

COMBUSTION, EXPLOSION,
AND SHOCK WAVES

Energy Abilities of Certain Derivatives of 1,2,4,5-Tetrazine *N*-Oxides as Components of Solid Composite Rocket Propellants

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Abstract—The energy capabilities of five real-life high-enthalpy derivatives of 1,2,4,5-tetrazine *N*-oxides as components composite solid rocket propellants (CSRPs), which do not contain metallic fuel, are considered. Various ways of reducing the combustion temperature of CSRPs to an acceptable value, if necessary, are studied.

Keywords: 1,2,4,5-tetrazine *N*-oxides, *s*-tetrazine *N*-oxides, 6-aminotetrazolo[1,5-*b*][1,2,4,5] tetrazine 2,5-dioxide, 3,6-diazido-1,2,4,5-tetrazine 1,4-dioxide, 6-amino-3-nitro[1,2,4]triazolo[4,3-*b*][1,2,4,5]tetrazine 7-oxide, composite solid propellant, CSRП, oxidizer, specific impulse, effective impulse

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INTRODUCTION

The aim of this study is to study the possibility of using some derivatives of 1,2,4,5-tetrazine *N*-oxides (I–V [1–6], Fig. 1) as components of composite solid rocket propellants (CSRPs). All five compounds have actually been synthesized and their structures have been proven by various methods, including X-ray diffraction analysis.

1,2,4,5-Tetrazine *N*-oxides (*s*-tetrazine *N*-oxides) are a relatively poorly studied subclass of high energy

heterocycles [1–13], the first representatives of which were described in 1993 [3]. Over the past 5–6 years, the intensity of works in this direction has sharply increased: during this period, eight articles were published, including 4 in 2019.

The main interest in *s*-tetrazine *N*-oxides is related to the prospect of their use as explosives. This is facilitated by the reduced proportion of carbon and hydrogen due to the high proportion of nitrogen and oxygen, high enthalpies of formation, and indicators α (the coefficient of providing the molecule with oxygen)

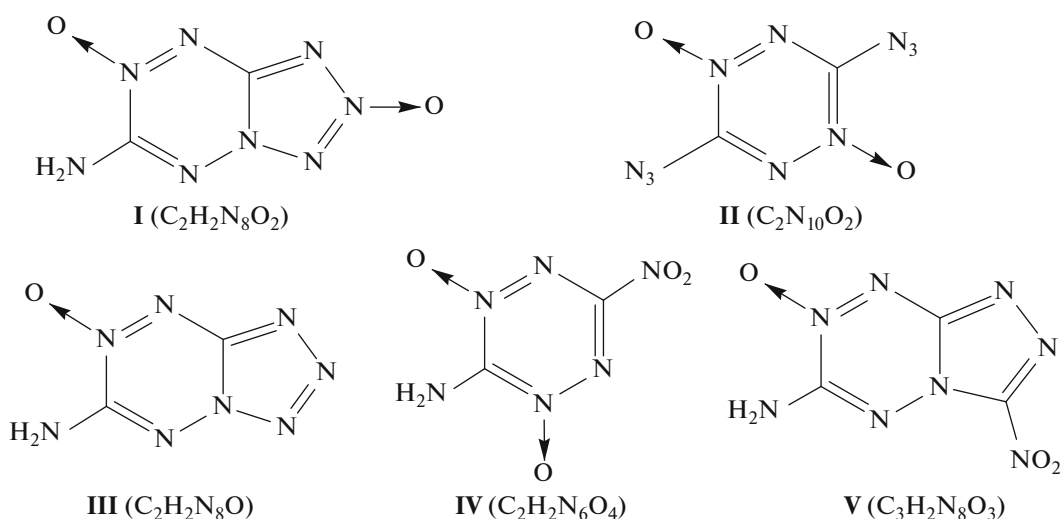
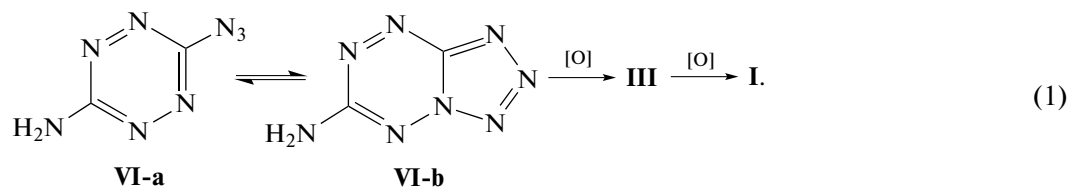


Fig. 1. Structural formulas of compounds I–V: I, 6-aminotetrazolo[1,5-*b*][1,2,4,5]tetrazine 2,5-dioxide [1]; II, 3,6-diazido-1,2,4,5-tetrazine 1,4-dioxide [1]; III, 6-aminotetrazolo[1,5-*b*][1,2,4,5]tetrazine 5-oxide [2]; IV, 3-amino-6-nitro-1,2,4,5-tetrazine 1,5-dioxide [3–5]; V, 6-amino-3-nitro[1,2,4]triazolo[4,3-*b*][1,2,4,5]tetrazine 7-oxide [6].

higher than *s*-tetrazine. *s*-Tetrazine *N*-oxides were not previously considered as potential components of CSRPs.

