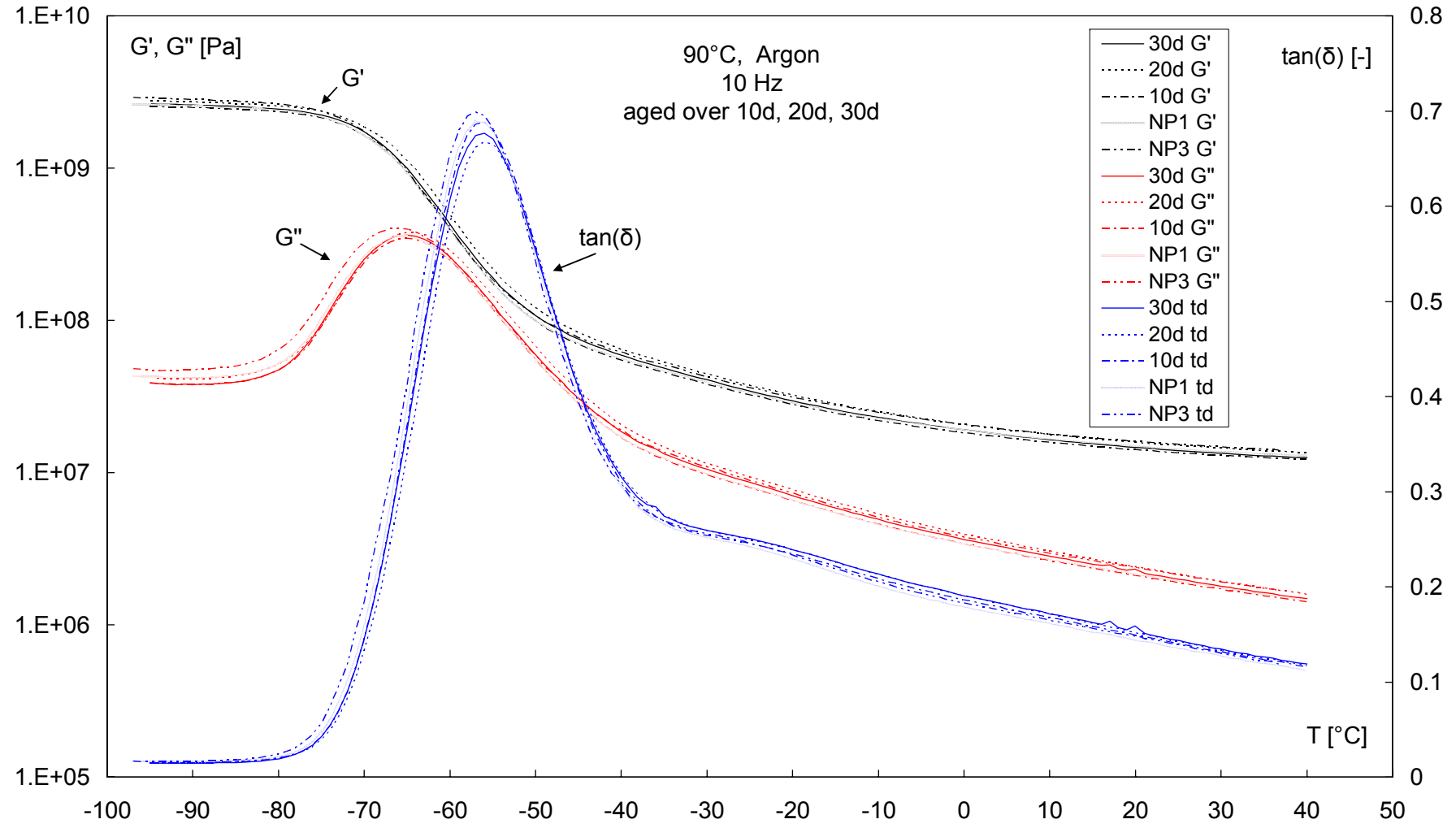
Shear modulus and loss factor tan(δ) – aged at 90°C under argon, 10d, 20d, 30d



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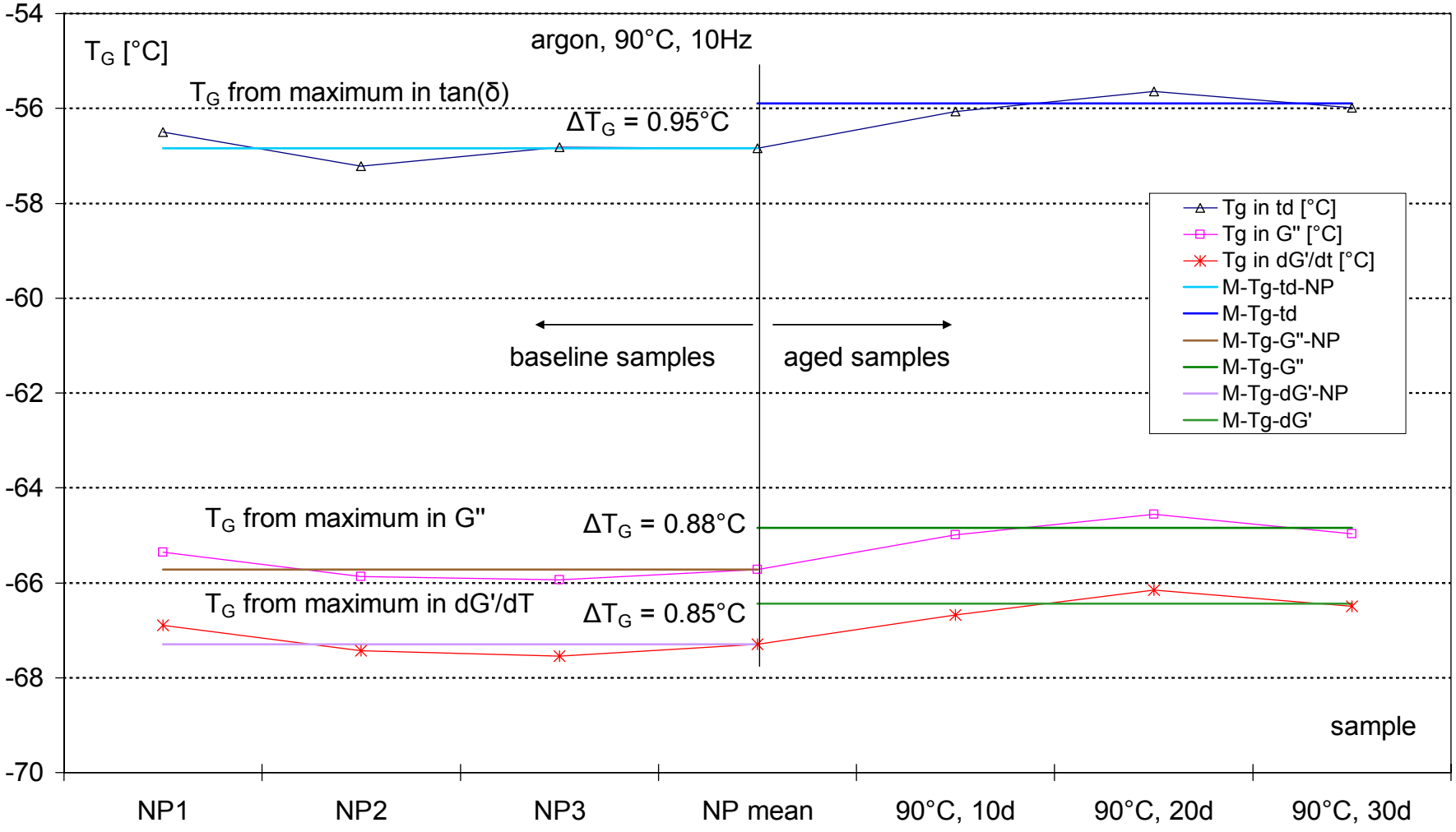
DMA results for glass transition temperatures - 90°C in argon, 10d, 20d, 30d



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HFMC- and CL-measurements

HFMC	Heat Flow Microcalorimetry
CL	Chemiluminescence

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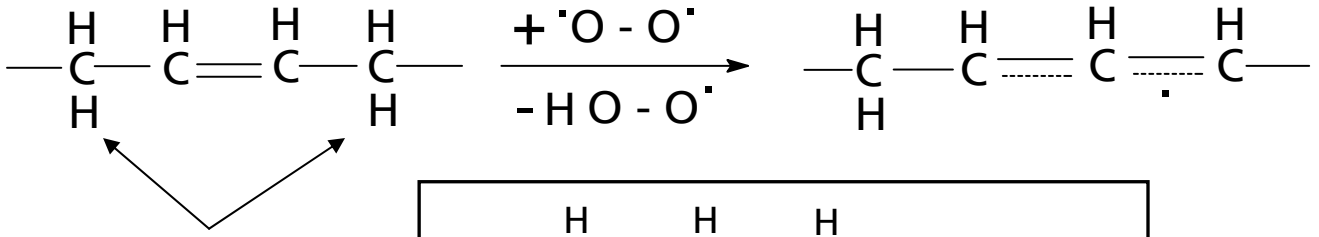
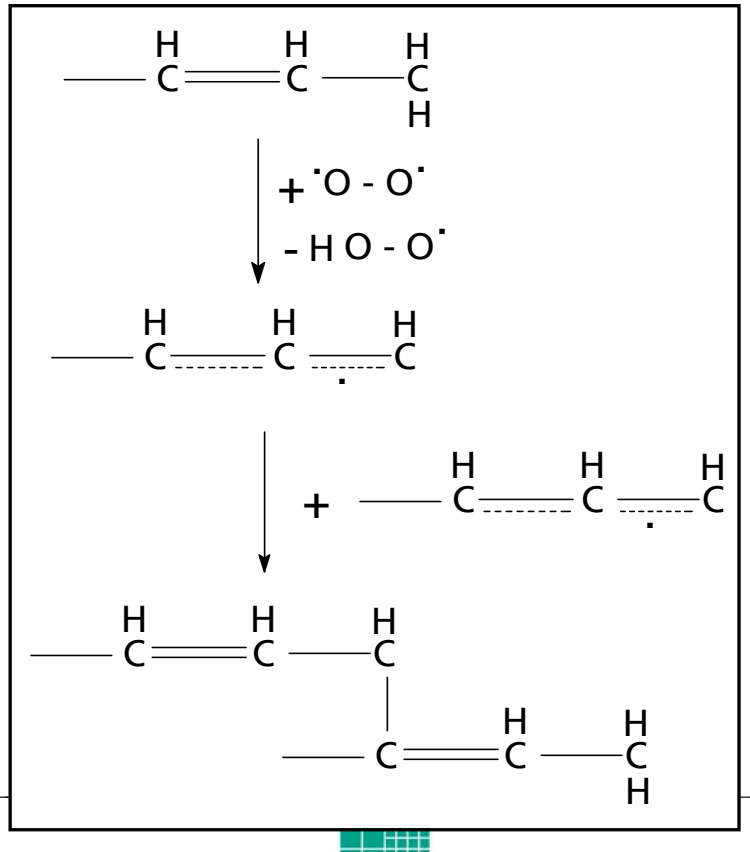
O_2-Attack sites on HTPB binder chain – resulting effect can be cross-linking



