Concept of a Theoretical Search for the Structure of Energetic Materials with Promising Physicochemical Characteristics

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Conclusions I:

(1,6,7) Some questions should evidently be answered "YES".

(2) What technical limitations are barriers?
I cannot answer.

(3) Should past "failed" candidates be reconsidered for future research investments?
It may turn out to be quite useful.

(4) Are there ideas that can be used to bypass problems with the traditional methods of synthesis?
It will be answered by synthetic chemists.

(5) How can we efficiently screen candidate materials with minimal time/cost investments?
We should trace the entire technological chain of manufacture and application.

(8) What can be done to further explore the link between energy content and sensitivity?
Introduction of non-ballast additives, or phlegmatization, cocrystallization, formation of eutectics, molecular complexes or solid solutions.

(9) Are there new concepts to help address issues with respect to Sensitivity, Compatibility, Shock, Thermal Sensitivity…
From basic theoretical standpoint the answer is "NO".

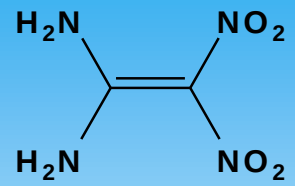
(10) What new predictive methodologies are required to assist screening of promising targets?
My lecture is just an attempt to answer it.

The main physical-chemical characteristics of energetic compounds:

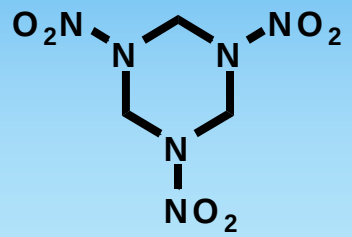
Enthalpy of formation
Molecular crystal density

Thermal stability
Sensitivity
Compatibility
Production cost
etc.

HMX



FOX-7



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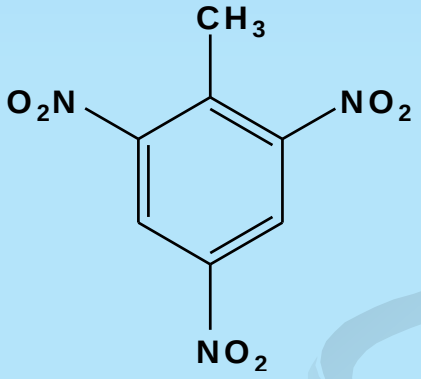

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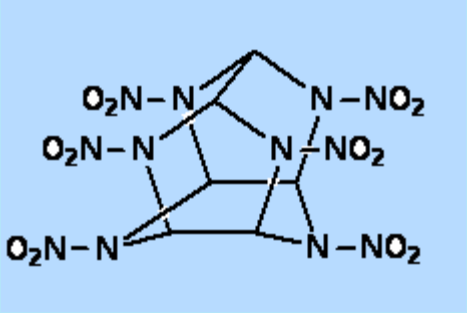

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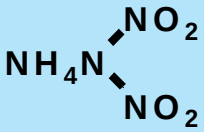

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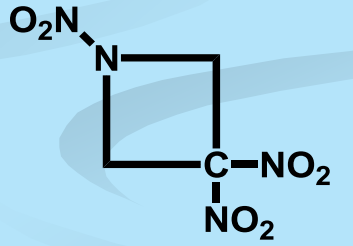

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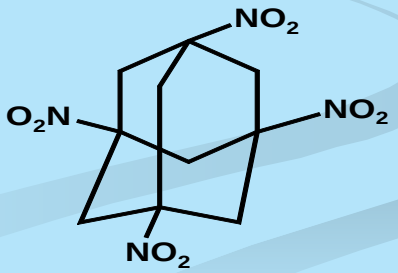

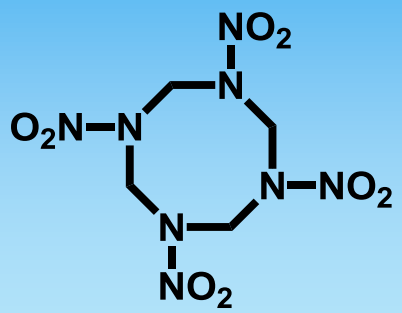

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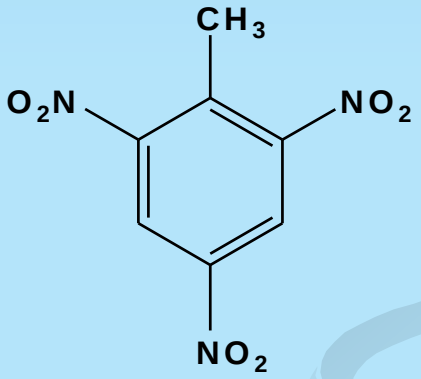

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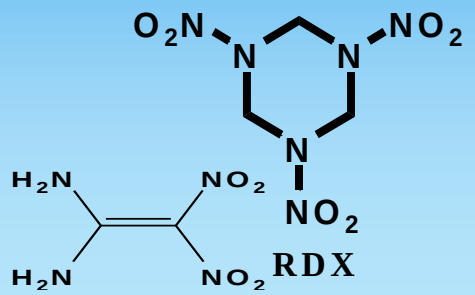
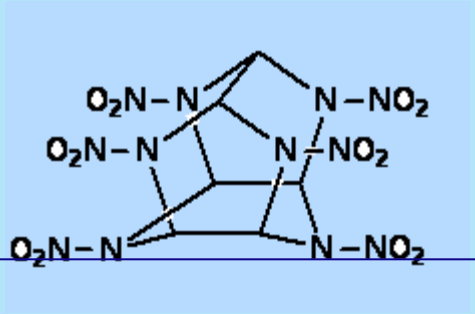
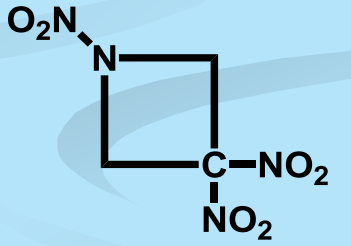


