

CONSTANT-VOLUME COMBUSTION ENERGY OF THE LEAD SALTS OF 2HDNPPb AND 4HDNPPb AND THEIR EFFECT ON COMBUSTION CHARACTERISTICS OF RDX–CMDB PROPELLANT

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The constant-volume combustion energies of the lead salts of 2-hydroxy-3,5-dinitropyridine (2HDNPPb) and 4-hydroxy-3,5-dinitropyridine (4HDNPPb), ΔU_c (2HDNPPb(s) and 4HDNPPb(s)), were determined as -4441.92 ± 2.43 and -4515.74 ± 1.92 kJ mol⁻¹, respectively, at 298.15 K. Their standard enthalpies of combustion, $\Delta_c H_m^\circ$ (2HDNPPb(s) and 4HDNPPb(s), 298.15 K), and standard enthalpies of formation, $\Delta_f H_m^\circ$ (2HDNPPb(s) and 4HDNPPb(s), 298.15 K) were as -4425.81 ± 2.43 , -4499.63 ± 1.92 kJ mol⁻¹ and -870.43 ± 2.76 , -796.65 ± 2.32 kJ mol⁻¹, respectively. As two combustion catalysts, 2HDNPPb and 4HDNPPb can enhance the burning rate and reduce the pressure exponent of RDX–CMDB propellant.

Keywords: combustion energy, lead salt of 2-hydroxy-3,5-dinitropyridine, lead salt of 4-hydroxy-3,5-dinitropyridine, standard enthalpy of formation

Introduction

Lead salts of 2-hydroxy-3,5-dinitropyridine (2HDNPPb) and 4-hydroxy-3,5-dinitropyridine (4HDNPPb) are two novel energetic compounds containing two $-\text{NO}_2$ groups, which can be used as energetic burning rate catalysts of solid rocket propellants because of their excellent catalytic effect and ability to reduce pressure exponent for RDX–CMDB propellant [1, 2]. As combustion catalysts, an understanding of their thermochemical and thermodynamic properties is very important. However, their standard enthalpies of formation, $\Delta_f H_m^\circ$ have not yet been reported in the literature, the aim of this work is to determine their constant-volume combustion energies by a precise rotating bomb calorimeter and to calculate their standard enthalpies of combustion ($\Delta_c H_m^\circ$), to investigate their application possibilities in cyclotrimethylenetrinitramine-composite modified double-base (RDX–CMDB) propellant and to enrich the thermochemical database and provide the theoretical basis for further study on properties of 2HDNPPb and 4HDNPPb and their applications.

Experimental

2HDNPPb and 4HDNPPb used in this work were prepared according to the reported method [3]. Anal. calcd for $\text{C}_{10}\text{H}_8\text{N}_6\text{O}_{12}\text{Pb}$ (2HDNPPb): C 19.64,

N 13.75; O 31.42, Pb 33.88, found C 19.36, N 13.12, O 31.30, Pb 33.06%; m/z : 567.27; IR (KBr): $\nu_{\text{O-H}}$: 3441 cm⁻¹, $\nu_{\text{C-H}}$: 3090 cm⁻¹, $\nu_{\text{C=C, N=C}}$: 1605, 1573, 1493 and 1419 cm⁻¹, $\nu_{\text{C-NO}_2}$: 1530 and 1326 cm⁻¹, $\nu_{\text{C-O}}$: 1245 cm⁻¹. Anal. calcd for $\text{C}_{10}\text{H}_8\text{N}_6\text{O}_{12}\text{Pb}$ (4HDNPPb): C 19.64, N 13.75; O 31.42, Pb 33.88, found C 20.03, N 13.41, O 31.24, Pb 33.25%; m/z : 566.84; IR (KBr): $\nu_{\text{O-H}}$: 3442 cm⁻¹, $\nu_{\text{C-H}}$: 3070 cm⁻¹, $\nu_{\text{C=N, C=C}}$: 1613, 1555, 1487 and 1422 cm⁻¹, $\nu_{\text{C-NO}_2}$: 1529 and 1350 cm⁻¹, $\nu_{\text{C-O}}$: 1245 cm⁻¹. Their structures are shown in Fig. 1.