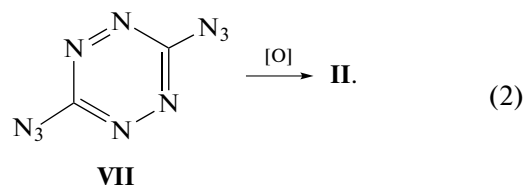
The obvious gain in the elemental composition during the oxidation of *s*-tetrazines into mono- and di-*N*-oxides is accompanied by an additional and completely unexpected bonus: a decrease in the sensi-

tivity of their azide derivatives (or tautomeric bicyclic tetrazolo[1,5-*b*][1,2,4,5]tetrazines) to mechanical stress. Thus, the oxidation of 3-amino-6-azido-1,2,4,5-tetrazine (**VI-a**), which exists in the crystal in the bicyclic form **VI-b**, into compound **III** (reaction (1)) leads to a sharp decrease in impact sensitivity (IS) from 1.5 to 10 J [2].

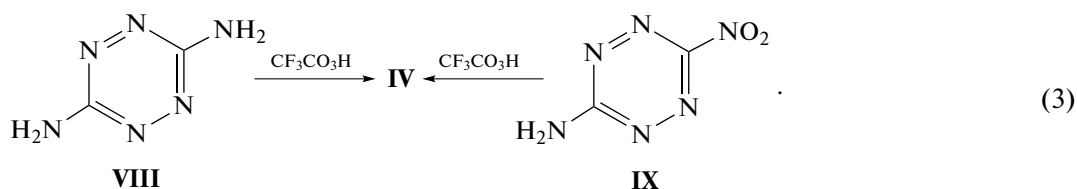


The deeper oxidation of compound **III** by the powerful oxidizing agent HOF goes through the tetrazole cycle with the formation of compound **I** (the last stage of reaction (1)), the IS = 6 J [1] of which, although it increased in comparison with compound **III** (IS = 10 J [1]), decreased in comparison with compound **VI** by a factor of four. It is curious that oxidation in the tetrazole cycle ends, for compound **I**, the possibility of reverse azido-tetrazole tautomerism, an example of which is the interconversion of tautomers **VI-a** and **VI-b** (reaction (1)).

A similar decrease in IS was observed upon the oxidation of 3,6-diazido-1,2,4,5-tetrazine (**VII**) (IS < 1 J [1]), which is extremely sensitive to impact, friction, and electrostatic sparks [14], to compound **II** (IS = 1.5 J [1]) (reaction (2)). Molecules **II** and **VII** in crystals have the azide form [1, 13].

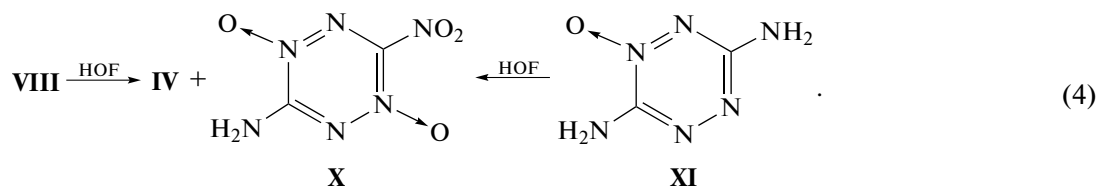


For completeness, we added compounds **IV** [3–5] and **V** [6] to compounds **I–III**. Compound **IV** has a higher value α (0.8), since there is a nitro group in its molecule and not one but two nitrogen atoms in the cycle are oxidized. For the first time, compound **IV** was synthesized with a yield of 7% in 1993 by oxidizing of 3,6-diamino-1,2,4,5-tetrazine (**VIII**) with trifluoroacetic acid [3]. Later, the yield was increased to 50% by taking 3-amino-6-nitro-1,2,4,5-tetrazine (**IX**) (reaction (3)) [5].



When using a stronger reagent (HOF) to oxidize compound **VIII** a mixture of compound **IV** with its structural isomer, 3-amino-6-nitro-1,2,4,5-tetrazine 1,4-dioxide (**X**)

(70 : 30), was obtained, and the oxidation of the other starting compound, 3,6-diamino-1,2,4,5-tetrazine 1-oxide (**XI**), gave an equal ratio of isomers **IV** and **X** [4] (reaction (4)).



The authors of [4] managed to isolate the minor isomer **X** using column chromatography (yields not shown) and even determine its structure. The density

of compound **X** turned out to be higher compared to compound **IV** (1.972 and 1.919 g/cm³, respectively). Judging by the rather high melting point with decom-

Table 1. Properties of compounds I–V and X

Compound	Gross formula	ΔH_f° ^a		ρ^b , g/cm ³	N ^c , %	α^d	P^e , GPa	D^f , m/s	IS ^g , J	FS ^h , H	T_{dec} , °C
		kJ/mol	kJ/kg								
I	C ₂ H ₂ N ₈ O ₂	576.0	3388.2	1.93	65.88	0.40	41.3	9.60	6	109	150 175 ^j (213) ^j
II	C ₂ N ₁₀ O ₂	967.3	4935.2	1.90	71.43	0.50	45.78	10.03	1.5	10	140 (167) ^j
III	C ₂ H ₂ N ₈ O	631.4	4100.0	1.87	72.73	0.20	36.4	9.33	10	60	185
IV	C ₂ H ₂ N ₆ O ₄	225.7	1297.1	1.92	48.28	0.80	39.4	9.32	3	10	110
V	C ₃ H ₂ N ₈ O ₃	744	3757.6	1.86	56.6	0.43	39.1	9.38	25	240	220
X	C ₂ H ₂ N ₆ O ₄	225.7 ^k	1297.1 ^k	1.972	48.28	0.80	–	–	–	–	168 ^l

