Research paper

Experimental and Theoretical Investigation of the Heat of Combustion of RDX-based Propellants

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Abstract: The main goal of the present work was to check whether it is possible to use a thermochemical model to predict the heat of combustion of new RDX-based propellants and to determine which calculation conditions ensure that the calculated heat obtained is close to the calorimetric value. Calorimetric measurements of the heat of combustion of selected new RDX-based propellants were carried out and their combustion characteristics were also obtained by thermochemical calculations. The combustion heats determined experimentally and theoretically were compared. On the basis of an analysis of the results obtained, the influence of the temperature of "freezing" of the composition of the combustion products on the calculated combustion heat was checked. The ballistic parameters of the tested propellants were also calculated.

Keywords: RDX-based propellants, combustion heat, thermochemical model

1 Introduction

The theoretical determination of the combustion parameters and the equilibrium composition of the combustion products based on the physical and chemical properties of propellants (atomic composition, energy or enthalpy

of formation and density) have become possible thanks to the principle of minimalization of thermodynamic functions formulated by Gibbs and by the use of the thermodynamic equations of state of the reaction products, describing their physical properties in a wide range of pressure and temperature changes. These principles have been used to develop a series of numerical models and programs (so-called thermochemical codes) for carrying out thermodynamic calculations of the combustion parameters of condensed energetic materials, such as BLAKE [1], BAGHEERA [2] and BARUT-X [3]. An option was also proposed in programs designed mainly to determine the detonation characteristics of explosives, such as CHEETAH [4], EXPLO5 [5] and ZMWNI [6], which allow calculation of the thermodynamic parameters of combustion products of propellants. In connection with the appearance of many thermochemical codes, a standardization agreement, STANAG 4400 [7], was created, the purpose of which is to standardize the methods for calculating the thermodynamic parameters needed in internal ballistics. This agreement defines and describes methods for the determination of the thermodynamic parameters that are necessary to resolve the problems of internal ballistics, and the agreed data used in calculations. The choice of the method of solving the equations given in the standard [7] was left to its users. In the literature there are also simplified methods for calculating the heat of combustion for selected compounds, for example [8].

In the present work, the CHEETAH code with the BLAKE product library [4] was used to calculate the ballistic parameters of propellants, including the heats of combustion. New RDX-based propellants were chosen for investigation. From a comparison of the measured and calculated values of the combustion heat for the selected propellants, the calculation conditions were determined for which the theoretical heat of combustion would be close to the measured calorimetric heat.

2   Experimental

For this research, new composite propellants based on RDX were chosen. RDX of reduced sensitivity (RDX-RS) with particle size from the range 2.5-5 µm was used. The other ingredients of the propellants were: cellulose acetate butyrate (CAB), acetyl triethyl citrate (ATC), glycerin triacetate (Triacetin), Akardite II and nitrocellulose (NC 12.6%N). The compositions of the tested propellants are listed in Table 1. The solid and liquid ingredients were mixed in a standard sigma blender with stainless steel blades for 4 h. The propellants

grains were then formed with a standard laboratory extruder.

The first propellant to be tested was P-1, whose composition is similar to that of XM39 [9]. Subsequent modifications of this propellant were aimed at obtaining ballistic parameters similar to the parameters of JA2 with the following composition:

– nitrocellulose (NC 13.2%N)   58.21%,
– nitroglycerine (NG)   15.79%,
– diethyleneglycol dinitrate (DEGDN)   25.18%,
– Akardite II   0.74%,
– magnesium oxide (MgO)   0.05%,
– graphite   0.03%.

Table 1.   Composition of propellants selected for testing

Propellant symbol	Content of the component [wt.%]					
	RDX	CAB	ATC	Triacetin	NC (12.6%N)	Akardite II
P-1	75.8	12.1	7.7	–	4.0	0.4
P-2	75.8	12.1	–	7.7	4.0	0.4
P-3	76.0	–	–	7.6	16.0	0.4
P-4	76.0	6.0	–	7.6	10.0	0.4
P-5	67.2	5.0	–	7.6	19.8	0.4

