Decomposition kinetics of RDX in cyclohexanone and gammabutyrolactone determined with ARC and HFMC

ARC[™]: accelerating rate calorimeter HFMC: heat flow microcalorimetry

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Objectives

- **RDX** is processed in solvents, for example to re-crystallize and to round the particles
- During recrystallization residual solvent is often trapped inside the particles
- In these saturated solutions inside RDX decomposition is possible

Questions

- Is RDX really decomposing in typical processing solvents?
- If decomposing: How fast is the degradation of RDX?
- What are the kinetic parameters of RDX decomposition in solvents?
- What are possible decomposition pathways?
- Is there an effect of the decomposition on the sensitivity of RDX?



Methodology - substances

The RDX (also called hexogen) types employed here have been used already in IMA (Insensitive Munitions Ageing) project of EDA, reports on this work see ICT conference 2014 and NDIA IMEMTS contribution # 16147, October 2013, San Diego, CA, USA.

RDX Types		mean particle diameter	R friction	S impact	
		[µm]	[N]	[Nm]	
RDX from SME-Eurence	o, Sorgues (accord. Woolwich process)				
I-RDX, class 1	coarse	225	96	7.5	
I-RDX M3C, class 5	fine	10.5	112	7.5	
RDX from Dyno (Chemr	nemring, Saetre, N) (accord Bachmann-process)				
S-RDX, Typ I, class 1	coarse	195	160	7.5	
S-RDX, Typ I, class 5	fine	17.6	168	10	



Melting point-26- 44Boiling point156204–206

Abbreviations

cyclohexanone as cycloh or similar

°C

 γ -butyrolactone as gBL



Here measurements of 8 mass-% solutions of I-RDX coarse and S-RDX coarse in these two solvents are investigated mainly.

I-RDX: insensitive RDX, trademark of Eurenco, France S-RDX or RS-RDX: sensitivity reduced RDX, trademark of Dyno / Chemring



Methodology – instrumentation: ES-ARC[™] and TAM[™]

ARC: adiabatic rate calorimeter Adiabatic self heating h = dT/dt



TAM: Thermal Activity Monitor Isothermal heat flow dQ/dt



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Basics of kinetic descriptions of data

Data obtained are adiabatic self heatrate h(T(t)) isothermal heat flow dQ(t)/dt



Evaluation of data from adiabatic self heating (ARC[™])

Connection between rate of substance change dA(t)/dt with self heatrate h

$$\frac{dA(T(t))}{dt} = -\frac{A(T(0))}{\Delta T} \cdot \frac{dT(t)}{dt} = -\frac{A(T(0))}{\Delta T} \cdot h(T(t)) = -\frac{A(T(0))}{\Delta T_{MS}} \cdot h(T_{MS}(t))$$

$$\frac{dA_{r}(T(t))}{dt} = -\frac{1}{\Delta T} \cdot h(T(t)) = -\frac{1}{\Delta T_{MS}} \cdot h(T_{MS}(t))$$

$$\frac{dA_{r}(T(t))}{dt} = -k_{n,r}(T(t)) \cdot A_{r}^{n}(T(t))$$

$$h(T_{MS}(t)) = k_{n,r}(T(t)) \cdot \Delta T_{MS} \cdot \left(\frac{T_{MS} - T_{MS}(t)}{\Delta T_{MS}}\right)^{n} \quad \text{with } \phi \neq 1$$
reaction of zero order
$$h(T(t)) = k_{0,r}(T(t)) \cdot \Delta T = \frac{k_{0}(T(t))}{A(T(0))} \cdot \Delta T$$

$$\frac{dA_{r}(T(t))}{dt} = -k_{n,r}(T(t)) \cdot \Delta T_{MS} \cdot \left(\frac{T_{MS} - T_{MS}(t)}{\Delta T_{MS}}\right)^{n} \quad \text{with } \phi \neq 1$$
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$$\frac{dA_{r}(T(t))}{dt} = -k_{n,r}(T(t)) \cdot \Delta T_{MS} \cdot \left(\frac{T_{MS} - T_{MS}(t)}{\Delta T_{MS}}\right)^{n}$$

$$\frac{dA_{r}(T(t))}{\Delta T_{MS}} \cdot \Delta T = T_{r} - T(0)$$
The kjr are normalized rate constants, unit is only 1/time