^a Standard enthalpy of formation (calculated);^b density (experimental);^c the percentage of nitrogen in the compound;^d oxygen supply coefficient for the molecule (for compound C_xH_yN_zO_w $\alpha = 2w/(4x + y)$);^e detonation pressure (calculated);^f detonation velocity (calculated);^g shock sensitivity (experimental);^h friction sensitivity (experimental);ⁱ decomposition temperature;^j the temperature of the onset of intensive decomposition was estimated by us from the DSC curves; in parentheses, the temperature at the maximum heat release [1, Sup. Inf.];^k ΔH_f° of compound **X** taken equal to ΔH_f° of compound **IV** [5];^l melting point with decomposition (°C/min).

position (168°C at a heating rate of 2°C/min [4]), compound **X** surpasses compound **IV** also in terms of thermal resistance (the decomposition temperature was 110°C according to the DSC data [3, 5]). Probably due to low yield and small amount of compound **X** extracted, we failed to measure its sensitivity to mechanical stress. There is not even a calculated enthalpy ΔH_f° of compound **X** or calculated detonation parameters in the literature. In this study for calculating the energy of CSRP compositions with compound **X**, its ΔH_f° was accepted by us as equal to ΔH_f° of compound **IV** [5]. Our immediate plans include the task of calculating ΔH_f° of this extremely interesting compound by modern quantum chemical methods in the same basis with isomer **IV** and some other similar structures for a correct comparison of the efficiency of *s*-tetrazine *N*-oxides as potential components of CSRP.

Compound **V** appears similar to **I**, formally molecule **V** is obtained by replacing the grouping N → O in the azole ring of molecule **I** on C–NO₂. The calculated enthalpy ΔH_f° of compounds **V** (744 kJ/mol [6]) raises some doubts in us (it seems overstated), since it is significantly higher than that of compound **I** (576 kJ/mol [1]), and tetrazoles have higher enthalpy heterocycles than triazoles. Perhaps this is due to the different calculation methods in [1] and [6]. Nevertheless, for the ther-

modynamic calculations, we used these published data on ΔH_f° [1, 6] (Table 1), but in the future we plan to recalculate ΔH_f° of compounds **I** and **V** together with compounds **IV** and **X** on the same basis and it is more correct to compare these four potential components of CSRP.

The properties of compounds **I**–**V** and **X** are presented in Table 1.

FORMULATION OF THE PROBLEM AND METHOD OF THE CALCULATION STUDIES

One of the two typical binders was taken to assemble the CSRP compositions: (i) a hydrocarbon binder (HB) (C_{72.15}H_{119.21}O_{0.68}; standard enthalpy of formation $\Delta H_f^\circ = -393$ kJ/kg; and density $\rho = 0.92$ g/cm³ [15]); and (ii) an active binder (AB) (C_{18.96}H_{34.64}N_{19.16}O_{29.32}; $\Delta H_f^\circ = -757$ kJ/kg; and $\rho = 1.49$ g/cm³) [15].

We studied the energy characteristics of not only binary compositions of CSRP (a binder and one of the investigated compounds **I**–**V**) but also more complex compositions containing an additional oxidizing agent: ammonium perchlorate (AP) (NH₄ClO₄; $\Delta H_f^\circ = -2495$ kJ/kg; $\rho = 1.95$ g/cm³; $\alpha = 2.25$) or HMX

($\Delta H_f^\circ = 295$ kJ/kg; $\rho = 1.9$ g/cm³; $\alpha = 0.67$). We also considered the possibility of increasing the energy of the composition through the use of a mixed binder AB + HB at various AB : HB ratios.

Binary CSRPs based on the oxidizing agents AP and ADN (ammonium dinitramide, NH₄N₃O₄, ADN, $\Delta H_f^\circ = -1129$ kJ/kg; $\rho = 1.82$ g/cm³; $\alpha = 2.0$ [16]) were selected as reference comparison compositions. It should be noted that due to the qualitative difference in the values α (2.00 versus 0.667) in the case of ADN, the most energy-intensive formulations are provided with the HB, while in the case of HMX, with the AB [17].

Specific impulse I_{sp} calculations and temperatures in the combustion chamber T_c (at a pressure in the chamber and at the nozzle exit of 4.0 and 0.1 MPa, respectively) was carried out using the TEPPA code for calculating high-temperature chemical equilibria [18]. The effectiveness of the components under study was analyzed according to the algorithm described in [19–22]. To compare the ballistic efficiency of compositions with different densities, when they are used in engines with different volume-mass characteristics, we used the so-called effective impulse values $I_{ef}(n)$ at different stages of rocket systems (n is the step number) [23].

$$I_{ef}(1) = I_{sp} + 100(\rho - 1.9),$$

$$I_{ef}(2) = I_{sp} + 50(\rho - 1.8),$$

$$I_{ef}(3) = I_{sp} + 25(\rho - 1.7).$$

These values characterize the ballistic efficiency of the fuel at the corresponding stages of the three-stage rocket systems.

To ensure satisfactory physical and mechanical characteristics of CSRP and the rheological properties of the uncured fuel mass, the compositions must contain a sufficient amount of polymer binder, which is usually achieved with a volume content of the binder of at least 18–19 vol %. For a correct comparison, all CSRP compositions considered in this study have approximately the same volume fraction of the binder, 18.0 ± 0.1 vol %.

RESULTS AND DISCUSSION

1. Binary Formulations: Test Compound + Binder (AB or HB)

Compounds I–III and V have low coefficients for providing the molecule with oxygen (α from 0.2 to 0.5); therefore, they are better combined with the AB. Compound IV and its isomer X ($\alpha = 0.8$) can be combined with both the AB and HB [24]. Since it was shown in [17] that with increasing ΔH_f° of the oxidizing agent, the advantage of HB over AB is increasingly manifest, and compound II with a very high enthalpy

of formation ($\Delta H_f^\circ = 4935$ kJ/kg) can also be tried in compositions with HB too. It is not excluded that a certain optimum is also possible in compositions with a binder, which is a mixture of the AB with the HB due to the higher hydrogen content in the HB than in the AB [24]. The calculated characteristics of the binary compositions are presented in Table 2. For comparison, there are also parameters of the binary compositions: HMX + AB and ADN + HB.