FOX-7



CL-20



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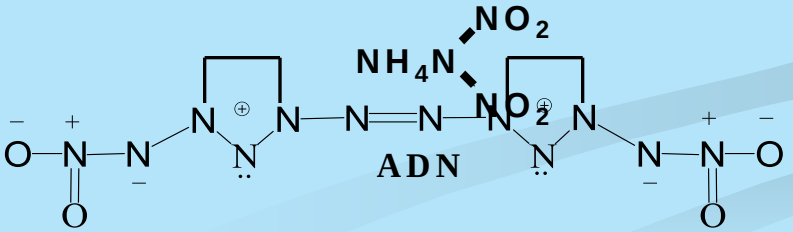
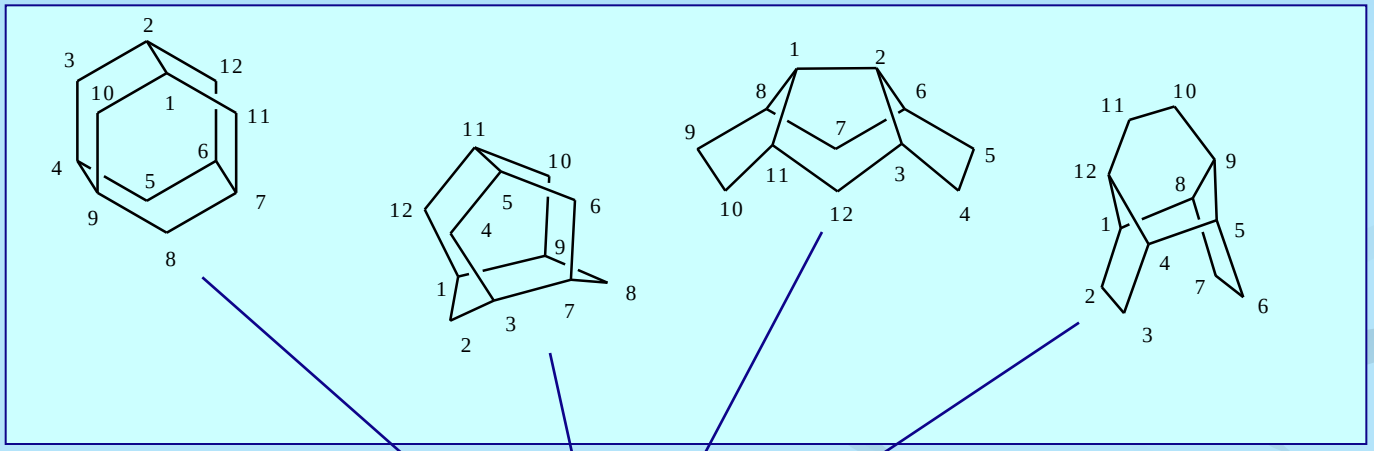


ADN

Molecular design

C_i N_j O_y H_z



Molecular screening

ΔH^0_f, kcal/mol

d, g/cm^3

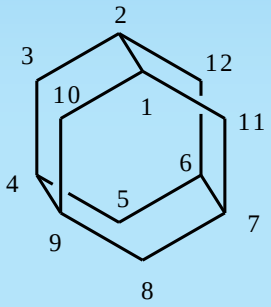
THE QUESTION WAS:

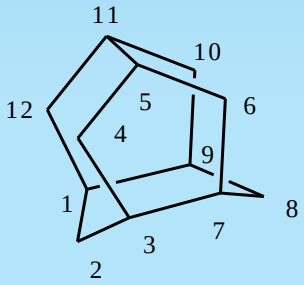
Is 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) the most usable high-energetic compound among caged structures of the same gross formula?

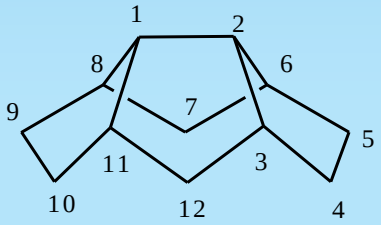
1. Tatyana Pivina, Marina Molchanova, Vladimir Shcherbukhin, and Nikolai Zefirov, *Computer Generation of Caged Frameworks Which Can be Used as Synthons for Creating High-Energetic Materials*, Propellants, Explosives, Pyrotechnics, 19 (1994).

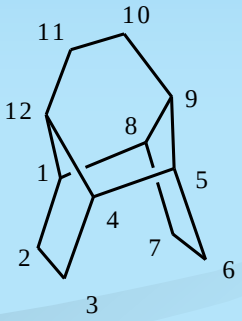
2. Tatyana Pivina, Marina Molchanova, Vladimir Shcherbukhin, and Nikolai Zefirov, *Computer-Assisted Prediction of Novel Target High-Energy Compounds*, Propellants, Explosives, Pyrotechnics, 20 (1995).