autocatalytic reaction (in first order formulation)

$$\frac{dA_{r}(T(t))}{dt} = -k_{1}(T(t)) \cdot A_{r}(T(t)) - k_{2}(T(t)) \cdot A_{r}(T(t)) \cdot (1 - A_{r}(T(t))) \qquad h(T(t)) = k_{1}(T(t)) \cdot (T_{f} - T(t)) + k_{2}(T(t)) \cdot (T_{f} - T(t)) \cdot (1 - \frac{T_{f} - T(t)}{\Delta T}) + k_{2}(T(t)) \cdot (T_{f} - T(t)) \cdot (T_{f} - T($$

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Typical shape of adiabatic selfheat curves from reaction types

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Basic reaction types and their connection to isothermal heat flow

$$\begin{aligned} & \textbf{Zero Order} \\ & \textbf{A} \xrightarrow{k_0} \textbf{B} + \textbf{C} + (-\Delta H_{R,0}) \\ & \left(\frac{d \textbf{Q}_A(t,T)}{dt} \right) \Big|_T = \textbf{k}_0(T) \cdot (-\Delta H_{R,0}) \\ & \textbf{Q}_A(t,T) - \textbf{Q}_A(0) = \textbf{k}_0(T) \cdot (-\Delta H_{R,0}) \cdot t \\ & \textbf{Q}_{Ar}(t,T) - \textbf{Q}_{Ar}(0) = \frac{\textbf{k}_0(T)}{A(0)} \cdot t \end{aligned}$$

first order

$$A \xrightarrow{k_1} B + C + (-\Delta H_{R,1})$$

$$\left(\frac{dQ_A(t,T)}{dt}\right)\Big|_T = k_1(T) \cdot (-\Delta H_{R,1}) \cdot A(0) \cdot \exp(-k_1(T) \cdot t)$$

$$Q_A(t,T) - Q_A(0) = (-\Delta H_{R,1}) \cdot A(0) \cdot (1 - \exp(-k_1(T) \cdot t))$$

$$Q_{Ar}(t,T) - Q_{Ar}(0) = (1 - \exp(-k_1(T) \cdot t))$$

Second order $A + A \xrightarrow{k_2} B + C + (-\Delta H_{R,2})$ $\left(\frac{dQ_A(t,T)}{dt}\right)\Big|_T = k_2(T) \cdot (-\Delta H_{R,2}) \cdot \left(\frac{1}{A(0)} + k_2(T) \cdot t\right)^{-2}$ $Q_A(t,T) - Q_A(0) = (-\Delta H_{R,2}) \cdot A(0) \cdot \left(1 - \frac{1}{1 + A(0) \cdot k_2(T) \cdot t}\right)$ $Q_{Ar}(t,T) - Q_{Ar}(0) = \left(1 - \frac{1}{1 + A(0) \cdot k_2(T) \cdot t}\right)$



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Example of appearance of autocatalytic decomposition in HFC



Determination of adiabatic self heatrate h with ES-ARC[™]

Measurement quantities are temperature and pressure in a closed system

The part of curve, where the adiabatic selfheating is determined is called also the 'exotherm'

Standard operation of ARC is the heat-wait-search mode



Exotherm data of 8 mass-% I-RDX in cycloh



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Adiabatic self heat rate h and pressure rate of 8 mass-% I-RDX in cycloh



Adiabatic self heat rate h and pressure rate of 8 mass-% I-RDX in gBL



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Adiabatic self heat rate h and pressure rate I-RDX alone



Comparison of I-RDX decomposition alone and in cyclohexanone







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difference recognizable The curves with gBL as solvent are shifted to higher

temperatures by about 17°C (onset) to 25°C in maximum

Evaluation of I-RDX decomp. in cycloh with nth order description



nth order description okay for the high temperature part Order n near 1

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Evaluation of I-RDX decomp. in cycloh with nth order + nth order autocatalytic



Direct analytical determination of RDX decrease

Ageing of RDX-solutions in TAM ampoules. Taking out TAM ampoules after certain time intervals. HPLC analysis of remaining RDX in ampoules



Autocatalytic decrease of RDX concentration in cyclohexanone



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Autocatalytic decrease of RDX concentration in gBL