From Table 2 it can be seen that in binary compositions with AB compounds II and V significantly outperform HMX (by 19.1 and 10.9 s, respectively) in terms of the values of the specific impulses I_{sp} ; and in terms of the effective impulse, $I_{ef}(3)$, the superiority is about the same (at 19.5 and 10.4 s, respectively). Compounds IV and X with the AB are slightly better than HMX (by I_{sp} , both by 0.8 s; and for $I_{ef}(3)$, by 1.5 and 2.6 s, respectively). Compounds IV and X have identical elements content (structural isomers) and ΔH_f° (our assumption), but compound X has a higher density (1.972 g/cm³) than compound IV (1.919 g/cm³). The superiority of compound X in terms of $I_{ef}(3)$ over compound IV (1.1 s) demonstrates the influence of the density of the main component on the ballistic efficiency of CSRP compositions, even for the third stage of the rocket complex. In the first and second stages, this advantage would be even higher. Compounds I and III with the AB (not to mention the HB) did not show a good result, which is explained by the lower values of coefficient α (0.4 and 0.2, respectively). It should be noted that compounds with low α (below 0.5) are impractical to use as independent oxidants, and even in binary compositions with the AB, they require the introduction of an additional oxidizing agent, for example, AP [25].

Compound II in the composition with the HB is superior to the ADN + HB composition in terms of I_{sp} and $I_{ef}(3)$ by 1.5 and 0.5 s, respectively, although α in compound II is significantly lower than that of ADN (0.5 versus 2). This is the result of the extremely high difference between the enthalpies of formation of compounds II and ADN. However, the binary II + HB composition still performs significantly (by ~20 s) worse than the II + AB composition; i.e., even such a high ΔH_f° (4935 kJ/kg) does not allow the component with $\alpha = 0.5$ to become more efficient with the HB than with the AB. Compositions II + AB with the maximum values I_{sp} and $I_{ef}(3)$ with the AB content of about 18 vol % have an unacceptably high T_c (~4050 K).

The layout of compound IV with the HB did not give good results, which is to be expected from a component with $\alpha = 0.8$ and value ΔH_f° at the level of 1300 kJ/kg. Thus, in binary compositions, the best result is demonstrated by compound II paired with the AB, which is not surprising for a compound with value ΔH_f° of about 5000 kJ/kg.

Table 2. Energy characteristics of binary CSRP compositions based on compounds **I–V**, **X** with **AB**, based on compounds **II** and **IV** with **HB** and compositions based on compound **II** with **AB + HB** at a volume content of the binder of about 18 vol % (and more than 18 vol % for compound **II**)

Oxidizing agent		Binder			ρ , g/cm ³	T_c , K	I_{sp} , s	$I_{ef}(3)$, s
no.	%	a type	wt %	vol %				
I	85.5	AB	14.5	18.0	1.851	3271	248.7	252.6
II	85.3	AB	14.7	18.0	1.826	4047	270.2	273.4
II	74.75	AB	25.25	30.1	1.777	3800	265.6	267.5
II	70.9	AB	29.1	34.4	1.759	3729	264.0	265.5
II	69.3	AB	30.7	36.1	1.752	3700	263.4	264.7
III	85.1	AB	14.9	18.0	1.802	2958	240.8	243.3
IV	85.45	AB	14.55	18.0	1.843	3413	251.9	255.4
V	85.05	AB	14.95	18.0	1.793	3570	262.0	264.3
X	85.75	AB	14.25	18.0	1.885	3413	251.9	256.5
HMX	85.2	AB	14.8	18.0	1.811	3177	251.1	253.9
II	90.4	HB	9.6	18.0	1.724	3398	252.4	253.0
IV	90.5	HB	9.5	18.0	1.740	2821	233.8	234.8
II	87.28	AB + HB 2.42 : 1	12.72	18.0	1.785	3800	263.1	265.2
II	87.95	AB + HB 1.39 : 1	12.05	18.0	1.771	3700	260.4	262.2
ADN	90.0	AB	10	18.0	1.658	3119	250.9	249.8

2. CSRP Compositions Based on Compound **II** and Possible Ways of Reducing the Temperature in the Combustion Chamber (T_c) to Technologically Permissible Values (3700–3800 K)

Separately, we should dwell on compound **II** and compositions based on it. As noted above, the binary composition **II** + **AB** at 18 vol % of the binder showed very high energy indicators; however, the temperature in the combustion chamber at the same time reached an unacceptably high value (4047 K, Table 2). Therefore, it is necessary to reduce T_c , moving it to technologically permissible values (3700–3800 K), since it is almost impossible to find structural materials for manufacturing a combustion chamber and a jet nozzle at $T_c > 3800$ K. T_c can be decreased in different ways.