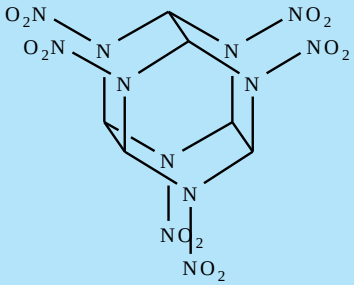
$C_{12}H_{18}$ → **49 caged structures**

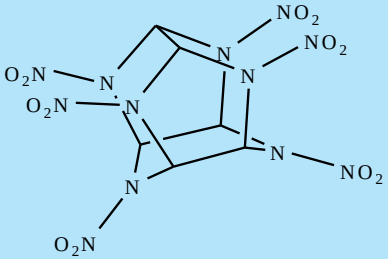


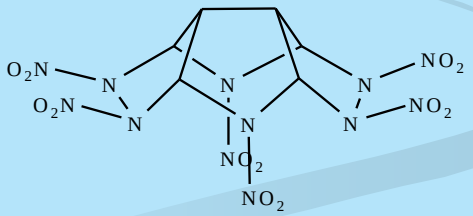


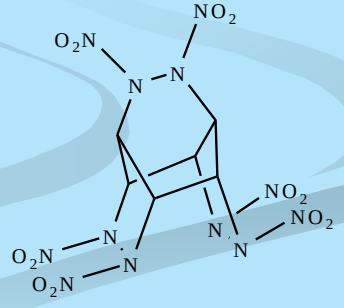


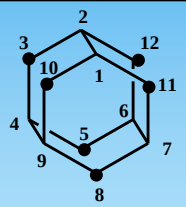
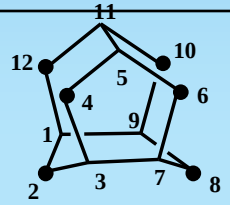
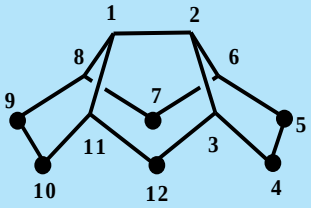
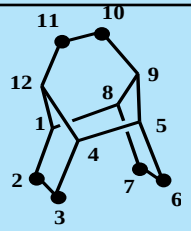










№	Structure Formula*	*d*, g/cm^3	*ΔH$_f$*, *kcal/mol*	*D*, m/s	*Qex*, cal/g	*I*	*P$_{CJ}$*, kbar
1		2,06	89,80	9835	1461	140,6	475
2**		2,00 (2.044)	97,30 (99.30)	9604 (9400)	1468	136,4	445
3		1,98	124,00	9619	1522	136,7	442
4		1,96	169,90	9699	1615	138,2	444

* The circles indicate the positions of NNO2 groups in the hydrocarbon frameworks.

** CL-20.

APPROACHES TO THE ENTHALPY OF FORMATION CALCULATIONS:

(1) Additive, molecular-mechanical, and quantum-chemical methods.
(2) QSPR (Quantitative Structure-Property Relationships).
(3) Artificial Neural Networks.

References:

T.S. Pivina: ***Hierarchy of calculation methods for evaluating and predicting the formation enthalpy of high-energy materials: from chemical intuition to computer chemistry methods,*** **Proc. of the 24th International Annual Conference of ICT, Karlsruhe, Germany, 1993.**

T.S. Pivina, D.V. Sukhachev, F.S. Volk, H.G. Bathelt: ***The theoretical estimating of energy content for energetic compounds in solid state: from additive methods to the QSPR approach,*** **Proc. of the 19th International Pyrotechnics Seminar, New Zealand, 1994.**

T.S. Pivina, D.V. Sukhachev, A.V. Evtushenko, L.I. Khmel'nitskii: ***Comparative characteristics of energy content calculating methods for the furazan series as an example of energetic materials,*** **Propellants, Explosives, Pyrotechnics, № 20, 1995, 5.**

T.S. Pivina, V.V. Shcherbukhin, M.S. Molchanova, N.S. Zefirov: ***Computer-assisted prediction of novel target high-energy compounds,*** **Propellants, Explosives, Pyrotechnics, № 20, 1995, 144.**

N.I. Zhokhova, T.S. Pivina, L.K. Maslova, Yu.N. Matyushin, and A.N. Zefirov: ***Artificial Neural Networks in Energetic Materials Enthalpy of Formations Calculations, Proc. of the 12th Seminar "New Trends in Research of Energetic Materials", Pardubice, Czech Republic, 2009.***

MOLECULAR CRYSTAL DENSITY CALCULATIONS:

Our approach is based on the method of Atom-Atom Potential Functions, developed by my compatriot and teacher Alexander Kitaigorodskii:

The based principles:

(1) Calculation of three-dimensional molecular structure

(2) Searching the crystal space for the possible crystal packings

(3) Assessing the generated structures to rank them in order of likelihood of formation

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A.V. Dzyabchenko, T.S. Pivina, E.A. Arnautova: Prediction of structure and density for organic nitramines, J. of Molecular Structure, 374, 1996, 137-145.