The thermal effect accompanying the combustion reaction of the tested propellants was measured and recorded using a water calorimeter KL-10 produced by *PRECYZJA-BIT* from Bydgoszcz. A scheme of the calorimetric system used to study the thermal effects of the combustion of the propellants is shown in Figure 1. A cylindrical steel calorimetric bomb with a capacity of approximately 0.350 dm³ was placed in a steel vessel with a capacity of 4.4 dm³ containing distilled water. The water was mixed with a stirrer from the beginning of the measuring cycle and its temperature was measured using a thermocouple and recorded by a microprocessor memory system. The vessel was placed inside the thermally insulated jacket with a capacity of 15.5 dm³, in which a constant temperature was maintained by means of a thermostat. The vessel and water jacket were closed by a cover.
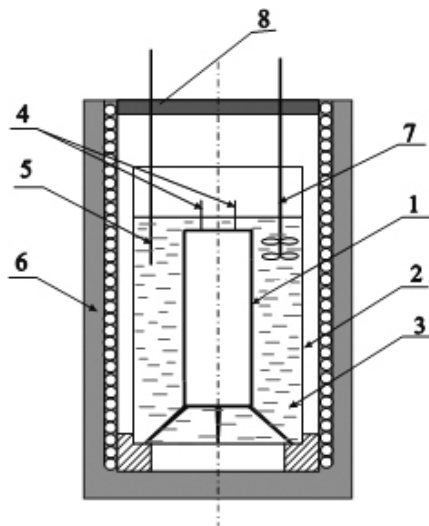
Figure 1.   Scheme of the calorimetric system: 1 – calorimetric bomb,
                2 – calorimetric vessel, 3 – water, 4 – electrodes, 5 – thermocouple,
                6 – thermal insulation coat, 7 – stirrer, 8 – cover

Calibration measurements were made by burning benzoic acid tablets with a weight of approximately 0.5 g in an oxygen atmosphere under a pressure of 2 MPa. The thermal capacity K of the calorimetric system was 54640 J/°C.

The measurements of the heat of combustion of the propellants were made in an argon atmosphere. Before each experiment the bomb was thoroughly cleaned and dried. The air in the bomb was removed by filling with argon three times to a pressure of 0.5 MPa and emptied, and finally the argon was left under this pressure. A sample of propellant with a weight of approximately 3 g in the form of 4 cylindrical grains was bonded with a spiral wire and a 6 cm long cotton cord. The heat of combustion of the resistance wire and cotton cord was not taken into consideration due to its insignificantly low impact on the final heat of combustion of a propellant. The thermochemical calculations showed that in the argon atmosphere the heat of combustion of the propellant samples with the wire and cord was smaller than the heat of combustion of the samples without these additives by less than 0.1%. Three tests were carried out for each type of propellant. The results of the combustion heat measurements are listed in Table 2.

Table 2.   Measurement of the heat of combustion of the tested propellants

Propellant symbol	Heat of combustion [J/g]	Average heat of combustion Q_{exp} [J/g]
P-1	3452	3500 ±50
	3534	
	3518	
P-2	3504	3520 ±50
	3492	
	3570	
P-3	4547	4560 ±20
	4554	
	4585	
P-4	4044	4060 ±40
	4098	
	4039	
P-5	3877	3900 ±30
	3906	
	3925	
JA-2	4655	4660 ±20
	4666	
	4646	

Table 2 shows that the applied method and conditions for measuring the heat of combustion give reproducible results (the maximum deviation of the measurement results did not exceed 1.5%). The propellant P-3 has a heat of combustion (Q_{exp}) comparable to the heat of combustion of JA-2 propellant, while propellants P-4 and P-5 have slightly smaller values. Hence, it is expected that the ballistic parameters of these propellants will be similar to the parameters of JA-2.

3   Calculation of the Ballistic Parameters

The so-called virial equation of state is often used to describe the physical properties of combustion products, for example in [1, 5, 7]. It has the following form:

$$pV = n_g RT \cdot \left[1 + \frac{n_g B(T)}{V} + \frac{n_g^2 C(T)}{V^2} \right] \qquad (1)$$

where $B(T)$ and $C(T)$ are the second and third molar viral coefficients of the gaseous combustion products, V – the volume occupied by the products, p – pressure, T – temperature, n_g – the number of moles of gaseous products.

The thermodynamic model of combustion of propellants with the virial equation of state has been implemented into the CHEETAH code [4] with the assumption that the third virial coefficient C in Equation 1 is constant for individual gaseous products.