The allylic hydrogen atoms are very susceptible for oxygen attack because the resulting radical is resonance stabilized



Recombination of two radicals on two neighbouring chains - cross-linking occurs

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Heat Flow Microcalorimetry (HFMC)

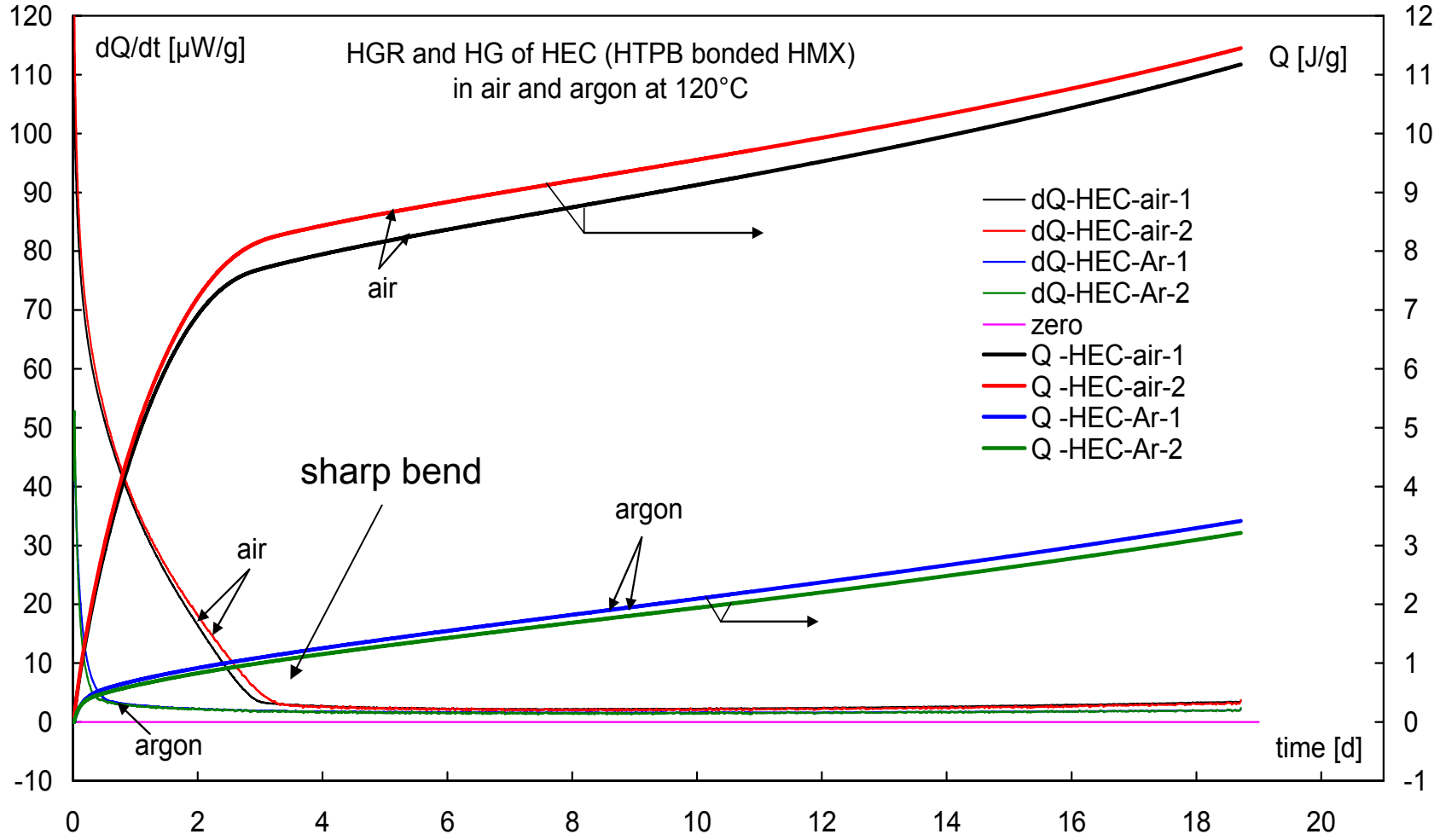
Used instrument

TAM II (high temp. version), TA Instruments (formerly Thermometric AB),
equipped with 4 microcalorimeter inserts (channels)
high long term baseline stability, better than 1 µW over 20 days

- Measured is heat generation rate (HGR) dQ/dt
  HGR is proportional to chemical reaction rate

- isothermal from 120°C to 150°C
- atmosphere: argon and air
- HEC sampled in Duran-vials inserted in Hastelloy-C22 ampoules
- sample masses around 1.0 to 1.25 g

Measurement results (HFMC)



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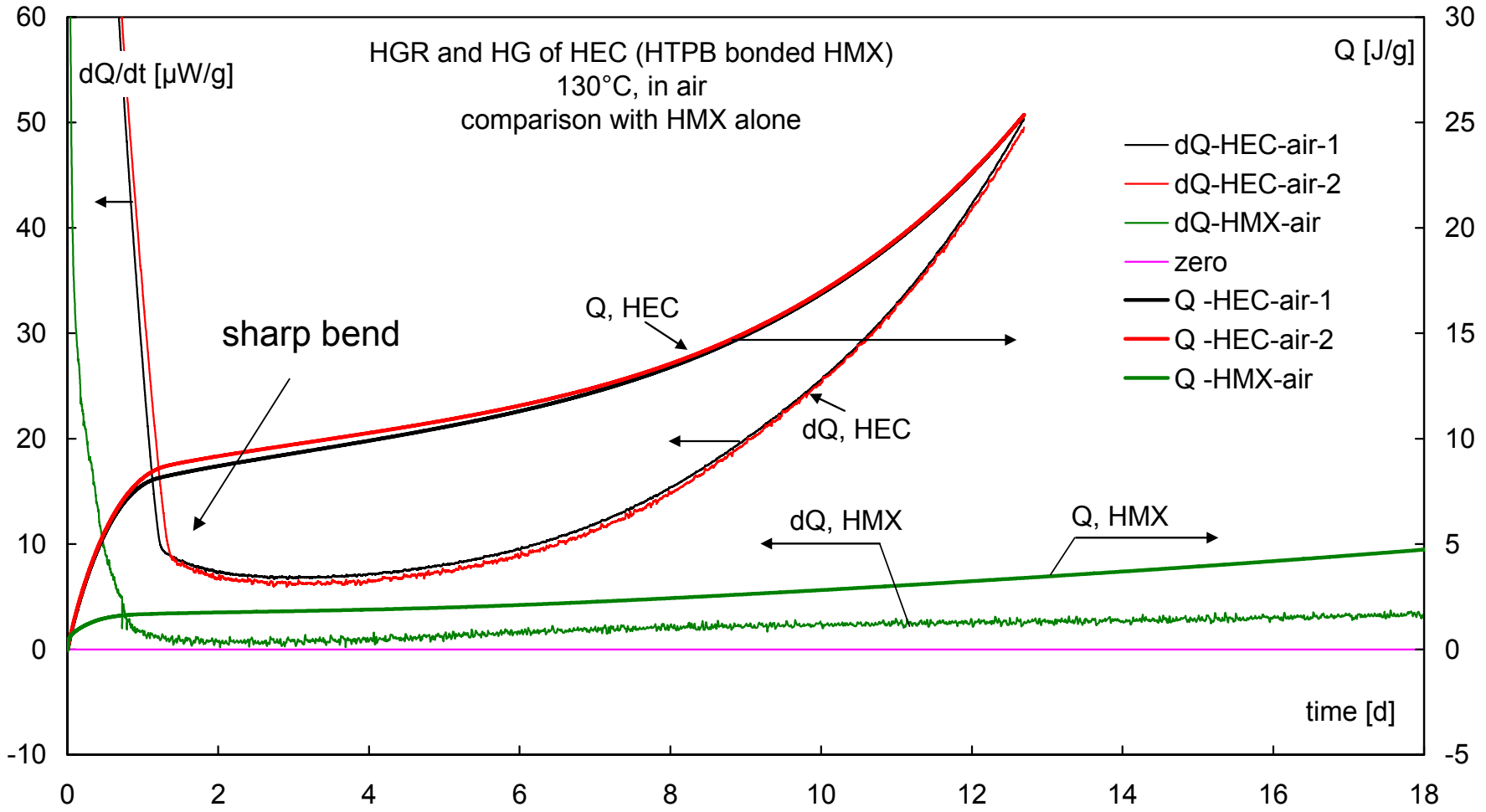
Measurement results (HFMC)