T.S. Pivina, M.S. Molchanova, E.A. Arnautova, and N.S. Zefirov: Computer search for the structure of high-density energetic compounds among hydrogen-free heterocycles, Proc. of the 24th International Pyrotechnics Seminar, Monterey, CA, 1998, 433-443.

Problem of Energetic Materials (EM-s) Decomposition

Formulation of Possible Schemes of Chemical Transformations

Thermodynamic and Kinetic Characteristics Investigations

The aim:

Development of the Methodology, Algorithms and Computer Program for *ab initio* Generation of a Whole Spectrum of the EM-s Decomposition Reactions

Tasks:

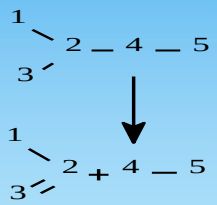
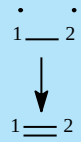
I. *Creation of the data base on mechanisms of Nitrocompounds decomposition.*

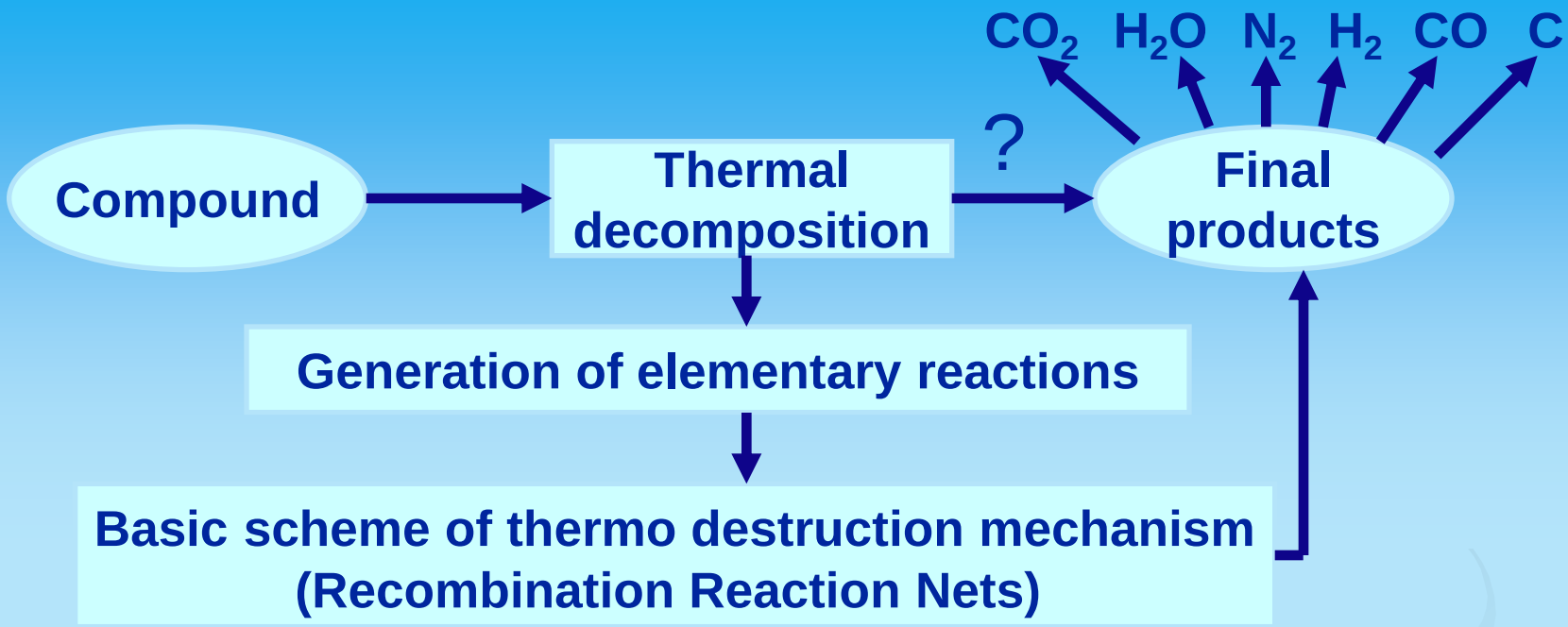
II. *Formalisation of structure-thermal decomposition mechanisms of different chemical classes compounds.*

III. *Differentiation of Nitrocompounds due to mechanisms of their decay.*

IV. *Computer simulation of Nitrocompounds decomposition mechanism to estimate the capability of the suggested methodology.*

Examples of the "If-Then" principles for the simulation of thermal decomposition reactions of nitro compounds.

Rule #	Graph	Description	Mode	Setting: Atom	Property	Relation	Value	Operation
1		HNO_2 elimination	transformation	1	atom type	=	C	no
					hetero atoms	=	1	BD
					hybridization	=	sp^3	BD
				2	atom type	=	C,N	no
				3	the same	=	C	no
					hetero atoms	=	1	BD
					hybridization	=	sp^3	BD
					atoms H	>	0	BD
				4	atom type	=	N	no
					charge	=	-1	set equal to 0
				5	atom type	=	O	no
					charge	=	-1	set equal to 0
2		closure of vicinal biradicals	stabilization	1	UE	≥	1	change to -1
				2	UE	≥	1	change to -1
3		non-vicinal biradicals	exclusion	1	valence	<	2	BD
					UE	>	1	no
				2	valence	<	2	BD
					UE	>	1	no