The basic calculated ballistic parameters are:

(a) the heat of combustion in a constant volume (Q_v):

$$Q_v = -\left[\sum_i n_i \left(\Delta E^0_{(298.15)}\right)_i - \Delta E^0_s\right] \tag{2}$$

where n_i is the number of moles of the i-th component of the combustion products, is the energy of formation of the i-th component, and ΔE^0_s is the energy of formation of the propellant at constant volume,

(b) propellant force (f):

$$f = n_g R T_v \tag{3}$$

where T_v is the isochoric combustion temperature,

(c) gas volume of combustion products α occurring in the Nobel-Abel equation:

$$p(V - \alpha) = n_g R T_v \tag{4}$$

(d) ratio of the "frozen" specific heat capacities, (κ):

$$\kappa = c_p / c_v \tag{5}$$

(e) ballistic energy (E_b):

$$E_b = f / (\kappa - 1) \tag{6}$$

(f) pressure of the combustion products in a constant volume (p_v).

The data used in the thermochemical calculations of the propellants are summarized in Table 3.

Table 3.   Data for thermochemical calculation of propellants

Component	Chemical formula	Density [g/cm³]	Molar mass [g/mol]	Molar volume [cm³/mol]	Enthalpy of formation [cal/mol]
CAB	$C_{147}H_{237}O_{77}$ [10]	1.25 [11]	3236.4 [10]	2589.2	–3 207 700 [12]
Akardite II	$C_{14}H_{14}O_1N_2$	1.236	226.27	183.07	–25 500 [7]
Triacetin	$C_9H_{14}O_6$	1.16 [11]	218.2 [11]	188.10	–318 070 [7]
DEGDN	$C_4H_8O_7N_2$	1.38	196.12	142.12	–99 400 [7]
NG	$C_3H_5O_9N_3$	1.60 [4]	227.1	142.29	–88 600 [7]
ATC	$C_{14}H_{22}O_8$	1.136 [9]	318.22	280.21	–400 000 [13]
RDX	$C_3H_6O_6N_6$	1.81 [4]	222.1	122.99	14 710 [4]
NC (13.3%N)	$C_6H_{7.312}O_{10.376}N_{2.688}$	1.660 [4]	283.90	171.02	–163 460 [7]
NC (12.6%N)	$C_6H_{7.549}O_{9.901}N_{2.451}$	1.655 [4]	272.73	164.79	–169 171 [7]

The ballistic parameters of the propellants were calculated using the CHEETAH code for a loading density of 0.2 g/cm³. However, the heat of combustion was calculated as the difference between the standard enthalpy of formation of the products resulting from combustion under isochoric conditions and the enthalpy of formation of the propellant, *i.e.*:

$$Q_v = -\left[\sum_i n_i (\Delta H^0_{(298.15)})_i - \Delta H^0_s - n_g R\, 298.15\right] \qquad (7)$$

where $(\Delta H^0_{(298.15)})_i$ is the enthalpy of formation of the *i*-th component, and ΔH^0_s is the enthalpy of formation of the propellant at constant pressure. The work of the expansion of the combustion products ($n_gR298.15$) is added so that the calculated heat corresponded to the definition (2), in which the standard energies of formation are used.

The two values of combustion heat were calculated from Equation 7. It was assumed that the water is in a gaseous state (Q_{v1}) or in a liquid state (Q_{v2}). The results of the calculations for the tested propellants are listed in Table 4.

Table 4.   Results of calculations of the ballistic parameters of the propellants

Propellant symbol	Q_{v1} [J/g]	Q_{v2} [J/g]	α	f_p [J/g]	c_p/c_v	E_b [J/g]	T_v [K]	p_v [MPa]	n_g [mol/kg]
P-1	3192	3421	1.165	1087	1.269	4046	2700	283.4	48.42
P-2	3181	3418	1.158	1083	1.267	4053	2712	282.0	47.98
P-3	4103	4468	1.070	1233	1.242	5094	3426	313.6	43.27
P-4	3663	3973	1.112	1167	1.254	4595	3076	300.3	45.65
P-5	3594	3913	1.103	1142	1.253	4512	3038	293.2	45.22
JA-2	4209	4667	0.983	1161	1.224	5193	3486	289.0	40.04

The results of these calculations from Table 4 indicate that some of the tested RDX-based propellants (P-3, P-4, P-5) have ballistic parameters comparable to those of JA-2 propellant.