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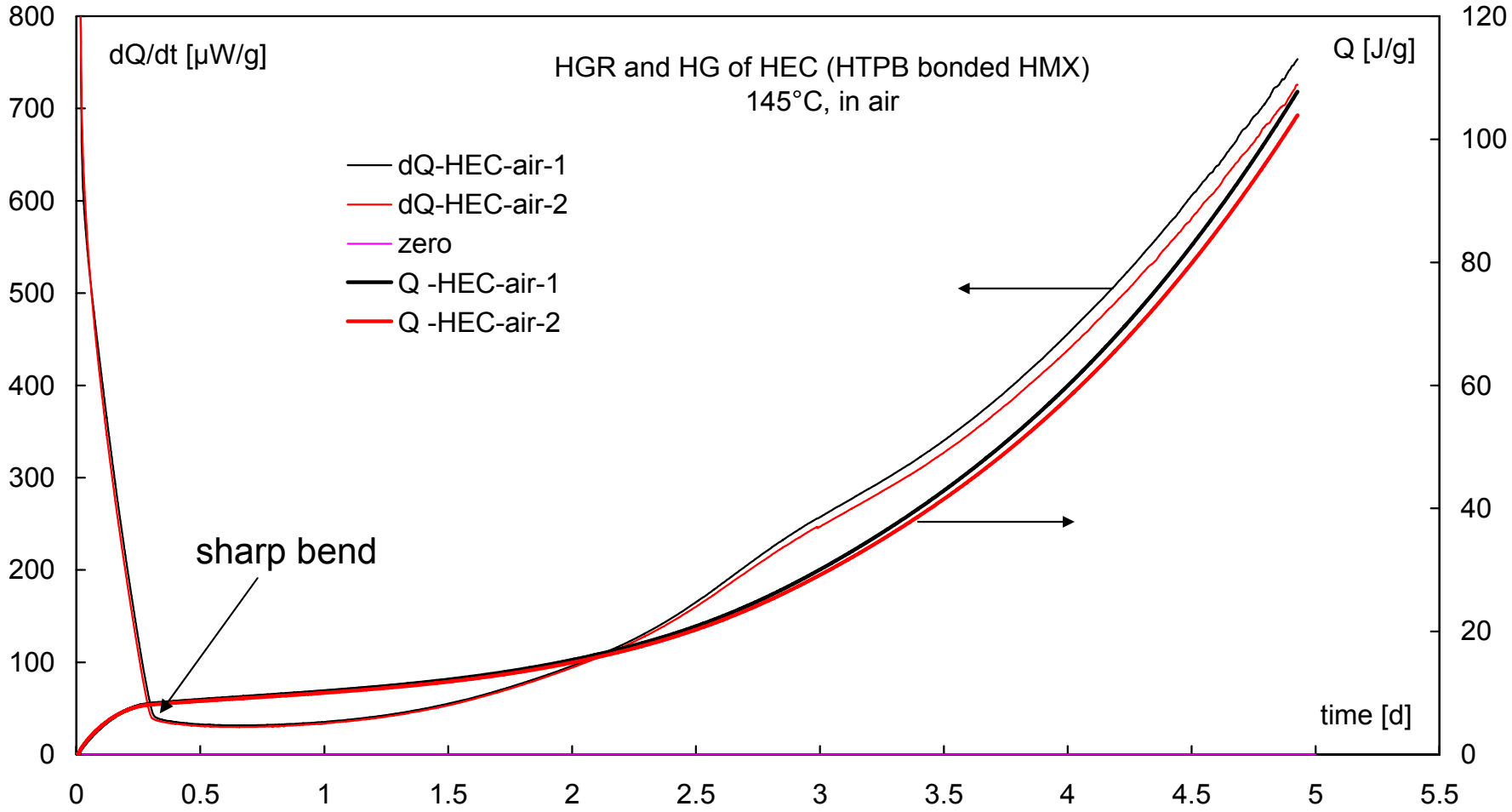
Measurement results (HFMC)



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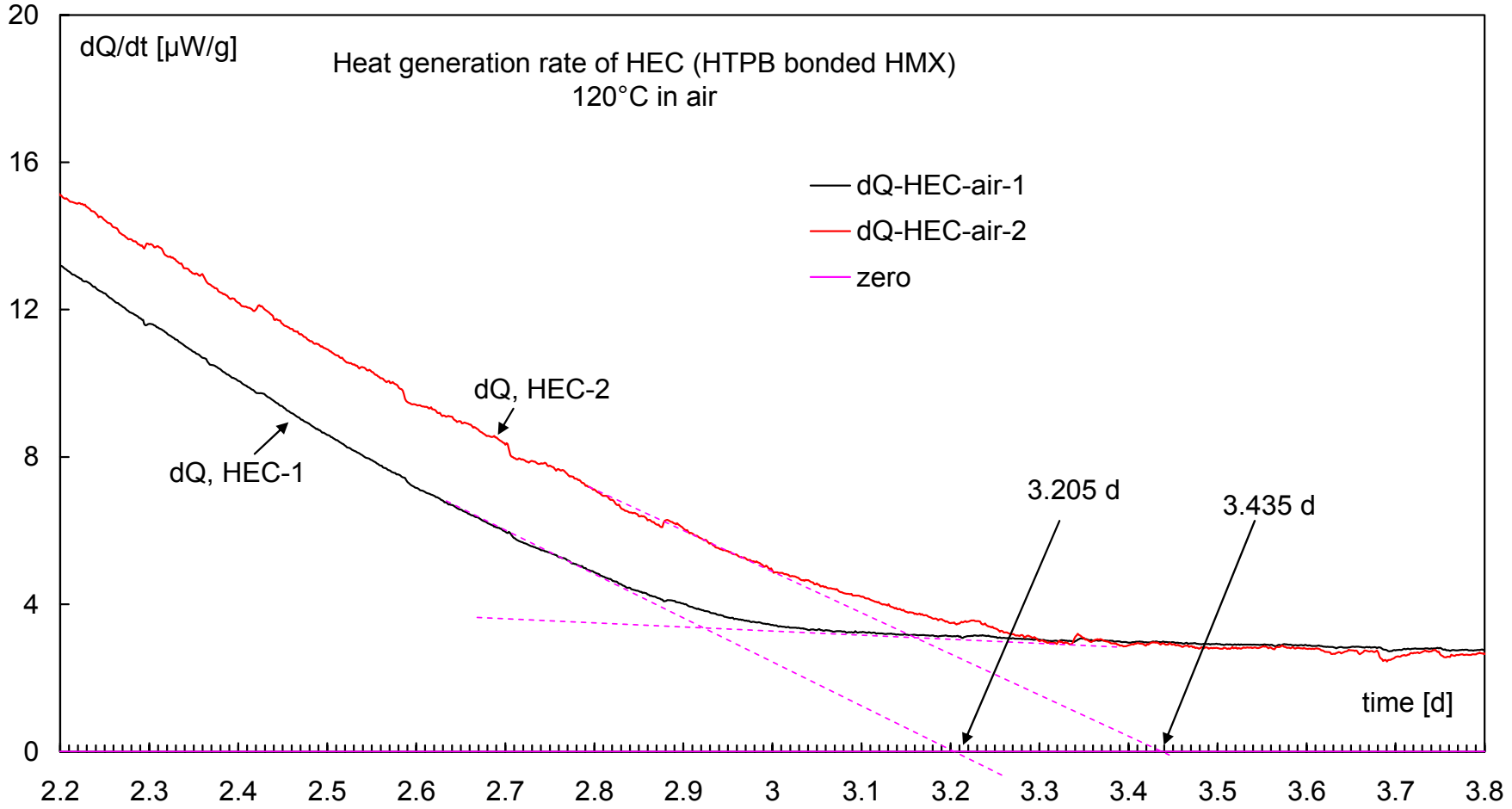
Data evaluation (HFMC) – times to sharp bend in HGR



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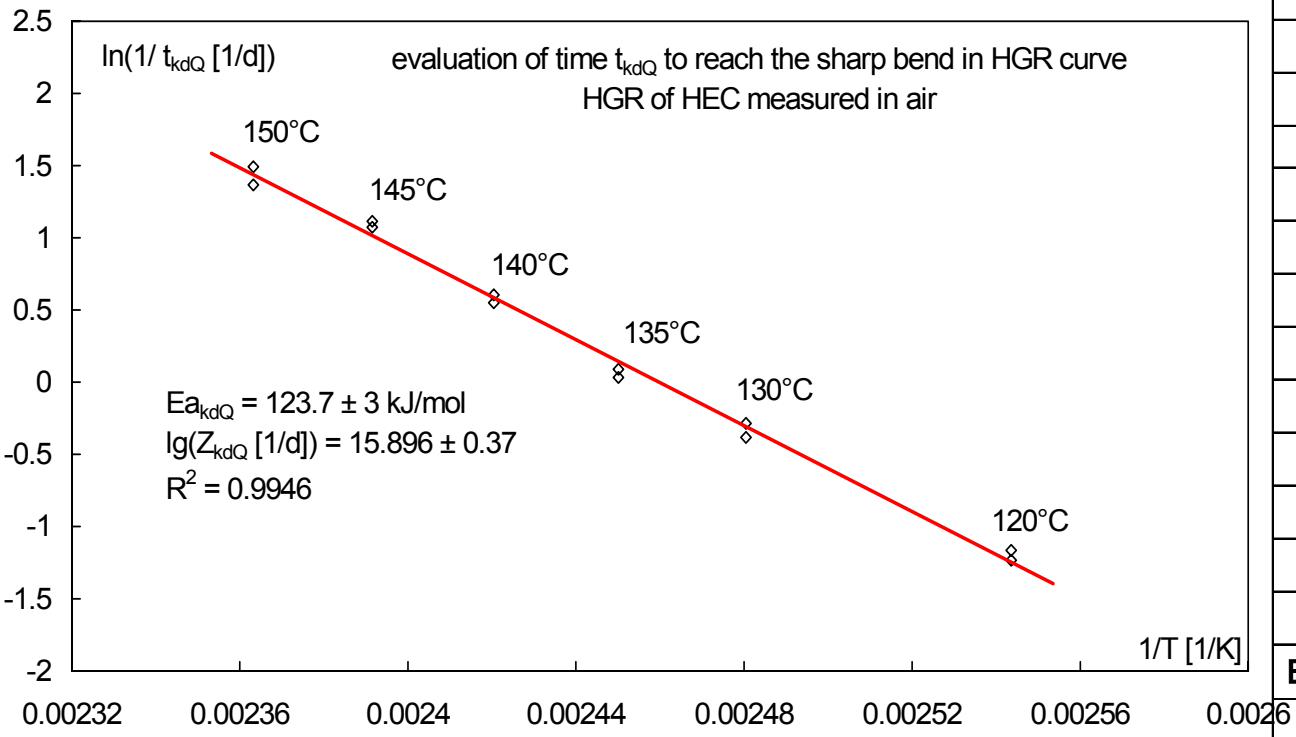
Results of sharp bend evaluation (HFMC)

Arrhenius parameterization of reciprocal times to sharp bends in HGR curves



	from HGR (dQ/dt) curves	
T [°C]	ln(1/ t_{kdQ} [1/d])	t_{kdQ} [d]
100	-	-
110	-	-
120	-1.164712	3.205
120	-1.234017	3.435
130	-0.285179	1.33
130	-0.381855	1.465
135	0.088831	0.915
135	0.032523	0.968
140	0.605136	0.546
140	0.549913	0.577
145	1.114742	0.328
145	1.072945	0.342
150	1.491655	0.225
150	1.366492	0.255
Ea_{kdQ} [kJ/mol]	123.7 ± 3	
$lg(Z_{kdQ}$ [1/d])	15.896 ± 037	
R^2	0.9946	

