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Calculation of Thermochemical and Explosive Characteristics of Furoxanes

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Abstract: Search of high-power energetic materials is one primary line of development of chemical physics of combustion and explosion.
Yield of such materials is usually very small, and its cost is very high. Calculation of unknown characteristics and properties is the only way out from this situation. There are different methods today that allow calculating unknown detonation performance and some of physicochemical properties.
Examination of calculated detonation performance of furoxanes and benzofuroxanes compounds that are not enough investigated is presented in this work. These compounds are new high-power energetic materials. Influence of error in enthalpy of formation of these compounds on their detonation performance is also examined in this work.
Furoxanes plays particular part among energetic materials. They are convenient blocks of molecules of high-power energetic materials. Joining of explosiphorus clusters of atoms are lead to obtaining of number of high-performance compounds. It is caused by flatten structure of furoxane ring, that lead to high density of compounds and are characterized by high and positive value of enthalpy of formation.
Detonation performance of furoxanes was not study practically. That is why 10 furoxanes have been chosen as object of study (see Nomenclature). 7 of 10 studied furoxanes have anomalous elemental composition, because they are hydrogen-free. In order to evaluate possible error in computational detonation performance, explosive characteristics of 6 hydrogen-free energetic materials with known experimental data have been calculated.

Keywords: furoxanes, benzofuroxanes, high-power energetic materials, heat of detonation, detonation velocity, detonation pressure

Calculation Method

All calculations have been performed by SD program that had been developed at Mendeleev University of Chemical Technology of Russia [1]. Conformity of SD code was examined repeatedly [2]. Influence of error in enthalpy of formation of these compounds on their detonation performance is also examined in this work. For that enthalpies of formation of all compounds examined in this work have been calculated by the quantum-chemical semiempirical method PM3 with the Gamess software [3]. All computed values of enthalpies of formation have been compared with experimental one and used in calculation by SD program. All computed values of detonation velocity and pressure have been compared with ones that were calculated in work [4].

Results and Discussion

Properties of furoxanes and benzofuroxanes that were calculated by means of the method [4] were described in paper [4]. In this paper we present the results of calculation of pressure, temperature and velocity of detonation, composition of detonation products and heat of explosion by means of the method [1].

Table 1. Comparison of experimental and calculated detonation parameters of hydrogen-free energetic materials

Compaund	Gross-formula	ρ_0, g/cm^3	ΔH_f^0, kJ/mol		D_{exp}, km/s	D_{calc}, km/s		
			Lit.	PM3		[4]	SD	SD*
Tetranitromethane	CN_4O_8	1.64	37.0	22.0	6.40	6.45	6.31	6.272
Hexanitroethane	$C_2N_6O_{12}$	1.86	83.6	108.3	7.58	7.54	7.23	7.261
Benzotrifuroxane	$C_6N_6O_6$	1.901	583.0	808.6	8.62	8.70	8.71	8.959
Hexanitrobenzol	$C_6N_6O_{12}$	2.00	200.0	181.84	9.50	9.63	8.99	8.979
Trinitrotriazido-benzol	$C_6N_{12}O_6$	1.74	1136.0	1025.8	8.58	8.63	8.59	8.486
Cyanurtriazid	C_3N_{12}	1.15	918.1	751.4	5.60	5.65	6.14	5.868

*- Detonation parameters have been calculated with using enthalpies of formation that have been calculated by PM3 method.

In order to evaluate possible error in computational detonation performance, explosive characteristics of 6 hydrogen-free energetic materials with known experimental data have been calculated (data are collected in Table 1). Difference between experimental results and calculated one by both methods [1] and [4] have

been compared. The literature data [4] for enthalpies of formation of considered compounds as well as values obtained by PM3 method are set up in Table 2.

Table 2. Literature and evaluated enthalpies of formation of investigated compounds

Compound number	ρ, g/cm^3	ΔH_f, kJ/mol	
		Lit.	PM3
1	2.002	670.3	695.97
2	1.96	422.9	501.45
3	1.7	1314.0	1272.6
4	1.71	260.4	238.31
5	1.93	692.2	732.34
6	1.945	637.1	572.43
7	1.906	307.4	453.17
8	1.85	348.6	511.67
9	1.88	203.7	135.76
10	1.915	233.1	363.41
11	1.92	357.0	588.41
12	1.98	83.6	331.75
13	1.87	383.0	600.47
14	1.91	175.1	348.070
15	1.99	104.5	347.03

*- Detonation parameters have been calculated with using enthalpies of formation that have been calculated by PM3 method.

Detonation performance of furoxanes and benzofuroxanes computed by means of SD code are presented in Table 3. For comparison, the results that were published in work [4] are also quoted.

Evidently, values of detonation performance calculated by means of SD program and data of work [4] are quite close. Difference is 3.6% for detonation velocity and 4.9% for detonation pressure. Unfortunately, computational heat of detonation data are absent in paper [4]. As one can see from Table 3, deviations in calculated enthalpy of formation from experimental values reveal small influence on evaluated detonation performance of considered compounds. Average range of error in enthalpy of formation is about 25%. However, even these quite remarkable errors in values of enthalpy of formation bring no important influence on obtained values of detonation velocity and pressure. The differences in values of enthalpy of formation regain on obtained values of heat of detonation. It should be noted that many furoxanes have very high detonation performances.