First, in binary composition **II** + **AB**, it is possible to increase the **AB** content in excess of the required 18% by volume by reducing the proportion of compound **II** (method A), but at the same time with decreasing T_c (Table 3) to acceptable values (3700–3800 K), the values of the target parameters I_{sp} and I_{ef} also decrease (3). Nonetheless, at the same time, the values of I_{sp} and $I_{ef}(3)$ remain very high (263.4–265.6 s for I_{sp} and 264.7–267.5 s for $I_{ef}(3)$). To bring down T_c to the maximum permissible value 3800 K, the mass fraction of the **AB** should be increased to 25.25%

(74.75% **II** + 25.25% **AB**), which corresponds to the volume fraction of the binder in 30.1 vol %, and values I_{sp} and $I_{ef}(3)$ will decrease to 265.6 and 267.5 s, respectively. To further reduce T_c and drop it up to 3700 K, the mass fraction of the **AB** should be increased to 30.7%. In the composition 69.3% **II** + 30.7% **AB**, the value of I_{sp} and $I_{ef}(3)$ will already be 263.4 and 264.7 s, and the volume fraction of the binder will exceed the minimum allowable value of 18% by an even greater margin to reach 36.1 vol % (Table 3), which should have a positive effect on improving the rheological parameters of the uncured fuel mass.

Second, paired with compound **II**, we can use a mixed **AB** + **HB** binder at a constant volumetric content (18 vol %) (method B). Partial replacement of **AB** with **HB** allows us to reduce T_c to 3800 K at the ratio of **AB** : **HB** = 2.4 : 1 at the cost of decreasing values I_{sp} and $I_{ef}(3)$ to 263.1 and 265.2 s, respectively. The same T_c is reduced to 3700 K with an even lower mass fraction of **AB** (**AB** : **HB** = 1.4 : 1), and the values I_{sp} and $I_{ef}(3)$ decrease to 260.4 and 262.2 s, respectively. Nevertheless, even these values are rather high for CSRP compositions without metal (Table 4).

Third, an additional low-enthalpy oxidant, **AP**, can be added to the composition due to compound **II**, keeping the volumetric content of the **AB** at the level

Table 3. Energy characteristics of binary CSRП compositions based on compound II with AB with a decrease in T_c by increasing the share of AB

II, %	AB		ρ , g/cm ³	T_c , K	I_{sp} , s	$I_{ef}(3)$, s
	wt %	vol %				
85.3	14.7	18.0	1.826	4047	270.2	273.4
84	16	19.5	1.820	4010	269.6	272.6
83	17	20.7	1.815	3983	269.2	272.0
82	18	21.9	1.810	3958	268.7	271.5
80	20	24.2	1.803	3910	267.9	270.4
75	25	29.8	1.778	3805	265.7	267.7
74.8	25.2	30.1	1.777	3801	265.7	267.6
74.75	25.25	30.1	1.777	3800	265.6	267.5
74.5	25.5	30.4	1.775	3780	265.5	267.4
70.9	29.1	34.4	1.759	3729	264.0	265.5
70	30	35.3	1.755	3713	263.6	265.0
69.3	30.7	36.1	1.752	3700	263.4	264.7

The compositions with the maximum values of the target parameters are highlighted in bold I_{sp} and $I_{ef}(3)$ with the T_c restriction not higher than 3700 or 3800 K.

Table 4. Energy characteristics of CSRП compositions based on compound II with a mixed binder AB + HB with a volume content of 18 vol %

II, %	AB, %	HB, %	AB + HB, vol %	ρ , g/cm ³	T_c , K	I_{sp} , s	$I_{ef}(3)$, s
85.3	14.8	0	18.0	1.826	4047	270.2	273.4
85.55	14.05	0.5	18.0	1.820	4035	269.7	272.7
85.85	13.3	1	18.0	1.815	4021	269.1	272.0
86.1	12.5	1.5	18.0	1.809	4000	268.4	271.2
86.9	10.1	3	18.0	1.793	3861	264.7	267.0
87.28	9.0	3.72	18.0	1.785	3800	263.1	265.2
87.3	8.95	3.75	18.0	1.785	3798	263.0	265.2
87.4	8.6	4	18.0	1.782	3777	262.5	264.6
87.7	7.8	4.5	18.0	1.777	3740	261.7	263.6
87.75	7.65	4.6	18.0	1.771	3733	261.3	263.2
87.75	7.6	4.65	18.0	1.775	3729	261.2	263.1
87.95	7.05	5	18.0	1.771	3704	260.5	262.3
87.95	7	5.05	18.0	1.771	3700	260.4	262.2
89	4	7	18.0	1.750	3566	256.8	258.1

The compositions with the maximum values of the target parameters I_{sp} and $I_{ef}(3)$ with the restriction T_c not higher than 3700 or 3800 K are highlighted in bold.

of 18 vol % (method C). In principle, it is possible to use the addition of the oxidizing agent ADN to reduce T_c , but in [26] it was shown that the addition of AP reduces T_c most efficiently. Thus, for the composition 74.75% II + 14.65% AB + 10.6% AP, $T_c = 3800$ K, and this is a permitted value. At the same time $I_{sp} = 266.4$ s and $I_{ef}(3) = 269.7$ s. The introduction of 16.9% AP, while maintaining 18.0 vol % of the binder, lowers

the temperature to 3700 K, further decreasing the values I_{sp} and $I_{ef}(3)$ to 264.0 s and 267.3 s, respectively (Table 5).