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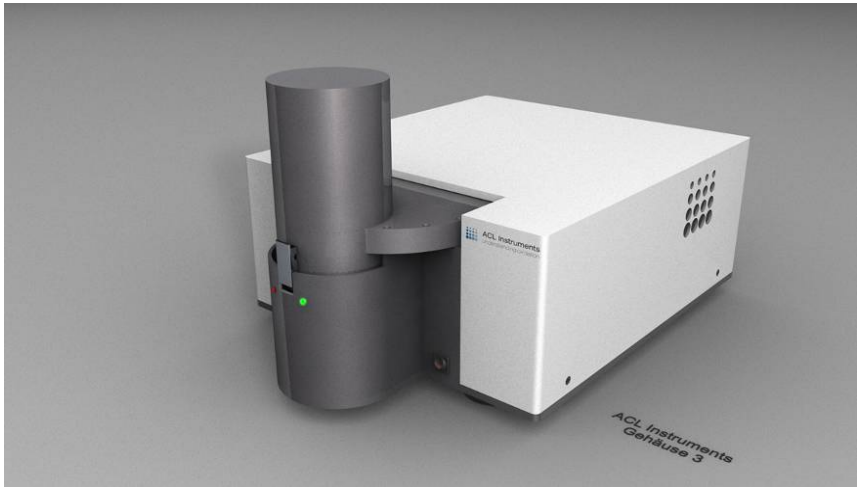
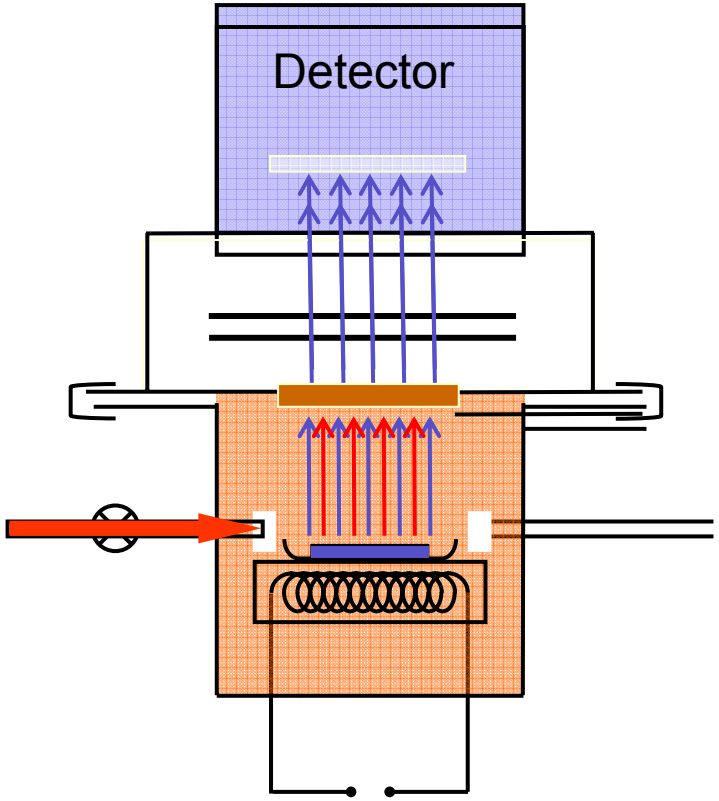
Chemiluminescence - instrument used

instrument from ACL Instruments Inc., Switzerland
Measured is light impulses per time per sample mass
Signal is proportional to the chemical reaction rate

- isothermal conditions from 100°C to 140°C
- atmosphere: air, 30 ml/min
- sample masses around 30 mg
- by reaction enthalpy excited oxygen





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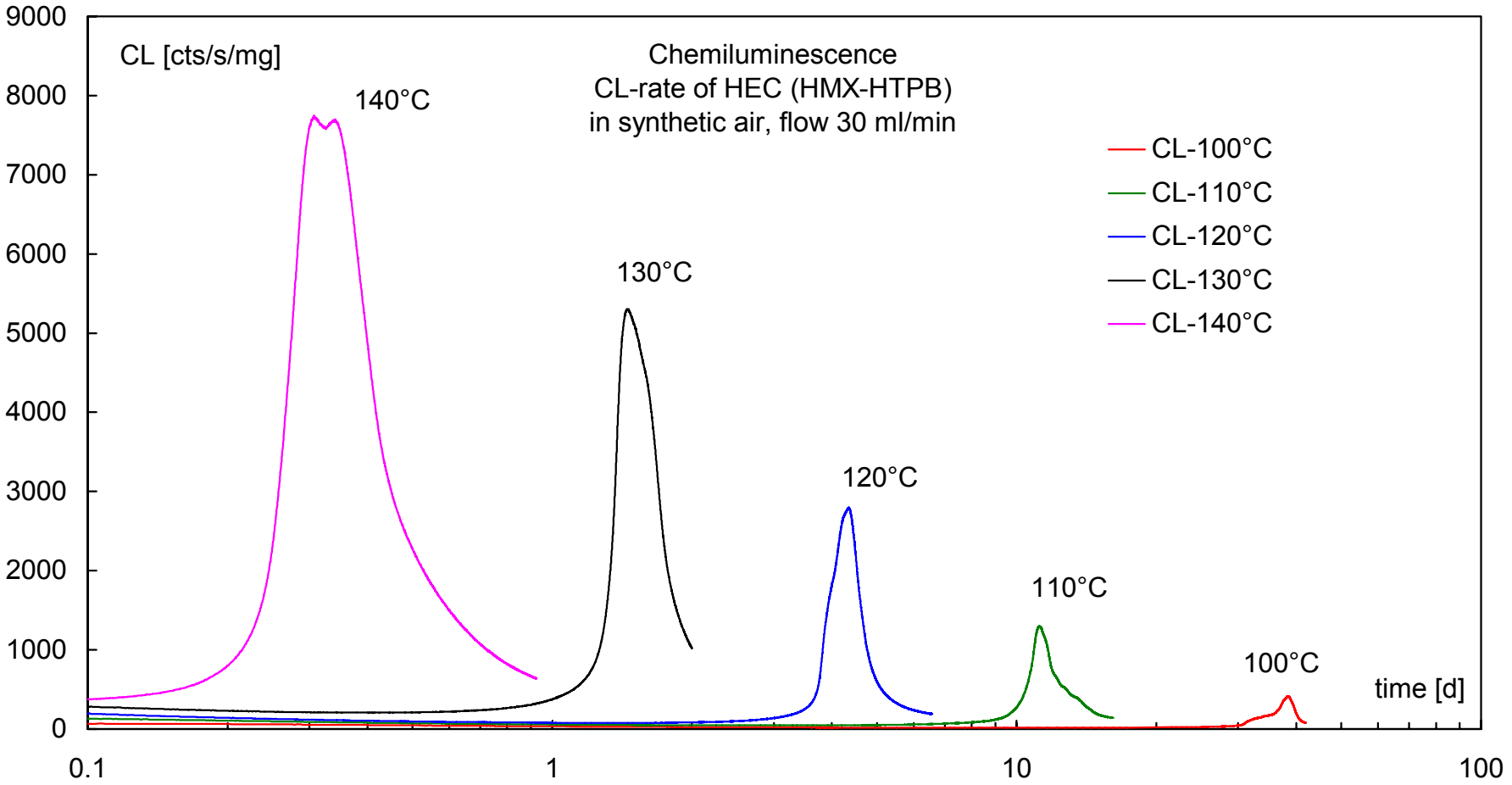
Measurement results on HEC (CL)



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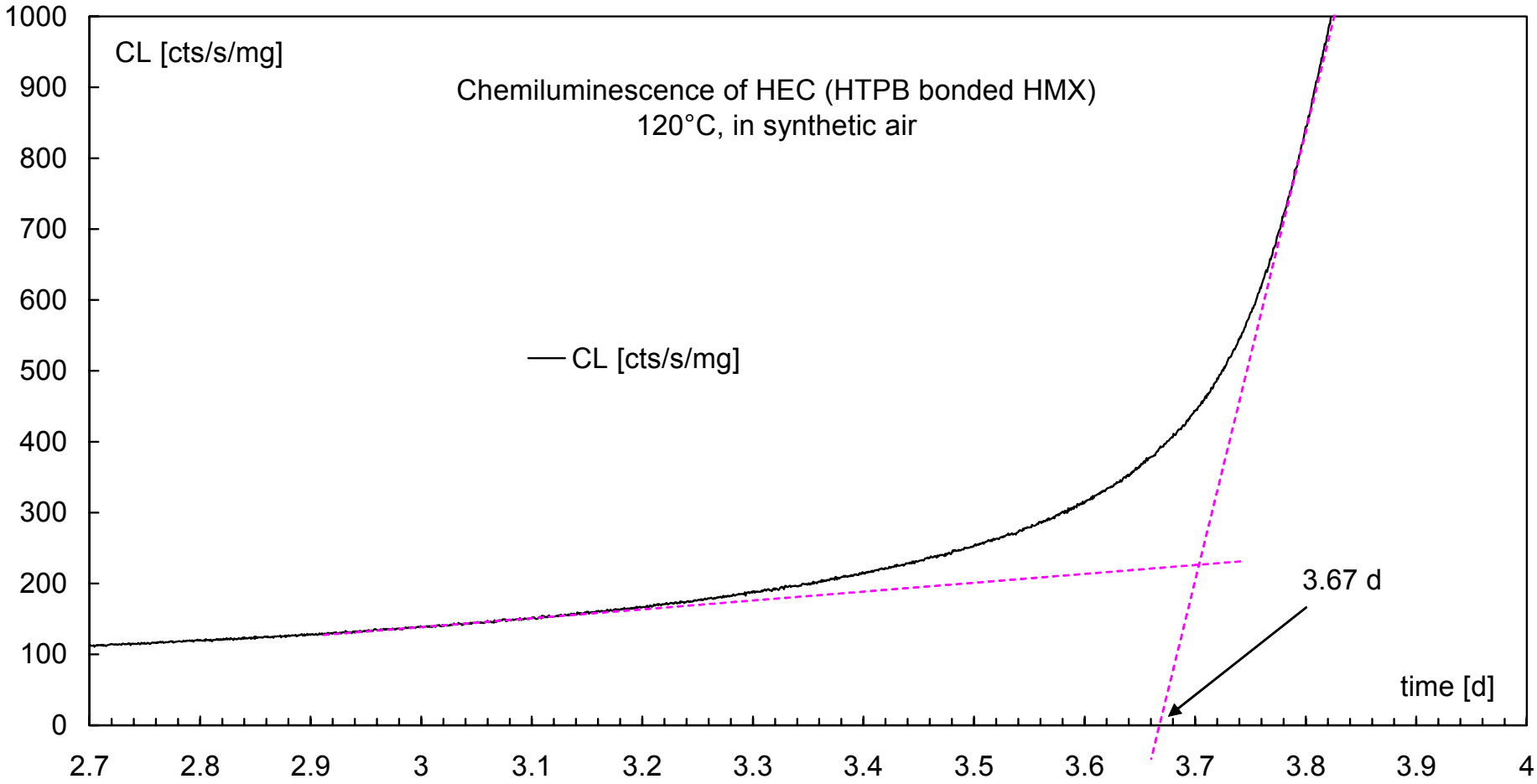
Data evaluation (CL) – times to sharp bend in CL rate