The constant-volume combustion energies of 2HDNPPb and 4HDNPPb were determined by a precise rotating bomb calorimeter (RBC-type II) [4]. The main experimental procedures were described previously [5]. The initial temperature was regulated to 25.000 $\pm 0.0005^\circ\text{C}$, and the initial oxygen pressure was 2.5 MPa.

The correct value of the heat exchange was calculated according to Linio–Pyfengdelel–Wsava formula [6].

The calorimeter was calibrated with benzoic acid of 99.999% purity. It had an isothermal heat of combustion at 25°C of -26434 ± 3 J g⁻¹. The energy

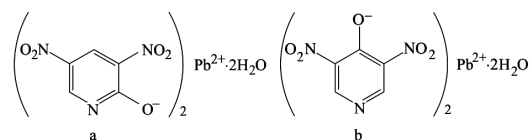


Fig. 1 Structures of a – 2HDNPPb and b – 4HDNPPb

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equivalent of calorimeter was determined to be $17936.01 \pm 9.08 \text{ kJ K}^{-1}$. The precision of the measurements was in $4.68 \cdot 10^{-4}$.

The analytical methods of final products (gas, liquid and solid) were the same as these in [7]. The analytical results of the final products showed that the combustion reactions were complete. As a result, either carbon deposits or carbon monoxide formed during the combustion reactions and the amount of NO_x in the final gas phase were negligible.

The burning rate was measured in strand burner filled with nitrogen. The sample prepared was the cylinder strand with $\Phi 5 \times 100 \text{ mm}$, coated by polyvinyl formal.

Results and discussion

Combustion energy of the compounds

The determination method of combustion energy for the compounds was the same as for the calibration of the calorimeter with benzoic acid. The combustion energies of the samples were calculated by the formula

$$\Delta_c U (2\text{HDNPPb}(s) \text{ or } 4\text{HDNPPb}(s)) = \frac{W\Delta T - aG - 5.983b}{m} \quad (1)$$

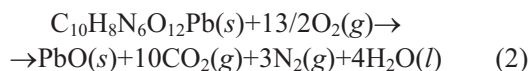
where $\Delta_c U (2\text{HDNPPb}(s) \text{ or } 4\text{HDNPPb}(s))$ denotes the constant volume combustion energy of the sample, W is the energy equivalent of the RBC-type 1 calorimeter (in J K^{-1}), ΔT is the correct value of the

temperature region, a is the length of the actual Ni–Cr wire consumed (in cm), G is the combustion enthalpy of Ni–Cr for ignition (0.9 J cm^{-1}), 5.983 is the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 mL of $0.1000 \text{ mol L}^{-1}$ solution of NaOH (in J mol^{-1}), b is the volume in mol of consumed $0.1000 \text{ mol L}^{-1}$ solution of NaOH, and m is the mass in g of the sample. The results of the calculation were given in Table 1.

Standard combustion enthalpies of the compounds

The standard combustion enthalpy of the compounds, $\Delta_c H_m^0 (\text{C}_{10}\text{H}_8\text{N}_6\text{O}_{12}\text{Pb}(s) \text{ 298.15 K})$, is referred to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 101.325 kPa.

- for 2HDNPPb and 4HDNPPb



The standard combustion enthalpies of the compounds were calculated by the following equations:

$$\Delta_c H_m^0 (\text{C}_{10}\text{H}_8\text{N}_6\text{O}_{12}\text{Pb}(s) \text{ 298.15 K}) = \Delta_c U (\text{C}_{10}\text{H}_8\text{N}_6\text{O}_{12}\text{Pb}(s) \text{ 298.15 K}) + \Delta nRT \quad (3)$$

$$\Delta n = n_g(\text{products}) - n_g(\text{reactants}) \quad (4)$$

where n_g is the total amount in mol of gases present as products or as reactants, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 298.15 \text{ K}$. The results of the calculations were given in Table 2.