Thus, comparing compositions based on II, reduced to the same permissible temperatures in the combustion chamber by the three methods described above (A–C), for example, when $T_c = 3800$ and 3700 K (Table 6), it can be argued that the third method (dilu-

Table 5. Energy characteristics of CSRP compositions based on compound **II** with AB and AP with the volume content of the binder of about 18 vol %

II , %	AP, %	AB, wt %	AB, vol %	ρ , g/cm ³	T_c , K	I_{sp} , s	$I_{ef}(3)$, s
85.3	0	14.7	18.0	1.826	4047	270.2	273.4
84.3	1	14.7	18.0	1.827	4015	269.9	273.0
80.3	5	14.7	18.0	1.828	3909	268.4	271.6
76.35	9	14.65	18.0	1.830	3829	267.0	270.2
75.35	10	14.65	18.0	1.831	3811	266.6	269.9
74.85	10.5	14.65	18.0	1.831	3802	266.4	269.6
74.75	10.6	14.65	18.0	1.831	3800	266.4	269.7
74.35	11	14.65	18.0	1.831	3793	266.2	269.5
73.35	12	14.65	18.0	1.832	3776	265.9	269.2
70.35	15	14.65	18.0	1.833	3729	264.7	268.1
68.45	16.9	14.65	18.0	1.834	3700	264.0	267.3
68.35	17	14.65	18.0	1.834	3699	263.9	267.3
65.35	20	14.65	18.0	1.835	3656	262.7	266.1
60.4	25	14.6	18.0	1.838	3589	260.5	264.0
55.4	30	14.6	18.0	1.840	3524	258.1	261.6

The compositions with the maximum values of the target parameters I_{sp} and $I_{ef}(3)$ with the restriction T_c not higher than 3700 or 3800 K are highlighted in bold.

tion with AP) leads to the smallest loss in values I_{sp} and $I_{ef}(3)$. This means lowering the temperature in the combustion chamber to acceptable values with less energy loss is best done by diluting compound **II** by AP. The other two ways of reducing T_c (increasing the mass fraction of the AB in the binary composition **II** + AB and dilution of AB with a hydrocarbon binder) are much less effective. However, each of the described methods of lowering the temperature in the combustion chamber has its own advantages and disadvantages. Method B (Table 6) (dilution of AB with a hydrocarbon binder) loses in terms of energy to method C (4.5 s in $I_{ef}(3)$ when T_c to 3800 K), but facilitates the work with the uncured composition and improves the physical and mechanical properties of the cured product, and there is no HCl in the combustion products. The same should be said about method A (increasing the mass fraction of the AB to 30.1 vol %); however, here the loss to method C is somewhat less (about 1 s). Obviously, from the energy point of view, the best way to reduce value T_c is method C; method A is inferior to it, and method B is the least effective. If it comes to the real development of such compositions, the choice will need to be made between methods A and C, depending on the intended purpose of such a fuel.

3. CSRP Compositions: Test Compound + AB + AP

Since most of the studied components (**I–III**, **V**) have low values of α , the energy characteristics of formulations containing, in addition to components **I–V** and a binder, an oxidizing agent (AP), were studied.

Earlier it was shown that such a technique can give a positive result at sufficiently high (approximately 700–1400 kJ/kg) values ΔH_f° of the main component (but not as high as components **I–III**, **V**) and with low values of α (0.2–0.54) [27]. Formulations based on HMX + AP + AB [27] are taken for comparison. Figures 2 and 3 show the dependences of $I_{ef}(3)$ and T_c on the content of compounds **I–V** or HMX in the composition of CSRPs with the active binder (18 vol %) and AP (the rest).

In other words, Figs. 2 and 3 demonstrate how the parameters $I_{ef}(3)$ and T_c are affected by the replacement of part of compounds **I–V** or HMX by PA in compositions with the AB. Figure 2 shows that for compounds **II**, **IV**, **V**, and **X** the introduction of PA is ineffective from the point of view of energy. There is an

Table 6. Changes in values I_{sp} and $I_{ef}(3)$ when decreasing T_c of the original composition 14.7% AB + 85.3% **II**

Method	T_c , K	I_{sp} , s	$I_{ef}(3)$, s
Original composition	4047	270.2	273.4
A	3800	265.6	267.5
	3700	263.4	264.7
B	3800	263.1	265.2
	3700	260.4	262.2
C	3800	266.4	269.7
	3700	264.0	267.3

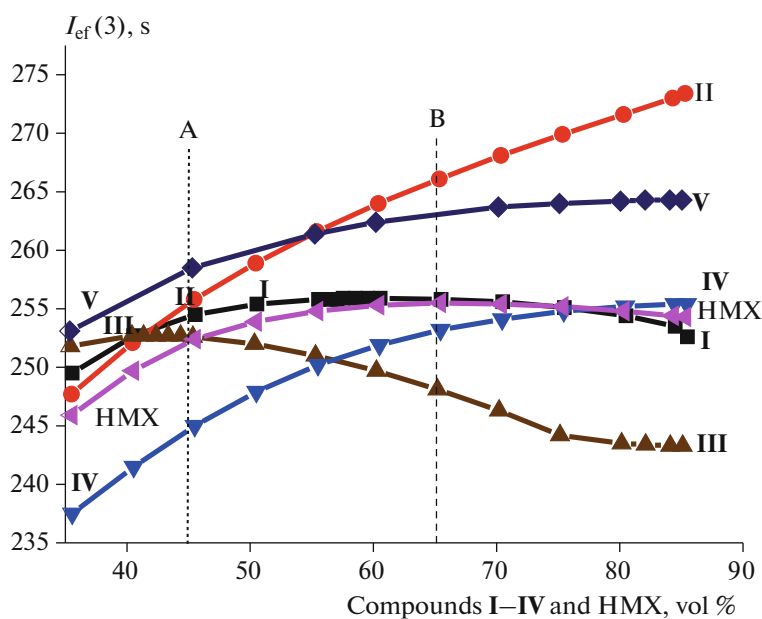


Fig. 2. Dependence of $I_{ef}(3)$ on the content of compounds I–V or HMX in CSRP formulations with active binder (18 vol %) and AP (the rest).