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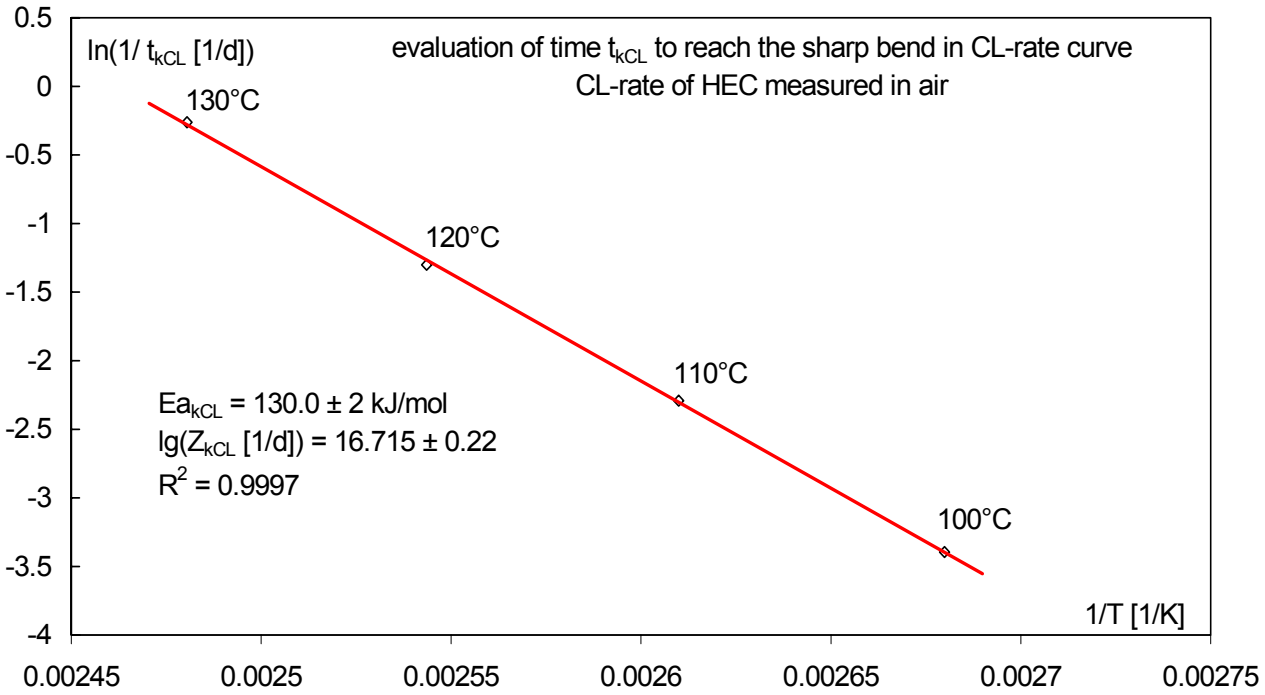
Results (CL) - reciprocal times to sharp bend

Arrhenius parameterization of reciprocal times to sharp bends in CL curves



	CL-rate curves	
T [°C]	**ln(1/t_{kCL} [1/d])**	**t_{kCL} [d]**
100	0.033557	29.8
110	0.101112	9.89
120	0.272479	3.67
130	0.769823	1.299
140	(1.452434) not used	0.234
Ea_{kCL} [kJ/mol]	130.0 ± 2	
lg(Z_{kCL} [1/d])	16.715 ± 0.22	
R^2	0.9997	

This result agrees with the corresponding evaluation of HGR data:

Ea_{kdQ} = 123.7 ± 3 kJ/mol

lg(Z_{kdQ} [1/d]) = 15.896 ± 0.37

R^2 = 0.9946

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Kinetic modelling of HFMC-data and CL-data

1 Start: radical formation at binder material

$Y\text{-}H + {}^{\bullet}O=O^{\bullet} \rightarrow Y^{\bullet} + HOO^{\bullet}$ formation of hydroperoxides by oxygen attack

2a Chain propagation: forms further radical sites at binder

$Y^{\bullet} + {}^{\bullet}O=O^{\bullet} \rightarrow YOO^{\bullet}$

$Y\text{-}H + HOO^{\bullet} \rightarrow Y^{\bullet} + HOOH$ formation of species, which can attack the starting material and re-formation of attacking species

$Y\text{-}H + YOO^{\bullet} \rightarrow Y^{\bullet} + YOOH$

2b Chain branching: increasingly autocatalytically effective

$HOOH \rightarrow HO^{\bullet} + {}^{\bullet}OH$

$2\,YOOH \rightarrow YOO^{\bullet} + YO^{\bullet} + HOH$

$YOOH \rightarrow YO^{\bullet} + {}^{\bullet}OH$

3 Radical neutralization by antioxidant Stabilization

$Y^{\bullet} + A-H \rightarrow Y-H + A^{\bullet}$

$YO^{\bullet} + A-H \rightarrow YOH + A^{\bullet}$ Radical neutralizing (trapping) by forming a more stable radical A•

$HO^{\bullet} + A-H \rightarrow HO-H + A^{\bullet}$

$Y^{\bullet} + A^{\bullet} \rightarrow Y-A$

$YO^{\bullet} + A^{\bullet} \rightarrow YOA$ Consumption of antioxidant A-H

The three main steps are approximated by three reactions, each summarizing the individual reactions in each step

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Kinetic model: autocat. reaction + 'side reaction' (= stabilizing reaction)

$$A + \mathrm{Ox} \xrightarrow{k_1} B + C + S \qquad (-\Delta H_{R,1}) \quad \text{primary radical formation}$$

$$A + B \xrightarrow{k_2} 2\,B + C + S \qquad (-\Delta H_{R,2}) \quad \text{chain branching / autocat. decomp.}$$

$$\mathrm{AO} + \mathrm{B} \xrightarrow{k_0} \mathrm{AO\text{-}B} \qquad (-\Delta H_{R,S}) \quad \text{stabilizing reaction by AO}$$

Approximation by three reactions;

B stands for all autocatalytically effective species

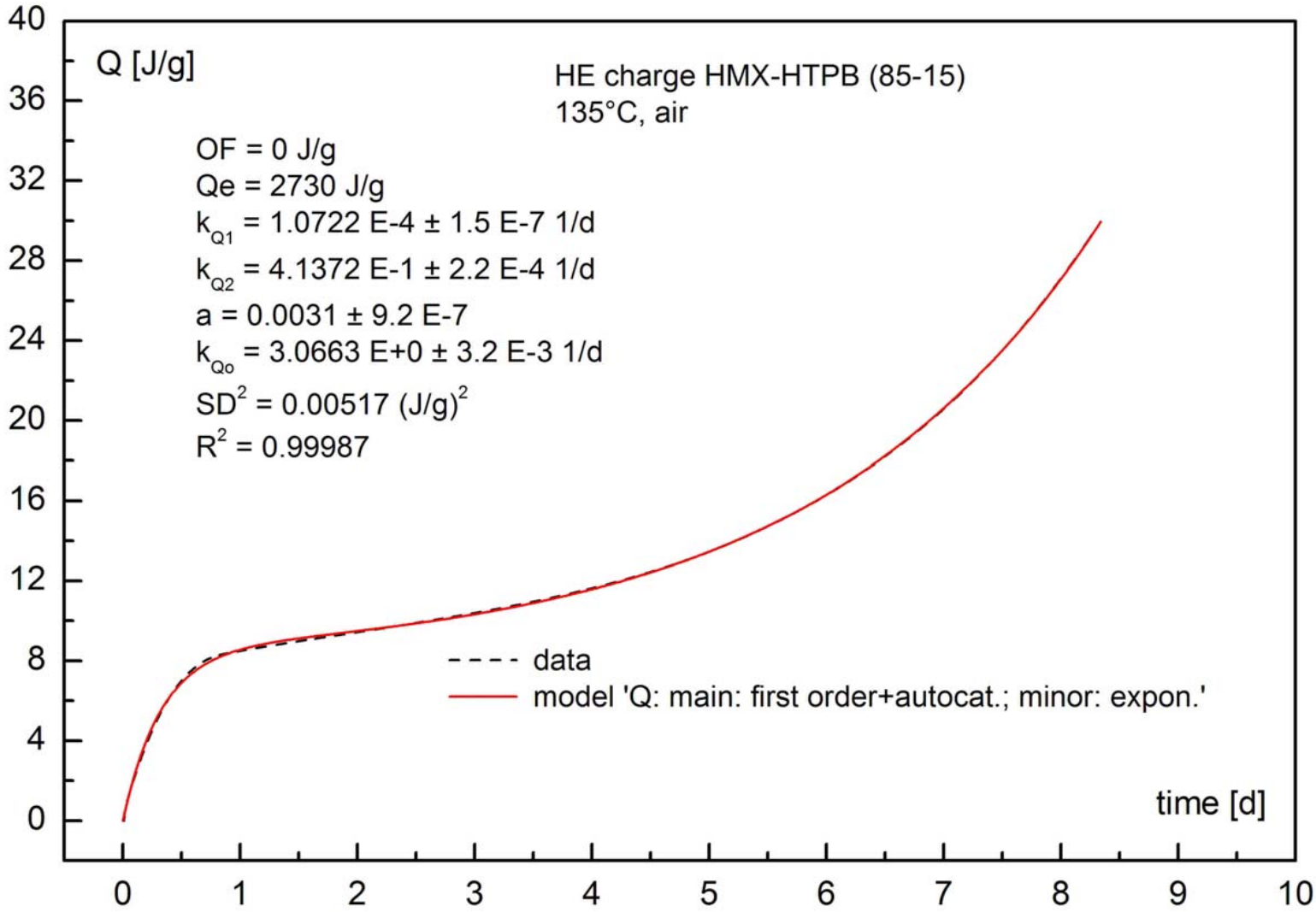
Model for HFCM-data: 'Q: main: first order + autocatalytic; minor: exponential'

$$Q(t,T) = OF_Q + Q(te)\cdot\left\{\begin{array}{l} a\cdot\left(1-\exp(-k_{Qo}\cdot t)\right)\ \ldots \\ \ldots + (1-a)\cdot\left(1-\dfrac{k_{Q1}(T)+k_{Q2}(T)}{k_{Q2}(T)+k_{Q1}(T)\cdot\exp\left(\left(k_{Q1}(T)+k_{Q2}(T)\right)\cdot t\right)}\right)\end{array}\right\}$$