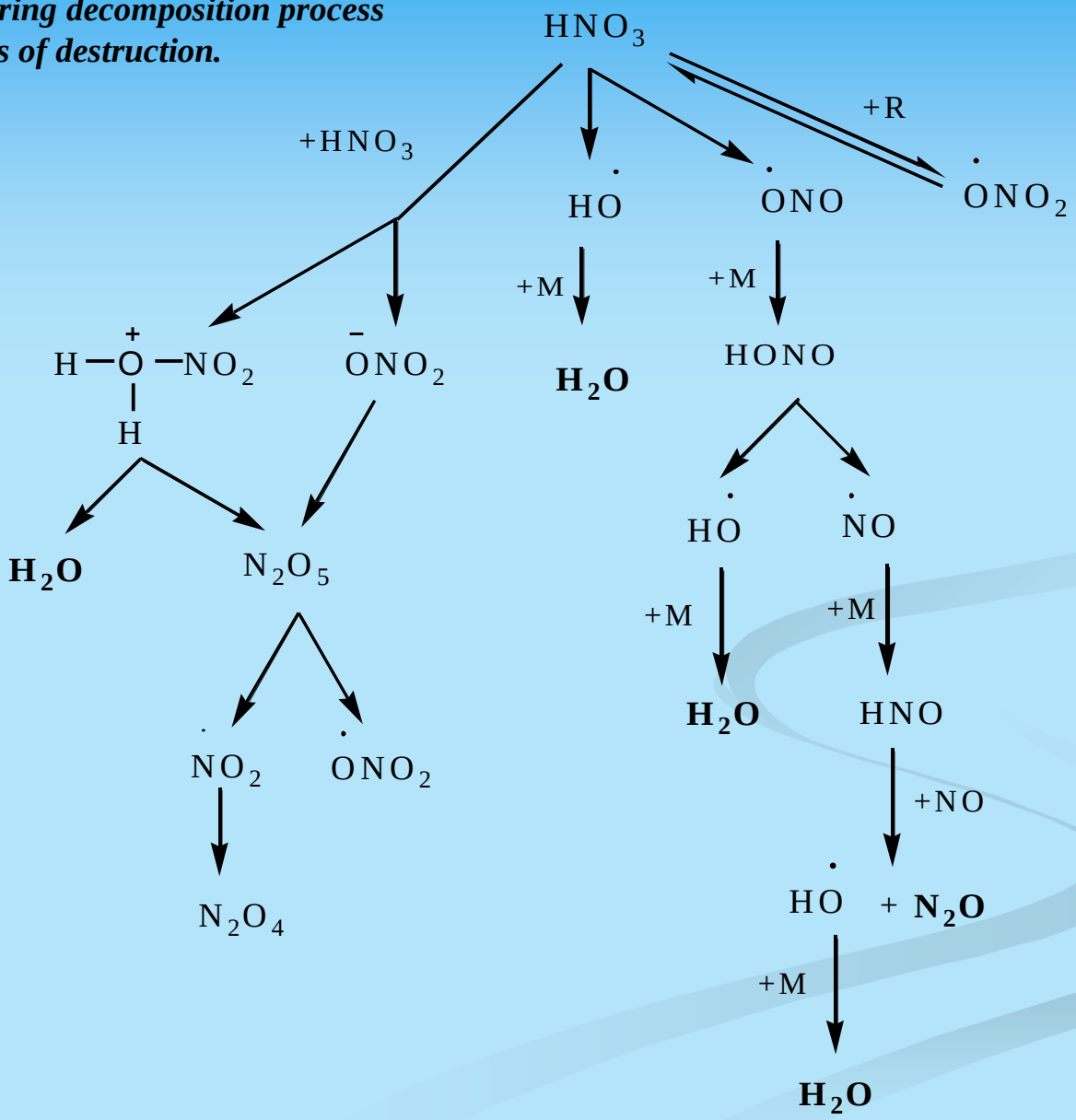
1. Basing on up-to-date experimental data a set of semi-empiric rules was formulated.

2. The rules were used for building of Recombination Reaction Nets (RRN) composed of intermediates and initial compounds.

3. Further estimations of the most favorable decomposition pathways were carried out on the basis of quantum chemistry methods calculations.

CASB (Computer Assisted Structure Building):

the computer simulation of different processes in chemistry, simulation the whole spectrum of reactions that are possible during decomposition process at the different steps of destruction.



