

COMBUSTION, EXPLOSION,
AND SHOCK WAVES

**Enthalpy of Formation and Explosive Properties
of 5,6-(3,4-Furazano)-1,2,3,4-Tetrazine-1,3-Dioxide**

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Abstract—The enthalpy of formation of 5,6-(3,4-furazano)-1,2,3,4-tetrazine-1,3-dioxide was determined, and the parameters of detonation, energetics, and performance characteristic were estimated.

Keywords: 5,6-(3,4-furazano)-1,2,3,4-tetrazine-1,3-dioxide, enthalpy of formation, explosive properties.

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INTRODUCTION

The explosive properties of compounds are determined by their chemical composition and structure. The enthalpy of formation and density of the monocrystal are characteristics of the structure of the high explosive. The power of HEs increases with the number of explosophoric groups in the HE molecule, being accompanied by a weakening of the chemical bonds and a change in the enthalpy of formation. The enthalpy of formation, density, and chemical composition are input parameters in calculating the detonation characteristics of HEs.

5,6-(3,4-Furazano)-1,2,3,4-tetrazine-1,3-dioxide (FTD) is a relatively new high explosive [1]. Its molecule contains a high-energy-content tetrazine dioxide group, the thermodynamic characteristics of which have been studied insufficiently. In the present work, we experimentally determined the enthalpy of formation of FTD and assessed its explosive properties and the prospects of practical applications.

EXPERIMENTAL

The energy of combustion of FTD was determined by burning this compound in a calorimetric bomb in excess of oxygen. The energy of combustion was measured on an automated hermetically sealed combustion calorimeter with a magnetic stirrer, isothermal jacket, and static calorimetric bomb, which was designed at the Institute of Chemical Physics of the Russian Academy of Sciences [2]. The design of the calorimeter was especially intended for burning energetic materials. The calorimeter was calibrated by burning K-1 benzoic acid certified at the Mendeleev Metrology Institute. The energy equivalent of the calorimeter was checked by burning secondary reference

compounds, such as succinic and hippuric acids. The calibration and tests of the calorimeter showed that the instrument makes it possible to measure the heat effect of combustion reactions to an accuracy of 0.02–0.03%.

The initial pressure of oxygen in the 200-cm³ bomb was 3×10^6 Pa. A 1-ml portion of water was introduced into the calorimetric bomb to create saturation vapor pressure and to dissolve the nitrogen oxides formed during combustion. The test materials were ignited with a cotton thread, which was tied to a platinum wire. The thread was ignited by heating the platinum wire by a preset-energy electric current pulse generated by a special device. The method used in the present work, with consideration given to the specifics of the combustion of nitrogen- and oxygen-containing organic compounds, was described in [3].

The results of measurements of the specific energy of combustion of FTD are summarized in Table 1. Since this compound is highly sensitive to mechanical impacts, it was burnt dissolved in dimethyl phthalate (DMP) to suppress its explosive combustion.

The calorimeter temperature rise was calculated with allowance for heat transfer from the calorimetric vessel to the thermal jacket. When determining the energy of combustion, we introduced corrections for the energy released during ignition and the heat of formation of nitric acid.

The enthalpy of formation of FTD in the DMP solution (ΔH_f°) was calculated according to the reaction of combustion of the compound:

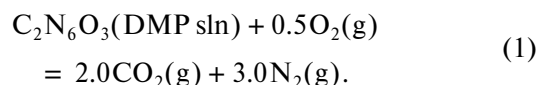


Table 1. Specific energy of combustion of FTD

HE number	Δm	ΔT	Q_t	q_{th}	q_{HNO_3}	q_{DMP}	$-\Delta U'_c$
1	0.05824	1.0999	1107.42	6.43	4.69	965.93	2238.5
2	0.05141	1.0807	1088.09	6.70	4.69	961.22	2246.2
3	0.05556	1.0358	1042.88	7.38	4.83	908.54	2198.2
4	0.05418	1.0714	1078.73	6.42	4.69	947.37	2220.3
5	0.06517	1.1073	1114.87	6.39	4.69	959.73	2210.4
6	0.08146	1.1330	1140.75	6.51	4.69	949.10	2215.2