Detonation performance is higher than HMX one.

Table 3. Calculated detonation parameters

Compound number	D_{calc}, km/s			P_{calc}, GPa			Q_{Vcalc}, kJ/kg	
	[4]	SD	SD*	[4]	SD	SD*	SD	SD*
1	10.098	9.44	9.463	47.6	45.89	46.35	7692	7773
2	9.65	9.136	9.212	42.4	41.21	42.03	7556	7831
3	9.136	8.897	8.849	36.5	35.45	34.95	7337	7204
4	7.845	7.869	7.832	24.8	26.42	26.06	5731	5615
5	9.676	9.274	9.327	44.8	42.72	43.35	7754	7931
6	9.845	9.324	9.24	48.3	43.79	42.56	7801	7541
7	9.498	8.887	9.07	42.6	38.40	40.48	6771	7320
8	8.987	8.908	9.032	35.1	37.14	38.56	7027	7446
9	9.163	9.032	8.953	37.7	38.17	37.3	7781	7478
10	8.811	8.611	8.72	34.9	34.08	35.48	6478	
11	8.776	8.737	8.986	33.2	35.18	37.84	6197	7066
12	8.793	8.920	9.178	31.9	36.80	39.79	5310	6253
13	8.64	8.371	8.74	45	31.72	35.15	6452	7392
14	8.44	8.682	8.906	34.7	31.88	34.33	5367	6226
15	9.16	8.873	9.11	39.9	37.69	40.49	6009	6819

*- Detonation parameters have been calculated with using enthalpies of formation that have been calculated by PM3 method.

Explosive DNAF (see Nomenclature) attracts special attention. Detonation velocity computed with maximum density $\rho = 2.002$ g/cm^3 is D = 9.44 km/s. Experiment [5] showed that real density of DNAF was lower than maximum one ρ=1.94 g/cm^3. Detonation velocity measured at real density is D = 9.7 km/s and heat of explosion is Q_v = 7450 kJ/kg [5]. We have calculated detonation velocity and heat of detonation of DNAF at real density $\rho = 1.94$ g/cm^3. Results of our calculations are D = 9.251 km/s, Q_V = 7665 kJ/kg. Differences between experimental values are several percents: ΔD= 4.6% for detonation velocity and ΔQ_v = 2.9% for heat of explosion.

It should be noted that in algorithm of both calculating methods [1] and [4] lays physically valid state equations of compounds under ultrahigh pressure (several tens GPa). Difference between detonation performances calculated by both methods is quite low. Computed detonation performances of hydrogen-free energetic materials and DNAF are close to experimental values.

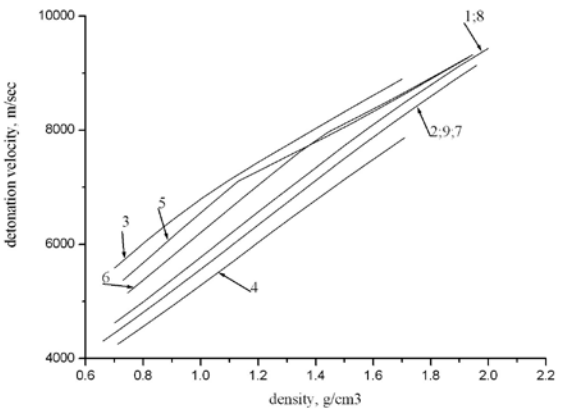


Figure 1. Detonation velocity as function of density for some furoxanes. Numerations in this column coincide with numeration in the table that is situated in the nomenclature issue.

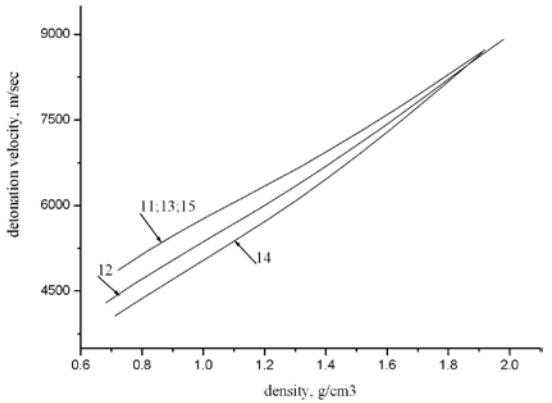


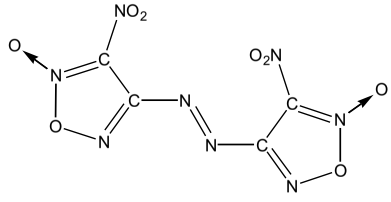
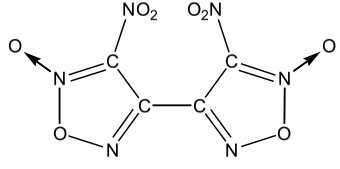
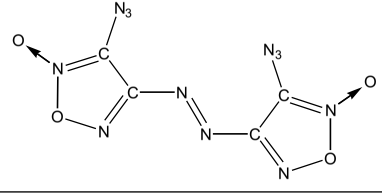
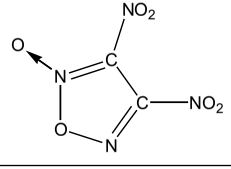
Figure 2. Detonation velocity as function of density for benzofuroxanes. Numerations in this column coincide with numeration in the table that is situated in the nomenclature issue.