Nitric acid decomposition mechanism computer simulation

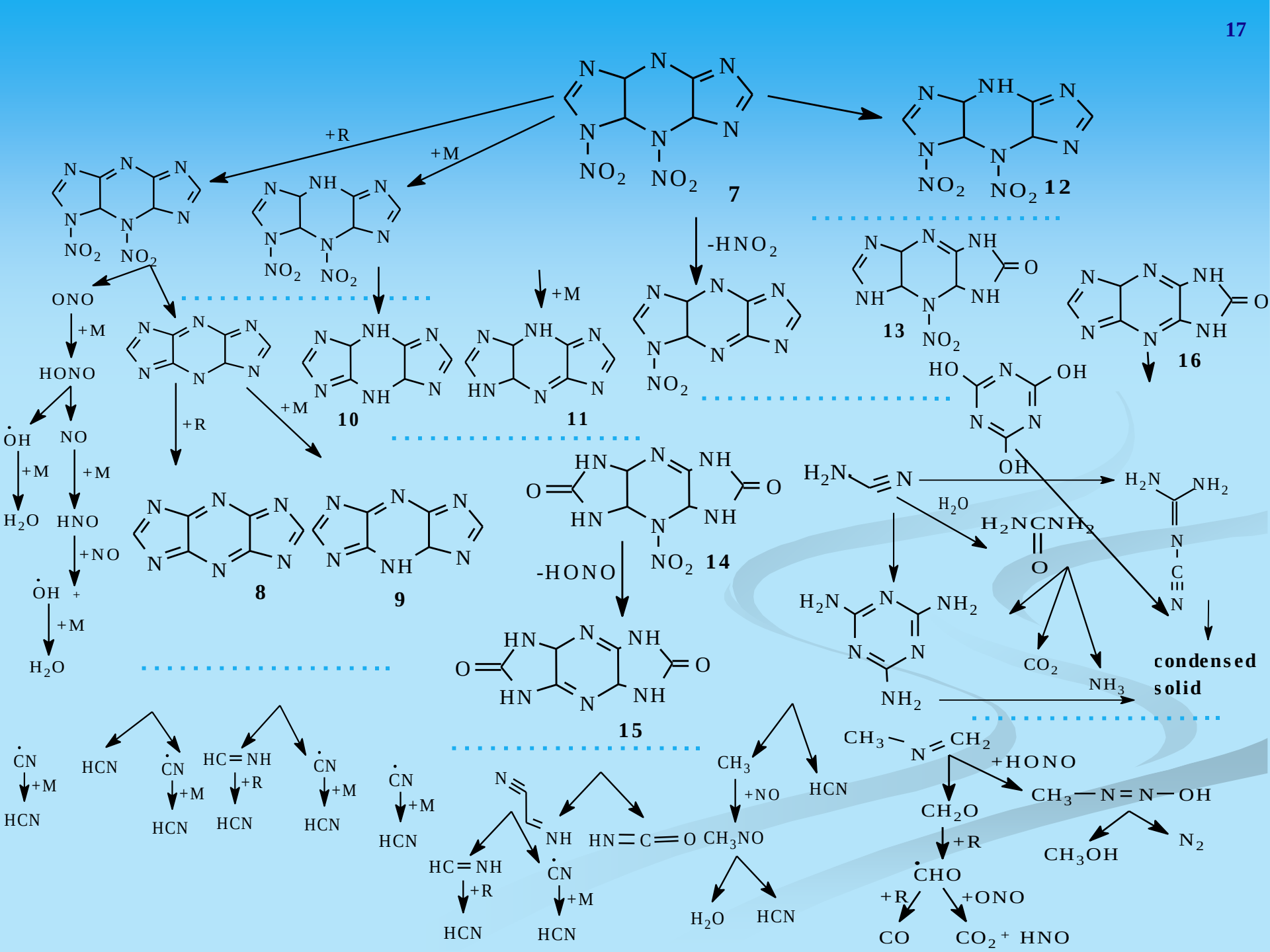
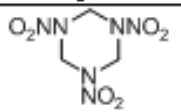
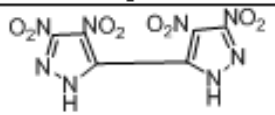
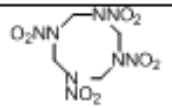
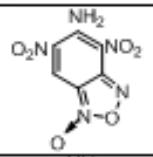
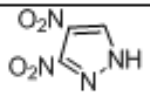
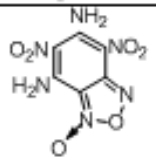
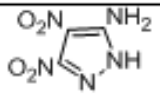
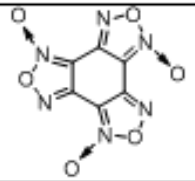
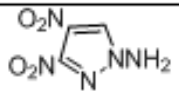
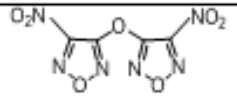
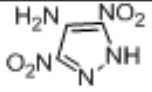
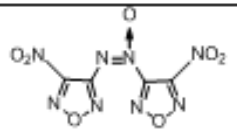

+R
+M
7
12
-HNO2
13
16
ONO
+M
HONO
10
11
+M
+R
+M
OH
NO
+M
+M
H2O
HNO
+NO
OH
+
+M
H2O
8
9
14
-HONO
15
H2O
H2NCNH2
O
CO2
NH3
condensed solid
CN
+M
HCN
HCN
CN
+M
HCN
HC=NH
+R
HCN
CN
+M
HCN
CN
+M
HCN
NH
HN=C=O
HC=NH
+R
HCN
CN
+M
HCN
CH3
+NO
HCN
CH3NO
H2O
HCN
CH3—N=CH2
+HONO
CH2O
+R
CHO
+R
CO
+ONO
CO2 + HNO
CH3—N=N—OH
CH3OH
N2

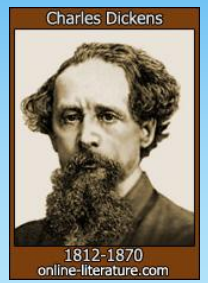
Table. Calculated (QSPR) and Experimental Values of the (Δcr) for Nitro Compounds.