Note: Δm is the mass of substance burnt, g; ΔT is the corrected temperature rise in the experiment, conventional degrees; Q_t is the total heat release, cal; q_{th} is the heat effect of combustion of the igniting cotton thread, cal; q_{HNO_3} is the heat effect of formation of nitric acid, cal; q_{DMP} is the energy of combustion of DMP, cal; $-\Delta U'_c$ is the specific energy of combustion of substance under conditions of a calorimetric bomb, cal/g; ΔH_c° is the standard enthalpy of combustion of the substance, kcal/mol; ΔH_f° is the standard enthalpy of formation of the substance, kcal/mol; $T = 298$ K, $-\Delta U'_c = 2221.5 \pm 7.3$ cal/g (SD), $\Delta H_c^\circ(\text{cr}) = -343.4 \pm 2.3$ kcal/mol, and $\Delta H_f^\circ(\text{DMP sln}) = 155.3 \pm 2.3$ kcal/mol.

In calculating the enthalpy of formation of FTD, we used the following enthalpies of formation of the combustion products:

$$\Delta H_f^\circ(\text{CO}_2)(\text{g}) = -94.051 \text{ kcal/mol},$$

$$\Delta H_f^\circ(\text{H}_2\text{O})(\text{l}) = -68.315 \text{ kcal/mol}.$$

To change over from the enthalpy of formation of FTD in DMP solution to the enthalpy of formation of FTD in the standard state, it is necessary to take into account the enthalpy of solution. The enthalpy of solution was measured on a Calvet calorimeter (Setaram, France). Before dissolution, the substances were placed into thin-walled glass ampules with a ground-in inlet tube, which were connected to a high-vacuum system and placed into thermostatically controlled heaters. Upon drying the substances at 30°C, the ampules were sealed off using a thin-flame burner and a special protective shield that prevented the substance from being affected by high temperature. In the course of dissolution, the substances were weighed on a Bunge balance to 2×10^{-6} g. The enthalpy of solution of FTD in DMP was found to be -5.6 ± 0.1 kcal/mol. The standard enthalpy of formation ΔH_f° of FTD in the crystalline state is related to the enthalpy of formation FTD in DMP solution as

$$\Delta H_f^\circ(\text{C}_2\text{N}_6\text{O}_3)(\text{cr}) = \Delta H_f^\circ(\text{C}_2\text{N}_6\text{O}_3)(\text{DMP sln}) - \Delta H_s^\circ(\text{C}_2\text{N}_6\text{O}_3)(\text{cr}), \quad (2)$$

where $\Delta H_s^\circ(\text{C}_2\text{N}_6\text{O}_3)(\text{cr})$ is the enthalpy of solution of FTD in DMP.

With account of the enthalpy of formation, the standard enthalpy of formation of FTD was determined to be 160.9 ± 2.3 kcal/mol or $1031.3 \pm$

14.6 cal/g. The error was defined as the double standard deviation at the 0.95 confidence level.

PARAMETERS OF THE DETONATION OF 5,6-(3,4-FURAZANO)-1,2,3,4-TETRAZINE-1,3-DIOXIDE

The enthalpy of formation, density, and chemical composition of the high explosive make it possible to estimate the detonation velocity and the temperature and pressure in the chemical reaction zone within the framework of a thermodynamic model [4] based on a theoretically substantiated state of the fluid phase (gas in a supercritical state) and the equation of state of the solid and liquid graphite and diamond nanoparticles formed in the detonation products. Table 2 lists calculated and measured parameters for a wide variety of HEs, which differ in chemical composition, enthalpy of formation, and density.