Model for CL-data: 'Ic: main: first order + autocatalytic; minor: exponential'

$$Ic(t,T) = OF_{Ic} + Ic(te)\cdot\left\{\begin{array}{l} a\cdot\left(1-\exp(-k_{Ico}\cdot t)\right)\ \ldots \\ \ldots + (1-a)\cdot\left(1-\dfrac{k_{Ic1}(T)+k_{Ic2}(T)}{k_{Ic2}(T)+k_{Ic1}(T)\cdot\exp\left(\left(k_{Ic1}(T)+k_{Ic2}(T)\right)\cdot t\right)}\right)\end{array}\right\}$$

Kinetic modelling of HFMC-data



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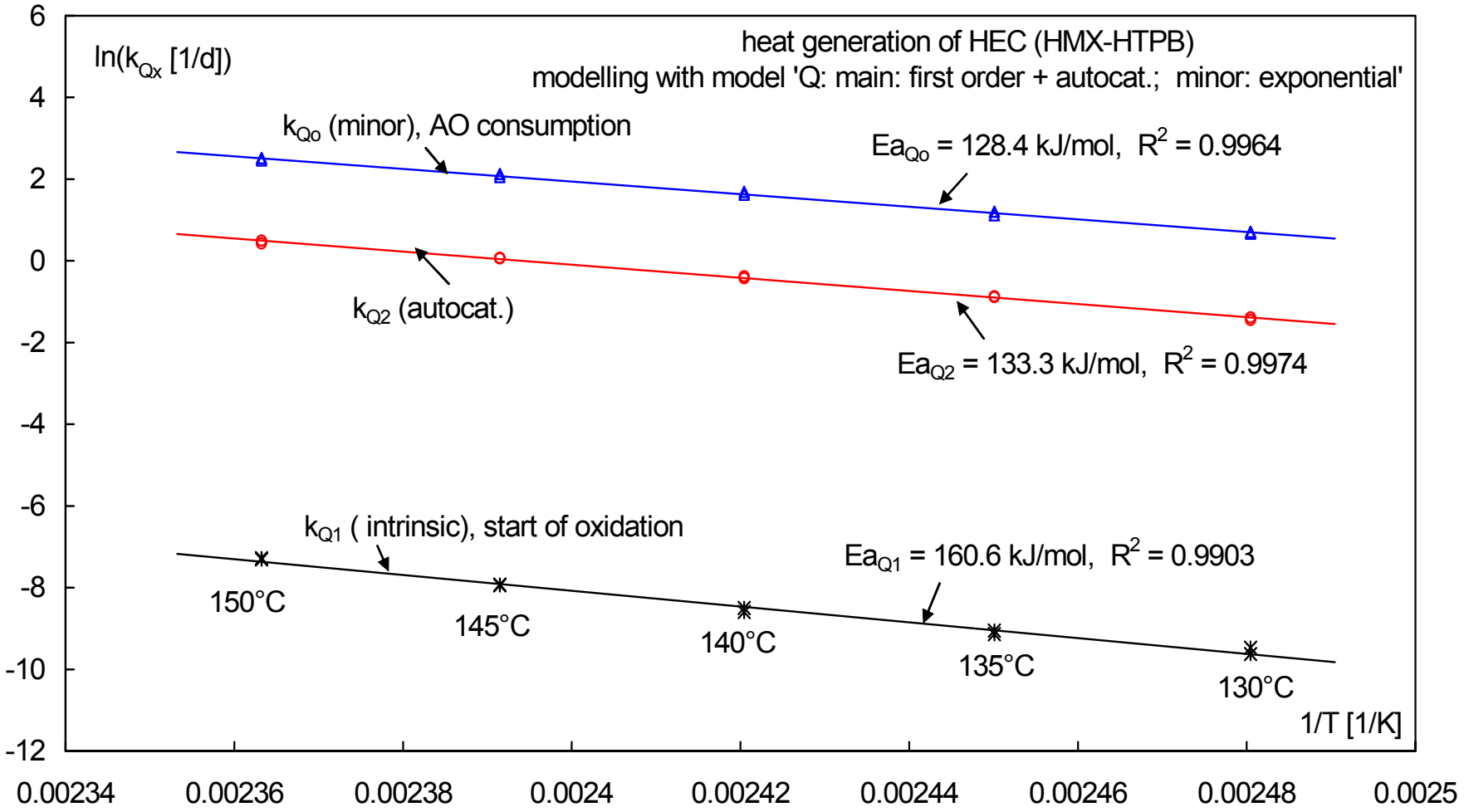
Kinetic modelling of(HFMC) - results

	primary radical formation	Chain branching / autocatalytical decomposition	AO - stabilizing
	k_{Q1} [1/d]	**k_{Q2} [1/d]**	**k_{Qo} [1/d]**
Ea_{Qx} [kJ/mol]	160.6 ± 5.6	133.3 ± 2.4	128.4 ± 2.7
$lg(Z_{Qx}$ [1/d])	16.629 ± 0.71	16.666 ± 0.31	16.943 ±0.34
R^2 [-]	0.9903	0.9974	0.9964
SD^2 [$ln(1/d)^2$]	0.00782	0.00145	0.00184

Results of kinetic modelling – HFCM data



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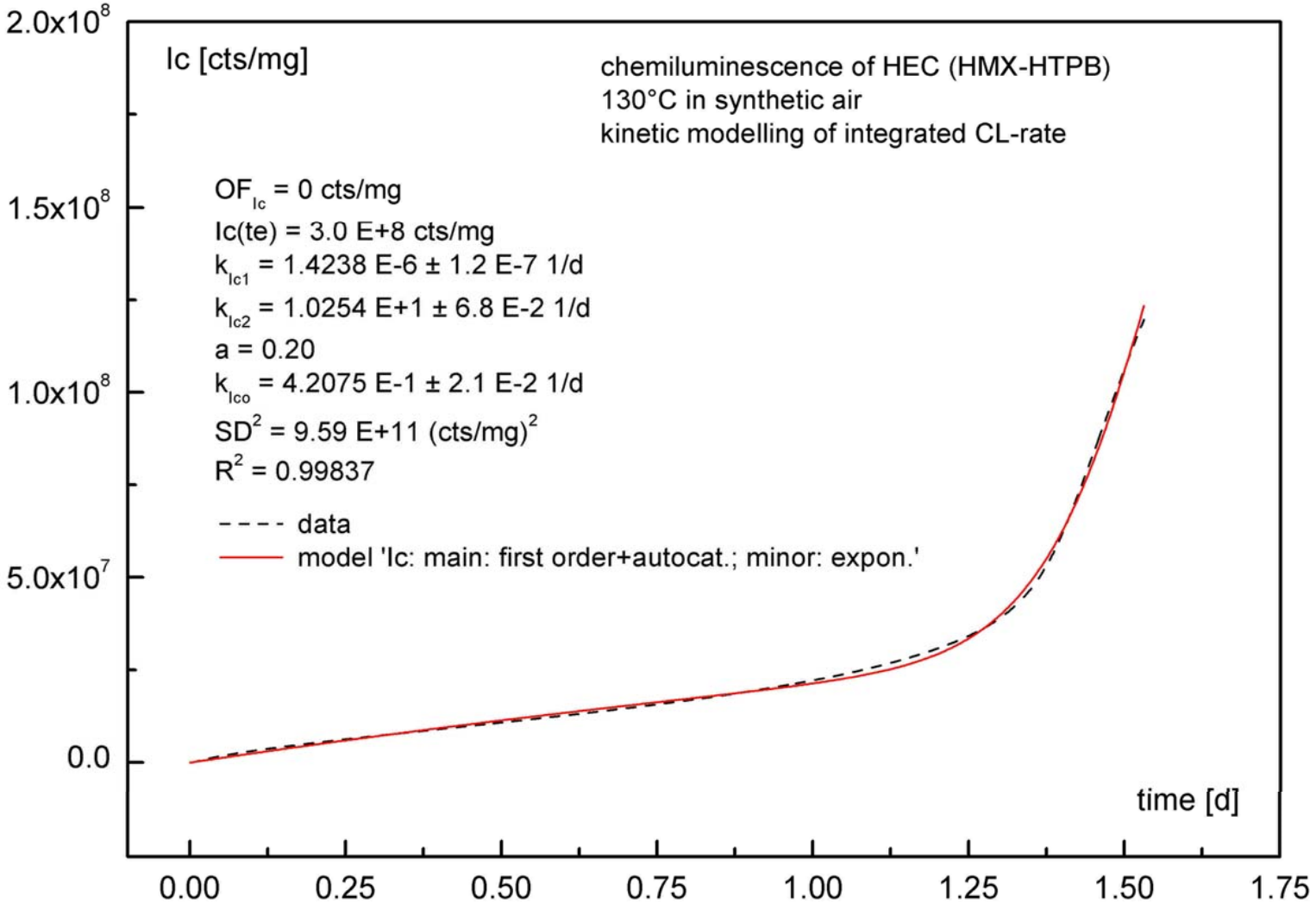
Kinetic modelling of CL-data