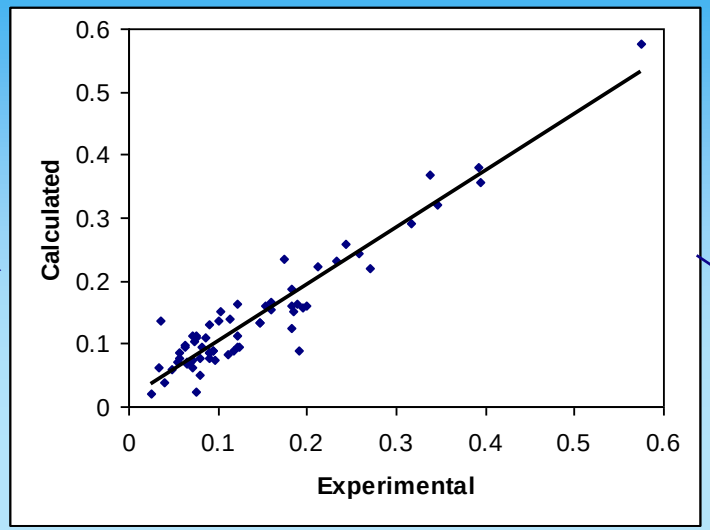
№	Compound	Molecular formula	$2\cdot\Delta_{cr}$ [μcm] exp.	$2\cdot\Delta_{cr}$ [μcm] calc.	№	Compound	Molecular formula	$2\cdot\Delta_{cr}$ [μcm] exp.	$2\cdot\Delta_{cr}$ [μcm] calc.
1		$C_3H_6N_6O_6$	52	48	7		$C_6H_2N_8O_8$	70	69
2		$C_4H_8N_8O_8$	68	60	8		$C_6H_3N_5O_6$	44	48
3		$C_3H_2N_4O_4$	93	80	9		$C_6H_4N_6O_6$	177	174
4		$C_3H_3N_5O_4$	--	261	10		$C_6N_6O_6$	21	16
5		$C_3H_3N_5O_4$	--	49	11		$C_4N_6O_7$	--	24
6		$C_3H_3N_5O_4$	115	116	12		$C_4N_8O_7$	--	8

German Afanas'ev, Tatyana Pivina, Dmitrii Sukhachev, PEP, 18, 309, 1993.

Correlation between the calculated and experimental values of 1/Ees obtained for the training set of compounds (Artificial Neural Networks model)

From “Great Expectations”
(not by Charles Dickens)





to “Lost Illusions”
(not from Honore de Balzac)

Some Experimental and (ANN)-calculated E_{es} ((J) RDAD) parameter of energetic materials

№	Chemical name	E_{es}, J (calc.)	E_{es}, J (exp.)
1	Pentaerythritol tetranitrate	1.74	1.74
2	1,3,5-Trinitro-1,3,5-triazacyclohexane	11.69	2.49
3	1,3-Dichloro-2,4,6-trinitrobenzene	2.63	2.55
4	2,2',4,4',6,6'-Hexanitrodiphenylsulfide	2.80	2.54
5	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	3.11	2.89
6	Hexanitrohexaazaisowurtzitane	8.85	4.70
7	2,6-Di(picrylamino)-3,5-dinitropyridine	7.23	8.90
8	2,4,6-Trinitro-2,4,6-triazaheptane	10.53	8.08
9	1,3-Dinitrobenzene	3.44	3.15
10	1,4,5,8-Tetranitro-1,4,5,8-tetraazadecaline	6.65	5.43

T. Pivina, N. Zhokhova, L. Maslova, A. Smirnov, and S. Smirnov: *Proc. of the EUCASS-2009 (European Conference for Aero-Space Sciences), Versailles, France, July 6-9, 2009.*

*Electric spark sensitivities E*es (J): RDAD and (mJ) ESZ KTTV instruments*

Chemical name	(J)	Ref.	(mJ)	Ref.
1,3-Dinitrobenzene	3.15	1	256.7±14.4	2
1,4-Dinitrobenzene	18.38	1	403.3±14.4	2
1,3,5-Trinitrobenzene	6.31	3	108.2±7.8	2
2,4-Dinitroaniline	40.88	1	--	
1-Hydroxy-2,4-dinitrobenzene	13.28	3	--	
1-Amino-2,4,6-trinitrobenzene	6.85	3	156.7±7.2	2
1-hydroxy-2,4,6 trinitrobenzene	9.98	1,3	115.5±6.8	2

** E_{es} – sensitivities to electric spark required for 50% initiation probability.*

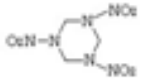
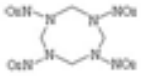
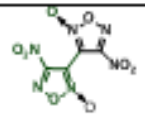
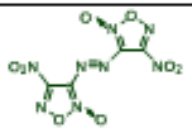
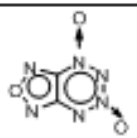
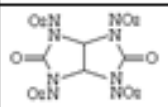
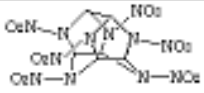
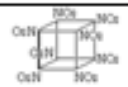
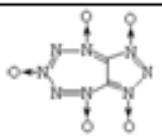
References:

[1] V. ZEMAN, J. KOČÍ, S. ZEMAN: *Spark Sensitivity of Polynitro Compounds. Part II. A Correlation with Detonation Velocities of some Polynitro Arenes,* HanNeng CaiLiao, No. 7, p. 127-132, 1999.