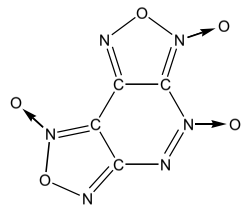
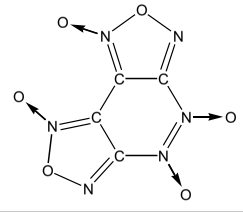
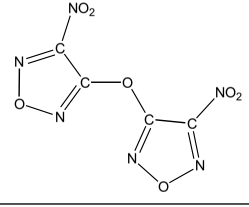
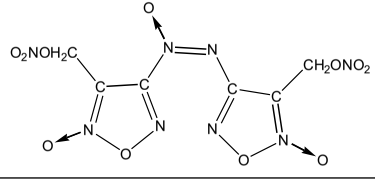
Conclusions

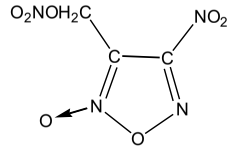
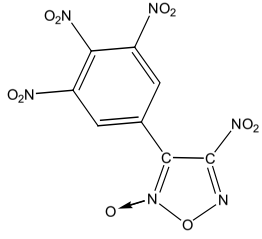
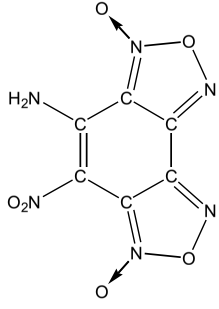
The results obtained in the paper have shown that furoxanes and benzofuroxanes are new high-power energetic materials. Their detonation performances are higher than HMX one. Deviation of calculated enthalpy of formation from experimental value has no influence on error of calculated detonation properties.

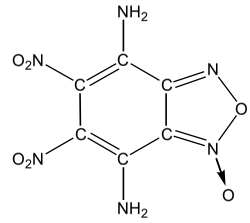
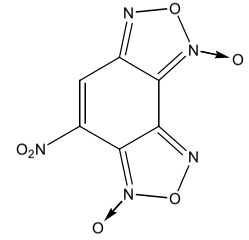
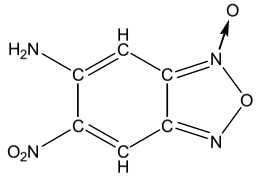
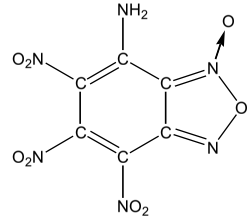
Nomenclature

Structural schemes, chemical formulas and names of considered compounds

No.	Formula	Gross-formula	Name
1		$C_4N_8O_8$	3,3'-diazene-1,2-diylbis-(4-nitro-1,2,5-oxidizole)-5,5'-dioxide Abbreviation: DNAF
2		$C_4N_6O_8$	4,4'-dinitro-3,3'-bi-1,2,5-oxidiazole-5,5'-dioxide
3		$C_4N_{12}O_4$	3,3'-diazene-1,2-diylbis-(4-azido-1,2,5-oxidizole)-5,5'-dioxide
4		$C_2N_4O_6$	3,4-dinitro-1,2,5-oxidiazole-5,5'-2-oxide

5		$C_4N_6O_5$	bis[1,2,5]oxidiazolo[3,4-c;3',4'-e]piridazin-1,5,6-trioxide
6		$C_4N_6O_6$	bis[1,2,5]oxidiazolo[3,4-c;3',4'-c]piridazin-1,4,5,8-tetraoxide
7		$C_4N_6O_7$	3,3'-oxibis-(4-nitro-1,2,5-oxidiazole)
8		$C_6H_4N_8O_{11}$	3,3'-diazeneoxide-1,2-diylbis-(4-nitroximethyl-1,2,5-oxidizole)-5,5-dioxide

9		$C_3H_2N_4O_7$	3- nitroximethyl-4nitro-1,2,5-oxidiazole-5,5'-dioxide
10		$C_8H_2N_6O_{10}$	4-nitro-3-(3,4,5-trinitrophenyl)-1,2,5-oxidiazole-2-oxide
11		$C_6H_2N_6O_6$	Aminonitrobenzofuroxane

12		$C_6H_4N_6O_6$	4,7-diamino—5,6-dinitrobenzouroxane
13		$C_6HN_5O_6$	5-nitro[1,2,5]oxidiazolo[3,4-e][1,2,3]benzoxadizole-1,6-dioxide
14		$C_6H_4N_4O_4$	6-amino-5-nitrobenzouroxane
15		$C_6H_2N_6O_8$	7-amino-4,5,6-trinitrobenzouroxane

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