Table 1 Experimental results for the combustion energies of the samples

Sample	No.	Mass of sample, m/g	Calibrated heat of combustion wire, Q_c/J	Calibrated heat of acid, Q_N/J	Calibrated $\Delta T/K$	Combustion energy of sample $-\Delta_c U/J \text{ g}^{-1}$
2HDNPPb	1	1.35720	12.60	60.45	0.5600	7280.43
	2	1.36237	10.80	60.68	0.5608	7264.56
	3	1.34535	11.70	59.92	0.5535	7259.74
	4	1.37302	12.60	61.15	0.5646	7255.59
	5	1.35084	12.60	60.17	0.5568	7272.81
	6	1.36027	12.60	60.59	0.5595	7257.36
	mean					7265.08 \pm 3.97
4HDNPPb	1	1.35236	12.60	59.61	0.5663	7389.91
	2	1.34728	11.70	59.38	0.5634	7380.36
	3	1.33524	12.60	58.85	0.558	7385.39
	4	1.35284	12.60	59.63	0.5672	7399.05
	5	1.34970	12.60	59.49	0.5646	7382.18
	6	1.34531	11.70	59.30	0.5624	7378.01
	mean					7385.82 \pm 3.14

Table 2 Combustion energy, standard combustion enthalpy and standard enthalpy of formation of the compounds (in kJ mol^{-1} at 298.15 K)

Sample	Molecular mass	$-\Delta_c U (\text{C}_{10}\text{H}_8\text{N}_6\text{O}_{12}\text{Pb}(s))$	$-\Delta_c H_m^0 (\text{C}_{10}\text{H}_8\text{N}_6\text{O}_{12}\text{Pb}(s))$	$-\Delta_f H_m^0 (\text{C}_{10}\text{H}_8\text{N}_6\text{O}_{12}\text{Pb}(s))$
2HDNPPb	611.406	444.92 \pm 2.43	4425.81 \pm 2.43	870.43 \pm 2.76
4HDNPPb	611.406	4515.74 \pm 1.92	4499.63 \pm 1.92	796.65 \pm 2.32

Standard enthalpies of formation of the compounds

The standard enthalpy of formation of the compounds, $-\Delta_c H_m^\circ(\text{C}_{10}\text{H}_8\text{N}_6\text{O}_{12}\text{Pb}(s) \text{ 298.15 K})$, were calculated by Hess's law according to the following thermochemical equations:

- the standard enthalpy of formation of 2HDNPPb

$$\begin{aligned} \Delta_f H_m^\circ [2\text{HDNPPb}(s) \text{ 298.15 K}] = & \\ = [\Delta_f H_m^\circ (\text{PbO}(s) \text{ 298.15 K}) + & \\ + 10\Delta_f H_m^\circ (\text{CO}_2(g) \text{ 298.15 K}) + & \quad (5) \\ + 4\Delta_f H_m^\circ (\text{H}_2\text{O}(l) \text{ 298.15 K})] - & \\ -\Delta_c H_m^\circ [2\text{HDNPPb}(s) \text{ 298.15 K}] & \end{aligned}$$

- the standard enthalpy of formation of 4HDNPPb

$$\begin{aligned} \Delta_f H_m^\circ [4\text{HDNPPb}(s) \text{ 298.15 K}] = & \\ = [\Delta_f H_m^\circ (\text{PbO}(s) \text{ 298.15 K}) + & \\ + 10\Delta_f H_m^\circ (\text{CO}_2(g) \text{ 298.15 K}) + & \quad (6) \\ + 4\Delta_f H_m^\circ (\text{H}_2\text{O}(l) \text{ 298.15 K})] - & \\ -\Delta_c H_m^\circ [4\text{HDNPPb}(s) \text{ 298.15 K}] & \end{aligned}$$

where $\Delta_f H_m^\circ (\text{PbO}(s) \text{ 298.15 K}) = -217.86 \text{ kJ mol}^{-1}$, $\Delta_f H_m^\circ (\text{CO}_2(g) \text{ 298.15 K}) = -393.51 \pm 0.13 \text{ kJ mol}^{-1}$, $\Delta_f H_m^\circ (\text{H}_2\text{O}(l) \text{ 298.15 K}) = -285.83 \pm 0.042 \text{ kJ mol}^{-1}$ [8].

The results of the calculations were also shown in Table 2. The fact of $\Delta_c H_m^\circ (2\text{HDNPPb}(s) \text{ 298.15 K}) < \Delta_c H_m^\circ (4\text{HDNPPb}(s) \text{ 298.15 K})$ shows that the thermal stability of 2HDNPPb is better than that of 4HDNPPb.