[2] S. ZEMAN, J. MAJZLÍK, and J. KOČÍ: *Spark Sensitivity of Polynitro Arenes. Part II. A Comparison of Two Instruments*, Central European Journal of Energetic Materials, No. 4(3), p. 15-24, 2007.

[3] J. KOČÍ, S. ZEMAN: *Spark Sensitivity of Polynitro Compounds. Part IV. A Relation to Thermal Decomposition Parameters*, HanNeng CaiLiao, No. 8, p. 18-26, 2000.

Table. The main parameters of some powerful explosives.

№	Compound	α	ρ_0, g/cm^3	ΔH_f^0 kJ/kg	Q_{vol} kJ/kg	D, m/s	P_{CJ}, GPa	η, %	P_{cr}, GPa
1	 **RDX**	**0.67**	**1.816**	**276.1**	**5564**	**8600**	**32.7**	**96.7**	**2.05**
2	 **HMX**	**0.67**	**1.907**	**251.0**	**5523**	**9100**	**36.1**	**100**	**2.4**
3	 **DNDF**	1.00	1.962	1606	7238	9450	43.9	107.8	0.2
4	 **ANF**	1.00	2.000	2320	7280	9700	40.6	110.3	0.2
5	 **FDTO**	0.75	1.852	4184	7530	9600	40.3	106	0.3
6	 **Sorguyl**	1.03	2.030	75.3	5440	9260	39.7	102	1.3
7	 **CL-20**	0.80	2.040	8.7	5857	9460	42.8	105.9	1.6
8	 **ONC**	1.00	1.982	937	7271	9350	39.0	108.2	0.9
9	 **GATO**	1.25	2.200	3170	6700	10800	53.0	119.0	0.4
10	 **OATE**	--	1.810	6200	6200	9950	42.0	99.0	0.4

A. Smirnov, D. Lempert, T. Pivina, D. Khakimov, Proc. of the14-th International Seminar "NTREM 2011", Pardubice, the Czech Republic, April 13-15, 2011.

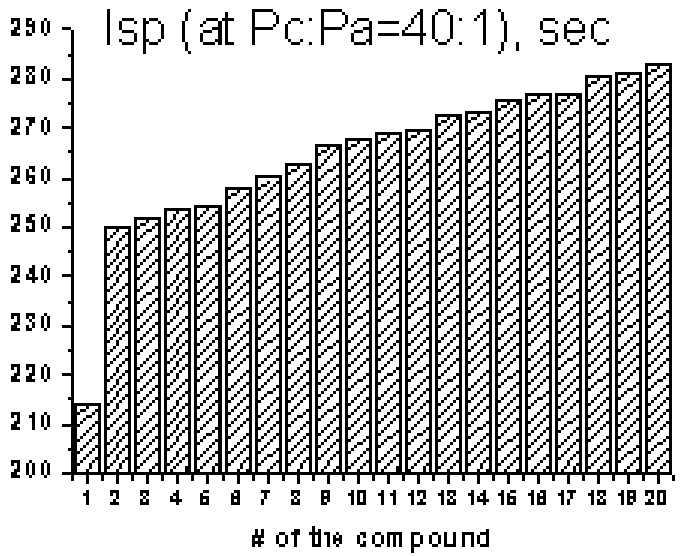


Fig. I_{sp} values (at pressure in the combustion chamber and in the exit nozzle section being 40:1 atm, respectively) for optimal mixture of the oxidizer with hydrazine.

1.
2.
3. NH_4ClO_4
4.
5.
6.
7. $(NO_2)_2\bar{N}\ NH_4^+$
8. NH_4ClO_5
9.
10.
11.
12.
13.
14.
15.
16. $O_2NN\left[CH_2C(NO_2)_2NF_2\right]_2$
17.
18. NO_2ClO_4
19.
20.

A. Smirnov, D. Lempert, T. Pivina, D. Khakimov, Proc. of the14-th International Seminar "NTREM 2011", Pardubice, the Czech Republic, April 13-15, 2011.

Summary

The extreme parameters of the (C,N,O) content explosives:

- monocrystal density close to 2.2 g/cm3,
- enthalpy of formation equal 6000 kJ/kg or so,
- heat of explosion ~7800 kJ/kg,
- detonation pressure 50÷60 GPa,
- acceleration ability (m-40) ~110÷120% (in comparison with HMX).

However all these explosives would have unacceptable safety properties:

- shock sensitivity (1.5÷5 kbar),
- critical thickness of detonation from a few mcm up to 50 mcm.

The estimation of performances for nitrogen allotropes (Nx) of very different structure shows that the most probable properties are the following:

- density ~2.0 g/cm3,
- enthalpy of formation (this time it is equal to the explosion heat) 6800 kJ/kg,
- detonation pressure ~50 GPa,
- acceleration ability (m-40) ~100÷110%/

Conclusions:

(I) Strategy in the field of energetic materials should not consist only in predictions. It should determine the future alternatives.

(II) The increasing uncertainties and risks, the technological problems require elaboration of a realistic and qualitative development strategy.

(III) Expert groups should elaborate the prospects of development via numerous polls, dialogs, and “brainstorms”.

(IV) The results should be structured so that it would be possible to make decisions.

(V) The necessary prerequisite for the foresight is sustainable feedback between the “strategists” and “experimentalists” at all stages.

Some statements are used from N. Krichevskiy's paper “Foresight”.