These data make it possible to compare the explosive properties of FTD with a number of regular HEs. In particular, the detonation velocity for DTD was found to be 9.7 km/s at the maximum density of 1.84 g/cm³, in close agreement with the respective values for dinitrodiazonofuroxan and hexanitrohexaazaisowurtzitane (compounds 12 and 13 in Table 2).

ENERGY CHARACTERISTICS AND SENSITIVITY OF 5,6-(3,4-FURAZANO)-1,2,3,4-TETRAZINE-1,3-DIOXIDE

The known enthalpy of formation makes it possible to readily estimate the maximum heat of explosion Q_{max} , which can be considered as an energy potential of FTD, an inherent characteristic of the HE. This quantity can be used to compare HEs according to the energy stored in their molecules. The energy potential

Table 2. Parameters of the detonation of HEs

HE number	Chemical formula	ΔH_f° , kcal/mol	ρ , g/cm ³	D , km/s		T , K	P , kbar
				expt	calc		
1	C ₇ H ₅ N ₃ O ₆	-17.8	1.64	6.94	6.90	3563	163.4
2	C ₄ H ₈ N ₈ O ₈	17.9	1.902	9.15	9.16	3653	381.0
3	C ₂ H ₄ N ₄ O ₄	-31.0	1.885	8.87	8.90	3142	327.5
4	CH ₃ N ₅ O ₄	0	1.88	9.20	9.21	3176	358.0
5	CN ₄ O ₈	8.8	1.64	6.40	6.46	2256	150.0
6	C ₂ N ₆ O ₁₂	20.0	1.86	7.58	7.58	2440	235.5
7	C ₆ N ₆ O ₆	138.8	1.901	8.62	8.72	4711	349.0
8	C ₆ N ₆ O ₁₂	47.5	1.973	9.33	9.34	4896	390.0
9	C ₆ N ₁₂ O ₆	270.4	1.74	8.58	8.60	4472	313.0
10	C ₅ H ₈ N ₄ O ₁₂	-125.5	1.77	8.30	8.35	4141	301
11	C ₃ N ₁₂	218.6	1.15	5.6	5.65	3954	89.0
12	C ₄ N ₈ O ₈	159.6	2.02	10.0*	10.1	5209	475.0
13	C ₆ H ₆ N ₁₂ O ₁₂	89.6	2.044	9.80*	9.91	4095	460.6
14	C ₂ N ₆ O ₃	160.9	1.84	—	9.70	5460	453.0

Notes: ρ is the monocystal density, D is the detonation velocity, T is the temperature, and P is the pressure; (1) TNT, (2) HMX, (3) diaminodinitroethylene (FOX-7), (4) dinitroguanidine, (5) tetranitromethane, (6) hexanitroethane, (7) benzotrifuroxan, (8) hexanitrobenzene, (9) trinitrotriazidobenzene, (10) PETN, (11) cyanurtriazide, (12) dinitrodiazenofuroxan, (13) hexanitrohexaazaisowurtzitane (CL-20), and (14) 5,6-(3,4-furazano)-1,2,3,4-tetrazine-1,3-dioxide.

* The detonation velocities obtained by extrapolating the experimental data to the monocystal density [5–7].

Table 3. Correlation between the sensitivity of HEs arranged in the order of increasing sensitivity and their energy characteristics

HE number	Chemical formula	ρ , g/cm ³	ΔH_f° , kcal/mol	Q_{\max} , kcal/kg	P_{cr} , kbar
1	CH ₄ N ₄ O ₂	1.77	-23.0	1091	13.8
2	CH ₃ N ₅ O ₄	1.88	0	1211	11.6
3	C ₇ H ₅ N ₃ O ₆	1.64	-17.8	1400	11.5
4	C ₆ H ₆ N ₆ O ₆	1.938	-39.4	1190	11.4
5	C ₂ H ₄ N ₄ O ₄	1.885	-31.0	1345	10.0
6	C ₇ H ₅ N ₅ O ₈	1.70	6.3	1518	9.7
7	C ₃ H ₆ N ₆ O ₆	1.80	14.7	1625	7.5
8	C ₅ H ₈ N ₄ O ₁₂	1.77	-125.5	1658	7.4
9	C ₄ H ₈ N ₈ O ₈	1.902	17.9	1619	6.5
10	C ₆ N ₆ O ₆	1.901	138.8	1670	5.9
11	C ₆ H ₆ N ₁₂ O ₁₂	2.044	98.5	1659	4.5
12	C ₆ N ₆ O ₁₂	2.00	47.5	1758	3.7
13	C ₂ N ₆ O ₃	1.84	160.9	1935	3.4
14	C ₄ N ₈ O ₈	2.02	159.6	1860	2.2