4   Comparison of Measured and Calculated Heats of Combustion

Burning a propellant sample with a mass of approx. 3 g in the 0.35 dm³-volume bomb filled with argon at a pressure of 0.5 MPa is a complex process. The sample burns gradually and hot combustion products at a temperature of about 3000 K mix with argon. The temperature of the products decreases towards room temperature since heat is transferred to the calorimeter vessel. The composition of the combustion products may change during this process. The question is whether the measured heat of combustion can be compared with the heat of combustion Q_v calculated for a loading density of 0.2 g/cm³.

To compare the results obtained from the thermochemical calculations (Q_v) and the calorimetric data (Q_{exp}), the relative difference between them (δ) was calculated according to Equation 8:

$$\delta = \frac{Q_v - Q_{exp}}{Q_{exp}} \ 100 \ [\%] \tag{8}$$

The differences calculated for Q_{v1} and Q_{v2} are listed in Table 5. As expected, a better agreement between the calculated combustion heat in a constant volume and the heat measured in the calorimeter was obtained when water in the liquid state was included in the calculations. This compatibility is quite good, although the compositions of the combustion products are significantly different in both cases, due to the fact that the measurement conditions and those adopted in the calculations are not the same.

Table 5.   Differences between the theoretical and experimental values of the heats of combustion

Propellant symbol	δ_1	δ_2
P-1	−8.8	−2.3
P-2	−9.6	−2.9
P-3	−10.0	−2.0
P-4	−9.8	−2,1
P-5	−7.8	+0.3
JA-2	−9.7	+0.2

The temperature of the combustion products decreases during the calorimetric measurement. From the thermochemical calculations it also follows that the composition of the combustion products changes as the temperature falls. It is not known exactly at what temperature in the calorimeter the chemical reactions in the products are actually interrupted. The measured thermal effect depends on this "frozen" composition.

An attempt was made to determine the conditions for calculating such a composition of combustion products that would be close to the final composition of products in the calorimeter, and which would cause the calculated and measured combustion heats to also be close to each other. Firstly, theoretical investigations of the effect of the freezing temperature (T_z) on the composition of the reaction products and the thermal effect of combustion were performed for the P-1 propellant. It was assumed that the initial state of the gases in the calorimetric bomb corresponded to the equilibrium state of the combustion products of a sample of propellant and argon. The loading density of the propellant sample and argon in the calorimetric bomb was 0.017 g/cm^3. The CHEETAH code was used to determine the equilibrium state of reagents in the calorimeter volume. The calculated equilibrium temperature (T_{eq}) varied from 2284 K (propellant P-1) to 2932 K (JA-2). The composition of the combustion products changed during cooling of the gaseous mixture in the calorimeter and was frozen at different temperatures in the calculations. The reaction heat (Q_z) was obtained from Equation 7. Water was assumed to be in the liquid state in the calculations of Q_z. The calculated number of moles of the main gaseous components and the corresponding heat of combustion as a function of the freezing temperature is shown in Figure 2.
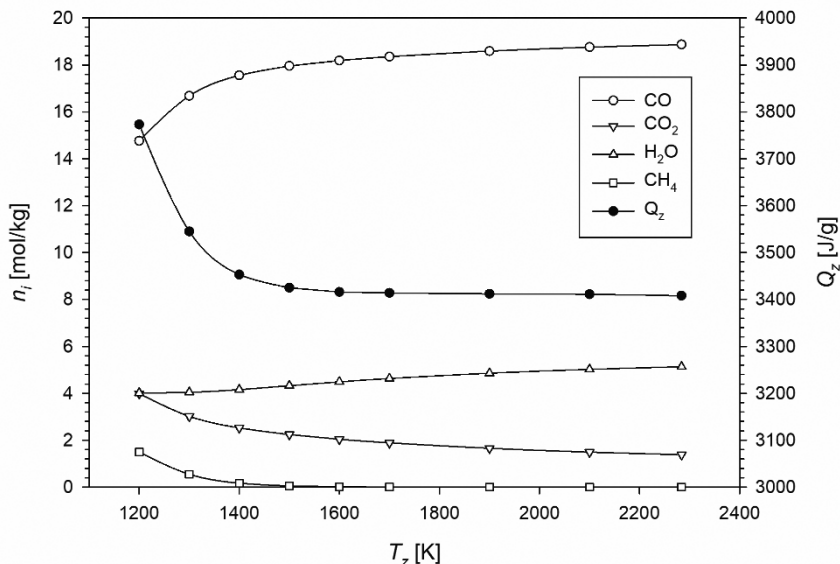
Figure 2.   Dependence of the calculated number of moles of the main
components of the combustion products and the heat of combustion
on the freezing temperature (P-1 propellant)

The graphs presented in Figure 2 show that the composition of the products
changes significantly below the initial temperature (the equilibrium temperature
in the bomb). This fact affects the heat of combustion calculated on the basis
of the composition of the reaction products. In the literature, a freezing
temperature of 1700 K, *e.g.* [10], is often used to calculate the combustion
heat of propellants.