Effect of 2HDNPPb and 4HDNPPb on combustion characteristics of RDX-CMDB propellant

In order to investigate the possible possibility of 2HDNPPb and 4HDNPPb as combustion catalysts, the burning rates of the three minimum smoke RDX-CMDB propellant, RDX-CMDB propellant DB-1 (binder/RDX/methyl centralite/additive, 66/26/2.0/6.0) (system I), RDX-CMDB propellant DB-2 (1/2HDNPPb/cupric 2,4-dihydroxybenzoate, 100/2.0/0.5) (system III), RDX-CMDB propellant DB-3 (1/4HDNPPb/cupric 2,4-dihydroxybenzoate, 100/2.0/0.5) (system II), at different pressures were determined by using a strand burner. The results were

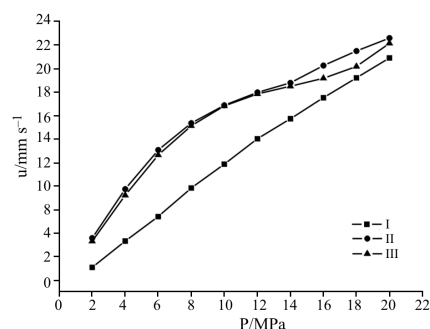


Fig. 2 Burning rate curves of systems I, II and III

shown in Fig. 2 and Table 3, indicating that (1) the burning rate for the propellants with 2HDNPPb and 4HDNPPb and cupric 2,4-dihydroxybenzoate is larger than that for the propellant without 2HDNPPb or 4HDNPPb and cupric 2,4-dihydroxybenzoate at the same pressures; (2) with increasing pressures, the burning rates of systems I–III increase; (3) the burning rates of system II is higher than that of system III, indicating that in comparison with 4HDNPPb, 2HDNPPb has the higher catalytic effect for RDX-CMDB propellants. In order to explain the influence of 2HDNPPb and 4HDNPPb on the combustion performance of system I, the pressure exponents (n) systems I–III and catalytic efficiency (\bar{Z}) for 2HDNPPb/cupric 2,4-dihydroxybenzoate and 4HDNPPb/cupric 2,4-dihydroxybenzoate on systems I–III are calculated using Eqs (7) and (8). By substituting the data in Table 3 into Eqs (7) and (8), the following values are obtained:

$$u_i = aP_i^n \quad i = 1 \sim 10 \quad (7)$$

$$\bar{Z} = \sum_{i=1}^k \frac{u_{\text{II(or III)}} / u_1}{k} \quad (8)$$

where a is coefficient, \bar{Z} is the average catalytic efficiency.

For system I in 2–20 MPa, $u = 1.69P$, $n = 0.843$, $r = 0.996$; for system II in 10–16 MPa, $n = 0.462$, $r = 0.9989$, $\bar{Z}_{2-6} = 1.61$, $\bar{Z}_{8-12} = 1.31$, $\bar{Z}_{14-18} = 1.11$; in 8–14 MPa, $n = 0.360$, $r = 0.9965$, $\bar{Z}_{8-14} = 1.3645$; for system III in 10–16 MPa, $n = 0.278$, $r = 0.9976$, $\bar{Z}_{2-6} = 1.72$, $\bar{Z}_{8-12} = 1.39$, $\bar{Z}_{14-18} = 1.10$, in 8–14 MPa, $n = 0.3599$, $r = 0.9886$, $\bar{Z}_{8-14} = 1.35$, showing that 2HDNPPb and 4HDNPPb possess better catalytic effect and abil-

Table 3 The burning rates of systems I–III at different pressure

System	$u/\text{mm s}^{-1}$ at different pressure/MPa									
	2	4	6	8	10	12	14	16	18	20
I	3.09	5.34	7.42	9.85	11.88	14.04	15.75	17.54	19.23	20.92
II	5.59	9.76	13.09	15.38	16.89	17.99	18.80	20.28	21.51	22.62
III	5.33	9.24	12.66	15.15	16.84	17.86	18.52	19.19	20.20	22.17

ity to reduce pressure exponent for RDX–CMDB propellant. In comparison with 4HDNPPb, 2HDNPPb has the higher catalytic efficiency. Therefore 2HDNPPb might have a good future for improvement of the burning rate of RDX–CMDB propellant. The position of the hydroxyl group in the molecules was the principal factor affecting the catalysis activity of 2HDNPPb and 4HDNPPb.

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