Note: (1) Nitroguanidine, (2) dinitroguanidine, (3) TNT, (4) triaminotrinitrobenzene, (5) diaminodinitroethylene, (6) tetryl, (7) RDX, (8) PETN, (9) HMX, (10) benzotrifuroxan, (11) hexanitrohexaazaisowurtzitane (CL-20), (12) hexanitrobenzene, (13) 5,6-(3,4-furazano)-1,2,3,4-tetrazine-1,3-dioxide, and (14) dinitrodiazenofuroxan.

of a HE is calculated using the equation of its explosive decomposition based on the Berthelot principle of maximum heat release. According to the Berthelot principle, the equation of explosive decomposition for FTD can be written as



which yields $Q_{\max} = 1935$ cal/g.

The energy characteristics of HEs can be correlated to their sensitivity to mechanical stimuli. Table 3 list organic HEs in the order of increasing experimentally measured sensitivity and maximum heat of explosion. As can be seen, the maximum heat of explosion correlates with the sensitivity, confirming the known empirical rule: the greater the power of the HE, the higher its sensitivity.

RESULTS AND DISCUSSION

For a number of reasons, the explosive properties of FTD have not been experimentally studied. The present work fills this gap by making use of the measured enthalpy of formation, density, and developed calculation methods. The chemical composition, along with the known enthalpy of formation and crystal density, makes it possible to reliably estimate the velocity, pressure, and temperature of FTD detonation (compound **14** in Table 2).

The authors of [8] proposed a criterion for assessing the sensitivity of organic HEs, which makes it possible to predict the sensitivity of HEs without invoking experimental data. This criterion is the maximum heat of explosion Q_{\max} , which provides a reliable method for arranging HEs in the order of increasing sensitivity. Table 3 shows that an increase in Q_{\max} is accompanied by a rise in the sensitivity to mechanical stimuli. The relationship between the sensitivity of and the chemical energy stored in the HE determines the boundaries within which all practically important HEs fall. The energy stored characterizes the safety hazards in handling a given HE. High explosives with an energy close to that stored in TNT (1400 cal/g) have a low sensitivity, and, consequently, high explosion safety. High

explosives with an energy of 1400 to 1700 cal/g have an acceptable sensitivity, but require strict observance of safety regulations. HEs with an energy higher than 1700 cal/g are highly sensitive dangerously explosive and, therefore, of no practical interest. The characteristics of the HEs presented in Table 3 completely support this classification. As the energy stored decreases, so does the sensitivity of the HE. 5,6-(3,4-furazano)-1,2,3,4-tetrazine-1,3-dioxide and dinitrodiazonofuroxan (compounds **13** and **14** in Table 3) are highly sensitive HEs, with $Q_{\max} = 1935$ and 1860 cal/g, respectively. As can be seen from Table 3, FTD has a record value of Q_{\max} , 1935 cal/g, being highly sensitive powerful HEs, with a sensitivity comparable with that of initiating explosives; therefore, these compounds are of no practical interest as explosives.

Thus, based on the experimental value of the enthalpy of formation of 5,6-(3,4-furazano)-1,2,3,4-tetrazine-1,3-dioxide, we estimated its detonation parameters and sensitivity and draw conclusions on the practical importance of this high-energy compound.

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