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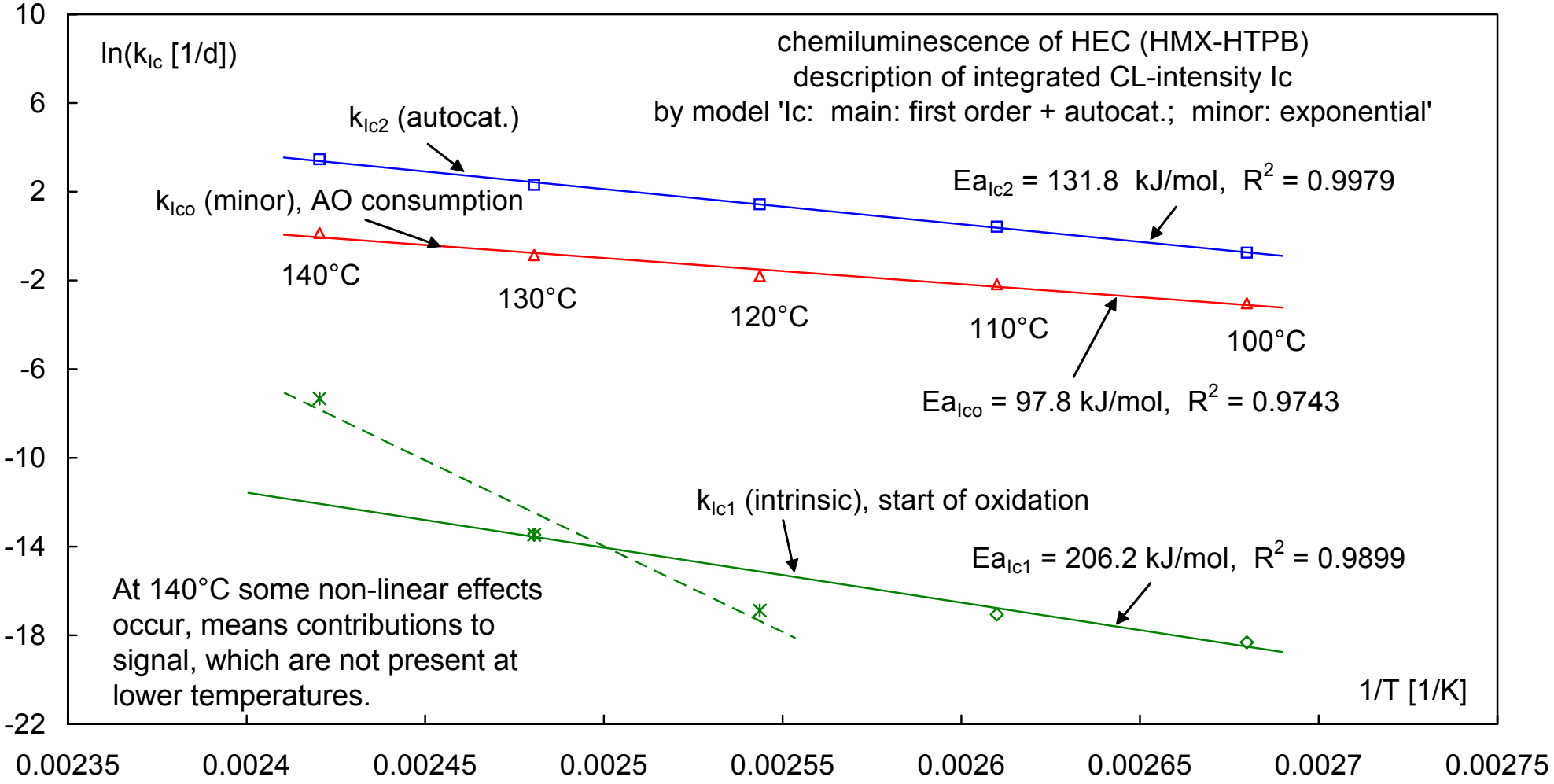
Results of kinetic modelling – integrated CL data

	primary radical formation	Chain branching / autocatalytical decomposition	AO - consumption
	k_{lc1} [1/d]	k_{lc2} [1/d]	k_{lc0} [1/d]
Ea_{lcx} [kJ/mol	206.2 ± 21	131.9 ± 3.5	97.8 ± 9.2
$lg(Z_{lcx}$ [1/d])	20.824 ± 2.80	18.137 ± 0.47	12.337 ± 1.22
R^2 [-]	0.9899	0.9979	0.9743
SD^2 [$ln(1/d)^2$]	0.128	0.0753	0.0511

Discussion of kinetic modelling – CL data



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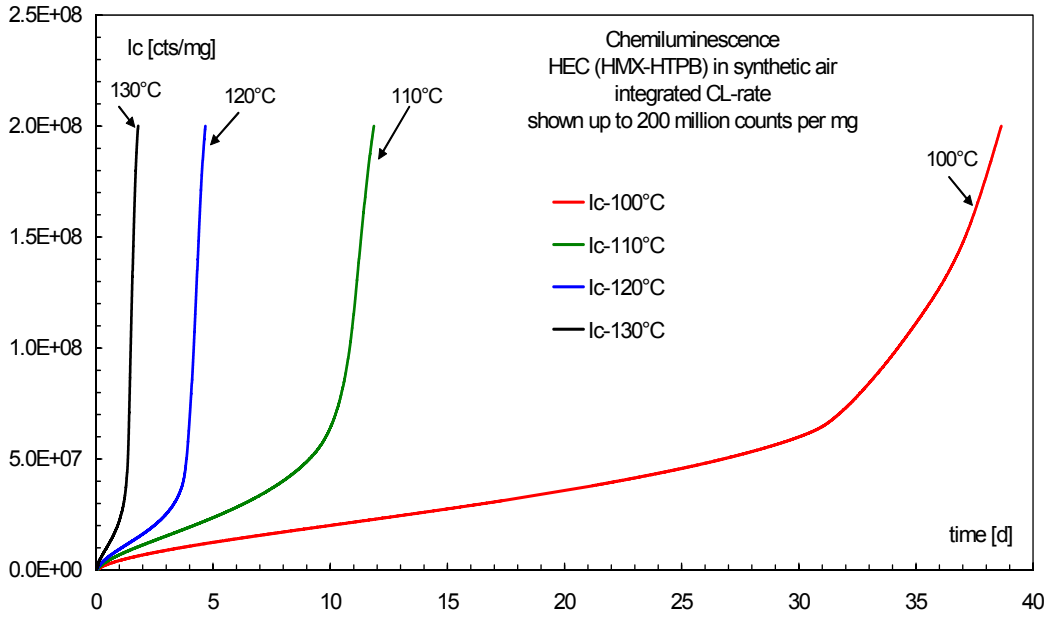
Results (CL) – slopes of Ic during 'induction period'

reaction rate constants k_{Ic} describing the part of stabilizer action and its consumption

k_{Ic} is obtained from the slopes of the integrated CL-intensity curves before the main oxidation peak (autocatalysis)

T [°C]	k_{Ic} [cts/mg/d]	R^2
100	1.4996E+06	0.99991
110	4.1697E+06	0.99928
120	6.9538E+06	0.99941
130	1.8886E+07	0.99913
140	3.2345E+07	0.99921
Ea_{Ic} [kJ/mol]	98.5 ± 5.6	
$lg(Z_{Ic}$ [cts/mg/d]	19.949 ± 0.75	
R^2	0.9903	



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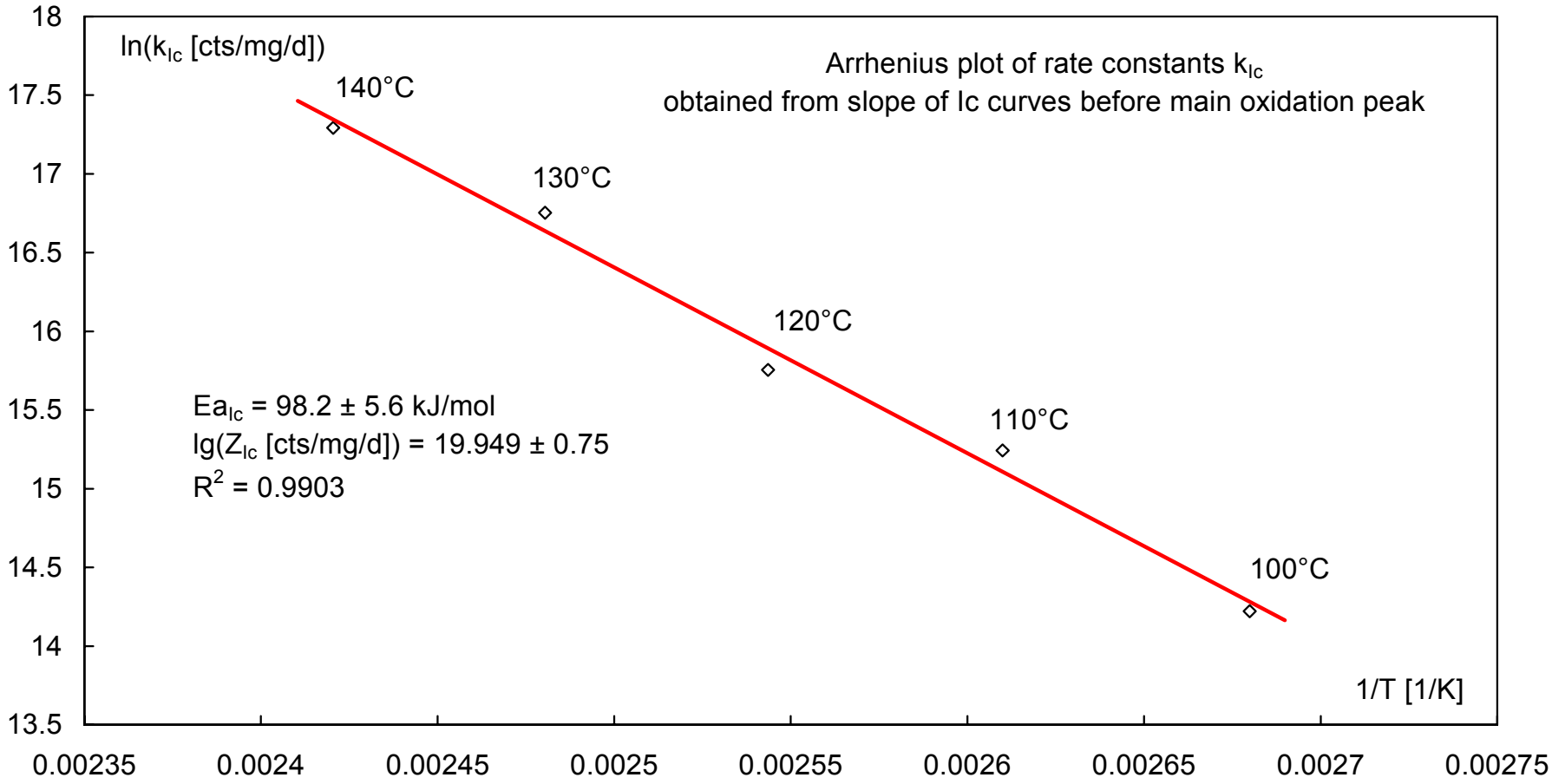
ACL Instruments understanding oxidation