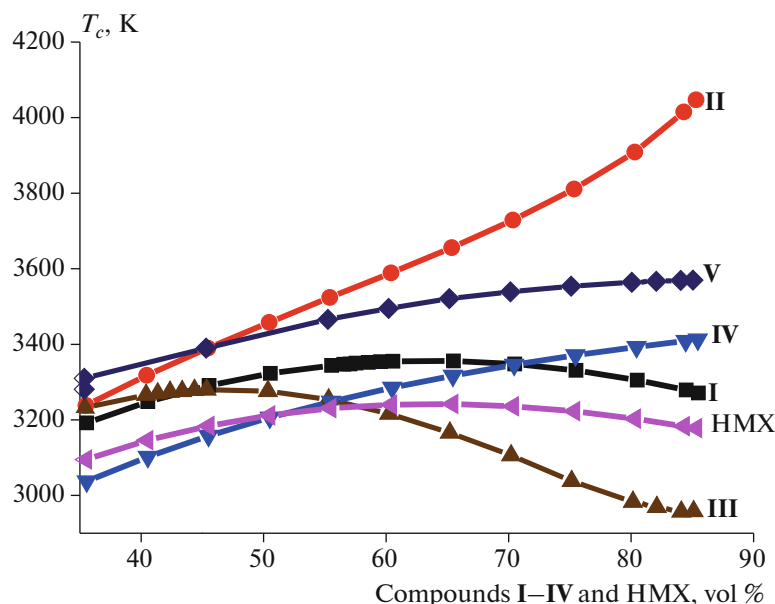


Fig. 3. Combustion chamber temperature dependence T_c on the content of compounds I–V or HMX in CSRP formulations with the active binder (18 vol %) and AP (the rest).

explanation for this: compounds **II** and **V** have such high ΔH_f° , that even at small values of α for these components (0.50 and 0.43), the introduction of low-enthalpy AP reduces ΔH_f° of the whole composition to such an extent that this drop is not compensated by the exothermic oxidation reaction of components **II** or **V** (and AB) with AP. For compound **II**, the introduction

of PA turned out to be the most effective way to reduce the unacceptably high T_c (method C, Section 2). There is no need to cool composition **V** + AB in this way (method C, Section 2), since its $T_c = 3570$ K and thus it lies in the allowed range, despite the high value of $I_{sp} = 262$ s. The same can be said about binary systems **IV** or **X** + 15 wt % AB. Taking into account the rather high value of α of compounds **IV** and **X** (0.8), they are

almost optimal in terms of the oxygen content. The curves for compound **X** in Figs. 2 and 3 are not shown. They practically repeat the course of the curves for compound **IV**, but are located slightly higher.

For component **I**, the values of α and ΔH_f° are significantly lower than for components **II** and **V**; therefore, the introduction of an additional oxidizing agent (for example, AP) in the compositions with compound **I** is entirely appropriate. The optimized 60.55% **I** + 14.45% AB + 25% PA composition outperforms binary composition **I** + AB by 3.3 s in terms of I_{sp} and 3.2 s in terms of $I_{ef}(3)$. The temperature in the combustion chamber of such a composition is 3355 K. This composition only slightly outperforms the optimized HMX + PA + AB composition in terms of $I_{ef}(3)$ (255.8 and 255.5 s). The curve for component **I** in Fig. 2 has the following feature: a weak dependence of $I_{ef}(3)$ on the content of component **I** in the fairly wide range of 45 to 65%, (marked in Fig. 2 by the vertical dashed lines A and B). HMX has the same feature (Fig. 2), but the range of weak dependence $I_{ef}(3)$ is shifted by ~5% towards the higher content of the component. Therefore, limiting the content of the organic high-enthalpy component due to its sensitivity to mechanical stress can make the advantage of component **I** more significant in comparison with HMX. Compound **I** and HMX are comparable in sensitivity to mechanical stress [1]. In particular, at a 40% content of the organic component, the composition based on compound **I** outperforms the HMX composition in terms of $I_{ef}(3)$ by 3 s.

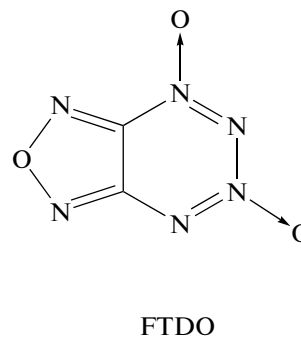
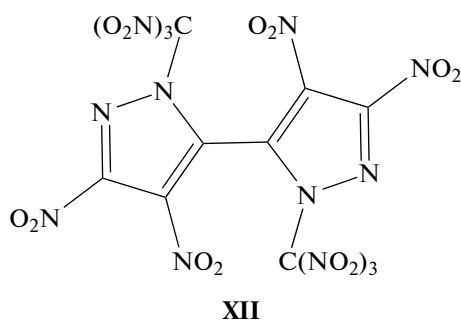
Adding 41% AP to the composition based on compound **III** with AB significantly increases values I_{sp} and $I_{ef}(3)$, by 8.6 and 9.4 s, respectively, which is

entirely expected for a compound with $\alpha = 0.2$. The maximum value $I_{ef}(3) = 252.7$ s is achieved when the content of component **III** in the composition is 44%; moreover, $I_{ef}(3)$ barely changes about this optimum in the range 40–50%. As a consequence, at a 40% limitation of the proportion of the organic high-enthalpy component, compound **III** surpasses HMX as part of the CSRP with AB and PA in terms of $I_{ef}(3)$ by 3 s; and at the 35% limit, by 6 s. Compound **III** is less sensitive to mechanical stress than HMX [1, 2]. Therefore, its content in the CSRP composition may not need to be limited.

In compositions with all the studied components, except **II**, the value T_c does not exceed the permissible level (3700–3800 K) (Fig. 3).