Modelling with first-order autocatalytic description

$$\begin{array}{ccc} A & \stackrel{k_1}{\longrightarrow} & B + C + S & (-\Delta H_R) & \text{intrinsic decomposition} \\ A + B & \stackrel{k_2}{\longrightarrow} & 2 B + C + S & (-\Delta H_R) & \text{autocatalytic decomposition} \end{array}$$

$$\left. \left(\frac{dA(t,T)}{dt} \right) \right|_{T} = -k_{1}(T) \cdot A(t,T) - k_{2}(T) \cdot A(t,T) \cdot B(t,T)$$

$$Ar(t) = A(t) / A(0)$$

 $k_{1,A}(T) = k_1(T)$ and $k_{2,A}(T) = k_2(T) \cdot A(0)$ and $F=B(0) / A(0)$

$$\left(\frac{dA_{r}(t)}{dt}\right)_{T} = -k_{1} \cdot A_{r}(t) - k_{2} \cdot A(0) \cdot A_{r}(t) \cdot (F + 1 - A_{r}(t))$$

$$Ar(t) = \frac{k_{1,A} + (F+1) \cdot k_{2,A}}{k_{2,A} + (k_{1,A} + F \cdot k_{2,A}) \cdot exp((k_{1,A} + (F+1) \cdot k_{2,A}) \cdot t)}$$

F can be zero

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Modelling with first-order autocatalytic description

$$Ar(t) = \frac{k_{1,A} + k_{2,A}}{k_{2,A} + k_{1,A} \cdot exp((k_{1,A} + k_{2,A}) \cdot t)}$$

$$k_{1,A} \quad \text{intrinsic decomposition}$$

$$k_{2,A} \quad \text{autocatalytic decomposition}$$

substance	k _{1,A} [1/d]	k _{2,A} [1/d]	R ² (COD)
I-RDX in cycloh. 120°C	0.0124 ± 0.004	1.997 ± 0.17	0.99747
I-RDX in gBL, 120°C	0.0043 ± 0.001	1.183 ± 0.05	0.99789
Ratio of rate constants	2.88	1.69	

RDX decomposition in cyclohexanone is much faster than in gBL



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Measurement of heat flow (heat generation rate) dQ/dt with TAM[™] microcalorimeters



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HFC-results from decomposition of I-RDX in cycloh at four temperatures



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HFC-results from decomposition of I-RDX in gBL at three temperatures



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Comparison of HFC-data between I-RDX and S-RDX in cyclohexanone



Comparison of HFC-data between I-RDX and S-RDX in gBL





Comparison of HFC-data between I-RDX in cycloh and in gBL



Strong difference in dQ/dt between the solvents.

The autocatalytic reaction starts in gBL later.

The Q- values are somewhat different

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HFC-results from decomposition of I-RDX in cycloh at 80°C



Evaluation of HFC data with differential iso-conversional description

Program system used was Thermokinetics V 4.23 (TK in short) from company AKTS, Switzerland



Ea and pre-factor In(Z) as function of conversion α : I-RDX in cyclohexanone



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Ea and pre-factor In(Z) as function of conversion α : I-RDX in gBL



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Prediction of isothermal conversion of I-RDX in cycloh, at 90°C to 135°C



Isothermal decomposition conversion calculated with AKTS TK program



Summary and conclusions

RDX decomposes in the solvents cyclohexanone (cych) and gamma-butyrolactone (gBL) With HFC this was recognized experimentally at temperatures as low as 80°C. The decomposition is autocatalytically accelerated.

This is confirmed by the shapes of HFC curves and by direct analysis of RDX decrease with time.

ARC determines also an autocatalytic behaviour, revealed by the special curvatures of the self heat rate.

With ARC the decomposition is seen mainly at higher temperature,

Maximum self heat rates are around 215°C with cych and 235°C with gBL.

The onset of the self heatrate is with gBL about 17°C higher.

gBL is a more stable solvent for RDX.

By extrapolation the significant decomposition in solvent holes in RDX can be reached between 10 and 40 years, depending on the temperature load.

Decomposition pathways: First hints are the formation of triazine type products from RDX. Effect on sensitivity: still an open question.

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Questions ?



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