Results (CL) – slopes of Ic in 'induction period'

reaction rate constants k_{Ic} describing the part of stabilizer action and its consumption



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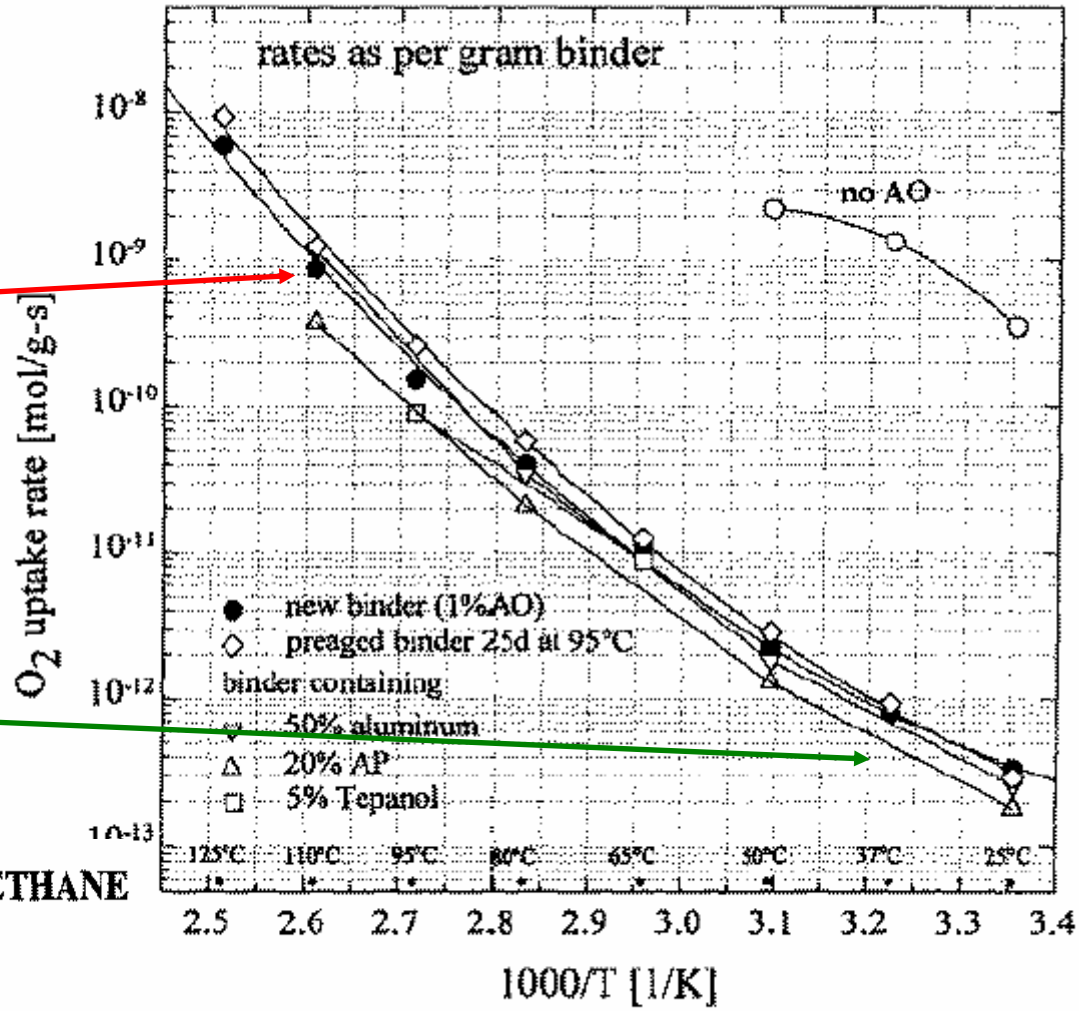
Oxygen uptake of HTPB-IPDI binder

Occurs temperature dependent at different mechanisms

120 to 130 kJ/mol

Switch temperature: 80°C

70 to 80 kJ/mol



Oxygen consumption rates of the binder and influence of other components.

THERMAL DEGRADATION STUDIES OF A POLYURETHANE PROPELLANT BINDER

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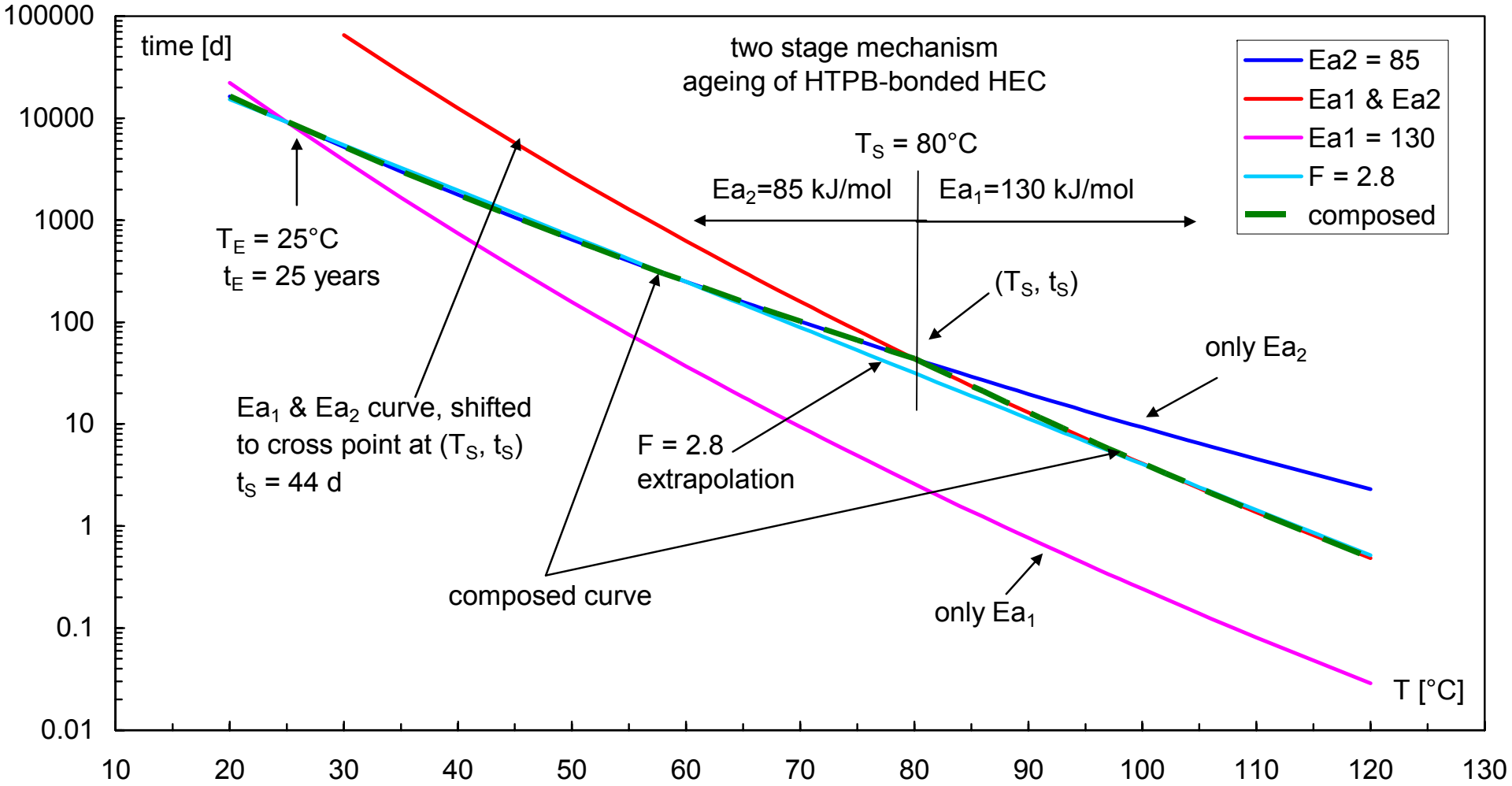
Ageing of HTPB bonded HEC using a two-step mechanism

For details and worked out examples with two mechanisms see: Manfred A. Bohn, Paper 78, 40th Conference of ICT, 2009



Summary and conclusions

Basic stability

The stability test data show that HEC of type KS32 is a very stable material.

Ageing program

The ageing times calculated with F = 2.5 in the factor extrapolation method seem appropriate, because the values of relevant ageing processes (AO consumption, time to sharp bend) are in the range 70 to 130 kJ/mol. F=2.5 is therefore a conservative extrapolation.

Gap-Test

A decrease of go detonation pressure was found with ageing: After 36 days at 80°C (corresponding to 15 years at 25°C) a 14% decrease resulted. This seems independent of surrounding atmosphere.

DMA (in torsion)

No essential shifts in glass transition temperature could be detected. Very slightly shifts between 0.5 and 1.7°C to positive values have been caused by ageing.
No significant difference between ageing in air and in argon.

Conclusions

HFMC and Chemiluminescence (CL)

Heat generation rate and Chemiluminescence (CL) measurements under oxidizing atmosphere revealed a kind of induction period – stabilizer (antioxidant) is active

In the curves well-defined bends occurred

With CL it could be shown that the end of induction period coincides with the well-defined bends in HFMC

After AO consumption autocatalytic oxidation / decomposition starts

Both methods give similar Arrhenius parameters of the 'reciprocal times to the bends' of about 130 kJ/mol

AO consumption rate is measured directly with CL, activation energy of 98 kJ/mol was found in kinetic modelling and in direct evaluation of integrated CL rate

AO consumption rate and time to end of AO activity can be used as ageing monitor.

The oxygen uptake rate has shown to follow a two-step mechanism with switching (turn-over) temperature Ts at about 80°C

For extrapolation below Ts a second process with much lower activation energy must be taken into account, about 65 to 85 kJ/mol.

Above Ts: oxygen uptake proceeds with higher activation energy: 120 to 130 kJ/mol

Thank you for your attention

Questions?