4. Comparison of Optimized CSRP Compositions Based on Compounds I–V and X with Each Other and with Some Known Compositions

The data from the optimized compositions based on the **I–V** and **X** compounds with the addition of AP (or without it) at the volumetric content of the AB of about 18% and provided $T_c < 3800$ K are presented in Table 7. The optimized compositions ADN + HB and HMX + AP + AB, as well as the compositions based on two promising components—4,4',5,5'-tetranitro-2,2'-bis(trinitromethyl)-2*H*,2'*H*-3,3'-bipyrazole (**XII**) [28, 29] and [1,2,5]oxadiazolo[3,4-*e*][1,2,3,4]tetrazine-4,6-dioxide (FTDO) [30, 31] with HB (for ADN, FTDO, and oxidizer **XII**, the hydrocarbon binder is more advantageous than the active one)—are given as the reference compositions.



For clarity, the data on values $I_{ef}(3)$ from Table 7 are shown in the histogram (Fig. 4).

From Table 7 and Fig. 4, it can be seen that in their optimized formulations, component **II** is at the level of FTDO and together with component **V**, significantly outperforms not only HMX and ADN but also the oxidizing agent **XII**, and component **V** significantly underperforms FTDO. Components **I**, **IV** and **X** are at the level of HMX and outperform ADN but underper-

form the oxidizing agent **XII**. Finally, component **III** is significantly inferior in terms of ballistic efficiency to HMX and oxidizer **XII**, but slightly more efficient than ADN.

Until recently, the energy characteristics of CSRP compositions based on FTDO remained record-breaking, far behind other actually synthesized compounds. The appearance of compound **II** and [1,2,3,4]tetrazino[5,6-*e*][1,2,3,4]tetrazine-1,3,6,8-tetroxide (TTTO)

Table 7. Energy characteristics of the CSRP compositions “test compound + AB + AP” based on compounds I–V and X at the volumetric content of AP at the volumetric content of AB of about 18% and the content of AP, providing the maximum values of I_{sp} and $I_{ef}(3)$ provided $T_c < 3800$ K compared to HMX, ADN, FTDO, and oxidizer XII compositions

Oxidizing agent		Binder			PHA, %	ρ , g/cm ³	T_c , K	I_{sp} , s	$I_{ef}(3)$, s
no.	%	type	wt %	vol %					
I	60.55	AB	14.45	18.0	25	1.856	3355	252.0	255.8
II	74.75	AB	14.65	18.0	10.6	1.831	3800	266.4	269.7
III	44.35	AB	14.65	18.0	41	1.832	3279	249.4	252.7
IV	85.45	AB	14.55	18.0	0	1.843	3413	251.9	255.4
V	85.05	AB	14.95	18.0	0	1.793	3570	262.0	264.3
X	85.75	AB	14.25	18.0	0	1.885	3413	251.9	256.5
HMX	65.4	AB	14.6	18.0	20	1.826	3242	252.1	255.5
ADN	90	HB	10	18.0	0	1.658	3119	250.9	249.8
XII	91	HB	9	18.0	0	1.820	3600	256.6	259.6
FTDO	90	HB	10	18.3	0	1.669	3770	270.4	269.6

[31, 32] destroyed this monopoly. It should be noted that compound II and FTDO, in terms of their sensitivity to mechanical stress, are related to the initiating explosives and their use as CSRP components is problematic.

The advantage of components I, IV, and X over HMX is small if any. Therefore, given the complex synthesis of these compounds, the prospects for their practical use are also questionable.

Of all the considered compounds, compound V with a high level of thermal stability and low sensitivity to mechanical stress appears to be the most promising CSRP component. However, as noted in the introduction, a more careful calculation of the value ΔH_f° of this compound and ideally an experimental measurement of this parameter are required.

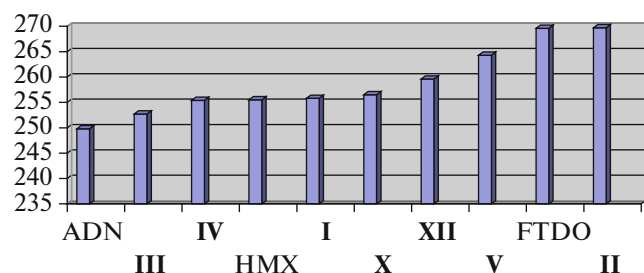


Fig. 4. Maximum achievable values $I_{ef}(3)$ of optimized I, II, III or HMX + binder (18 vol %) contents + PHA and IV, V, X, XII, FTDO or DNAA + binder (not less than 18 vol %) with limitation $T_c < 3800$ K. Binder for all fillers except ADN, FTDO, and XII is active; and for ADN, FTDO, and XII, hydrocarbon.

CONCLUSIONS

In this study, it is shown that some derivatives of 1,2,4,5-tetrazine *N*-oxides can be considered as promising components of CSRPs. Compound II, due to its high nitrogen content (two azide groups in the *s*-tetrazine di-*N*-oxide cycle in the molecule), high values of the standard enthalpy of formation and density with the content of the polymer binder in the composition of the formulation at least 18 vol %, can provide rather high impulse values. Thus, even with the restriction $T_c < 3800$ K for compositions with AB and AP, I_{sp} and $I_{ef}(3)$ values of 266.4 and 269.7 s, respectively, can be obtained. The method of reducing T_c to 3800 K compositions with compound II by using the mixed AB + HB binder turned out to be somewhat less effective. Nevertheless, the achieved values $I_{sp} = 263.1$ s and $I_{ef}(3) = 265.2$ s significantly outperform the reference compositions based on DNAA and HMX in terms of energy characteristics.

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