Despite the change in the composition of the combustion products, the thermal
effect differences do not exceed 4% for the P-1 propellant when the temperature
is decreased from T_{eq} to 1300 K. This can be explained by the similar thermal
effects of two competing reactions:

$$CO + 0.5O_2 \leftrightarrow CO_2 + 281.79 \text{ J} \qquad\qquad\qquad\qquad (a)$$

$$H_2 + 0.5O_2 \leftrightarrow H_2O + 240.58 \text{ J} \qquad\qquad\qquad\qquad (b)$$

For this reason, despite the relatively large variation in the number of moles
of CO_2 and H_2O in Figure 2, the change in reaction heat is small.

In the next step, it was checked whether it was possible to estimate the final composition of the combustion products and a corresponding combustion heat close to the measured thermal effect. For all of the tested propellants, the heat effects for the compositions of the products frozen at temperatures $T_{z1} = T_{eq}$ (heat Q_{z1}), $T_{z2} = 1700$ K (heat Q_{z2}) and $T_{z3} = 1300$ K (heat Q_{z3}) were calculated from Equation 7. The compositions were calculated for a sample of propellant and argon in the calorimeter using the CHEETAH code. The temperature of 1300 K was chosen because it was noted that below this freezing temperature solid carbon was present in the calculated combustion products of P-1. However, there was no appearance of solid products of combustion from the tested propellants in the bomb filled with argon. In order to compare the results obtained from the thermochemical calculations and the experimental data, the relative difference between them (δ) was calculated according to the Equation 8. The results are listed in Table 6.

Table 6.   Differences between the experimental values of the heat of combustion and the theoretical heat of reaction

Propellant symbol	Q_{z1} [J/g]	δ_1	Q_{z2} [J/g]	δ_2	Q_{z3} [J/g]	δ_3
P-1	3395	−3.0	3402	−2.8	3535	1.0
P-2	3418	−2.9	3424	−2.7	3541	0.6
P-3	4459	−2.2	4530	−0.7	4548	−0.3
P-4	3963	−2.4	3988	−1.8	4040	−0.5
P-5	3907	0.2	3928	0.7	3974	1.9
JA-2	4664	0.1	4763	2.2	4770	2.4

Based on an analysis of the results in Table 6, it may be concluded that a similar scale of differences exists between the calculated and measured values of the heat of combustion of the tested propellants for different temperatures of freezing of the composition of the products. The maximum value of the relative difference δ does not exceed 3%. However, the average deviation calculated for all propellants according to Equation 9:

$$\bar{\delta} = \sqrt{\sum_{i=1}^{n} \delta_{ki}^2 / n} \tag{9}$$

where n is the number of tested propellants ($n = 6$), and $k = 1, 2, 3$, is 0.66%, 0.61% and 0.41% for T_{eq}, 1700 K and 1300 K, respectively. Therefore, the best agreement between the calorimetric heat and the theoretical one is that obtained

when the composition of the combustion products is assumed to be frozen at 1300 K. Therefore, a temperature of 1300 K should be taken as the freezing temperature of the reaction products in the procedure for calculating the theoretical heat of combustion for propellants.

5   Summary

In the present work, the heat of combustion of selected RDX-based propellants was measured using a calorimeter. The differences between the measured results for a given propellant do not exceed 1.5%. The ballistic parameters of the propellants were calculated using the CHEETAH thermochemical code with the BLAKE product library. The heat of combustion of the propellants was calculated taking into account the argon filling the calorimetric bomb and the freezing of the composition of the products at different temperatures. Based on an analysis of the measured results and calculations, it was found that the best agreement between the calorimetric heat and the theoretical one was obtained when the composition of the combustion products was assumed to be frozen at 1300 K.

The results of the thermochemical calculations indicate that some of the new RDX-based propellants are characterized by ballistic parameters comparable to those of JA-2. Their potential use in ammunition will be determined by other propellant characteristics, such as burning velocity, thermal stability or sensitivity to mechanical and thermal stimuli.

Acknowledgments

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