Thermochimica Acta 614 (2015) 85–92

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Combustion behavior and physico-chemical properties of dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate (TKX-50)

V.P. Sinditskii[a,*], S.A. Filatov[a], V.I. Kolesov[a], K.O. Kapranov[a], A.F. Asachenko[b], M.S. Nechaev[b], V.V. Lunin[b], N.I. Shishov[c]

[a] *Mendeleev University of Chemical Technology, Moscow, Russia*
[b] *Topchiev Institute of Petrochemical Synthesis, RAS, Moscow, Russia*
[c] *Federal Centre for Dual-use Technologies "Soyuz", Dzerzhinsky, Moscow region, Russia*

ARTICLE INFO

Article history:
Received 26 March 2015
Received in revised form 9 June 2015
Accepted 10 June 2015
Available online 17 June 2015

Keywords:
Dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate (TKX-50)
Thermal decomposition
Enthalpy of formation
Burning behavior and flame structure
Surface temperature
Temperature dependence of vapor pressure

ABSTRACT

The physico-chemical characterization (thermal decomposition under non- and isothermal conditions, enthalpy of formation, burning behavior and flame structure) of a new explosive dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate is detailed. Combustion studies have shown that TKX-50 burns slightly faster than HMX and approaches the burning rate of CL-20. The combustion of TKX-50 has been shown to obey mechanism with the leading reaction in the condensed phase. The rates of TKX-50 decomposition in both solid and liquid phases proved to be slightly higher than the corresponding rates of decomposition of RDX. Decomposition of TKX-50 is determined by decomposition of free hydroxylamine formed in the reaction of dissociation of the salt. An intermediate decomposition product is ammonium salt of 5,5′-bis (2-hydroxytetrazole), which further decomposes in the second stage at elevated temperatures. The enthalpy of formation of TKX-50 has been measured with the help of bomb calorimetry, however the resulting value is quite different from the enthalpy reported earlier.

1. Introduction

Concerns about the environmental impact of energetic materials have grown in recent years, demanding new green energetic materials, first of all polynitrogen compounds, which decomposition releases mainly environmentally friendly N_2. Tetrazole derivatives are among these compounds. In order to improve energetic properties of the tetrazoles, N-oxides were proposed in several studies as providing even higher densities and stabilities, lower sensitivities and better oxygen balances [1–3]. A new explosive dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate (TKX-50), which belongs to this chemical class and outperforms all other commonly used explosives, has recently been synthesized [4]. According to published data, TKX-50 can be easily prepared; its explosive performance exceeds the performance of RDX and is comparable to that of CL-20. At the same time, it possesses good thermal stability, low toxicity, and safety of handling is comparable to that of RDX.

The detonation velocity of TKX-50 ($D = 9698\ \mathrm{m\,s^{-1}}$), calculated at maximal density of $1.918\ \mathrm{g\,cm^{-3}}$ (100 K), is higher than that of β-HMX [5] ($D = 9221\ \mathrm{m\,s^{-1}}$) and also of ε-CL-20 ($D = 9455\ \mathrm{m\,s^{-1}}$) [6]. At room temperature (298 K), the density of TKX-50 is $1.877\ \mathrm{g\,cm^{-3}}$. Next to its impressive performance, the impact sensitivity of TKX-50 is 20 J which is much lower than sensitivities of RDX, HMX, and CL-20, ranging from 4 to 7.5 J [4]. Friction sensitivity of TKX-50 with 120 N is comparable to or lower than sensitivity of RDX, HMX or CL-20 [4]. TKX-50 has an electrostatic sensitivity of 0.1 J [4], which is far higher than the human body can generate (0.025 J). Thermal stability of TKX-50 with a decomposition onset of 221 °C is comparable to that of RDX.

High energetic performance along with high safety allows considering TKX-50 as not only powerful explosive [4,7], but a promising propellant ingredient also, which could result in superior compositions [8,9]. Calculations have shown that TKX-50 is a better replacement of RDX in the composite modified double base (CMDB) propellants [8]. Substitution of HMX by TKX-50 in the nitrate ester plasticized polyether (NEPE) propellants results in a two- to five-second increase in the specific impulse. At the same time, neither combustion behavior nor combustion mechanism of TKX-50 has been studied up to date, that are required for purposeful design and adjustment of TKX-50-based rocket propellants.

It is obvious that high energetic characteristics of TKX-50 are primarily due to its high enthalpy of formation. Gas phase enthalpy of formation (131.2 kJ/mol for neutral form of charged components and 1962.3 kJ/mol for noninteracting ions [10]) was computed by

---

[*] Corresponding author. Fax: +7 495 4966027.
E-mail address: vps@rctu.ru (V.P. Sinditskii).

http://dx.doi.org/10.1016/j.tca.2015.06.019
0040-6031/© 2015 Elsevier B.V. All rights reserved.

combining the atomization method and quantum mechanics [11] (CBS-4 M method [12]). The last value was converted into the solid state enthalpy of formation (446.6 kJ/mol) [4] by subtraction of lattice enthalpy calculated according to Jenkins et al. [13]. The usability of the above method to calculate lattice enthalpy of salts is discussed in [14], indicating that the experimental enthalpy of formation of TKX-50 (439 kJ/mol) proved to be in a good agreement with the calculated one (446.6 kJ/mol).

Without going into discussion on the calculation methods, we note that the present value of the enthalpy of formation of TKX-50 is highly questionable. Indeed, a simple sum of enthalpies of formation of TKX-50 constituents—hydroxylamine (−114.18 kJ/mol [15]) and 5,5′-bis (2-hydroxytetrazole) (~481 kJ/mol, estimation based on enthalpy of formation of 5,5′-bistetrazole [16]) gives a much lower value of 253 kJ/mol. Heat of reaction between an acid and a base, so-called heat of salt formation, is a difference between enthalpy of formation of salt and sum of enthalpies of formation of salt constituents. Based on comparison of enthalpies of formation of hydroxylammonium perchlorate [17], hydroxylammonium nitrate [15], liquid perchloric acid [15], nitric acid and hydroxylamine [15], heat of salt formation for hydroxylamine salts averages 67 kJ per one mole of hydroxylamine. Taking into account heat of salt formation for two hydroxylamine molecules (~134 kJ, estimation), the enthalpy of formation of TKX-50 can be calculated as ~119 kJ/mol, that is more than three times less than the value reported in [4].

The thermal behavior of TKX-50 and the kinetics of its thermal decomposition were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in nonisothermal condition only [18], the decomposition mechanism of TKX-50 remains unknown. By applying multiple heating rate DSC measurements and Ozawa's isoconversional model-free method the activation energy of 143.2 kJ/mol, and pre-exponential factor of $1.99 \times 10^{12}\ s^{-1}$ were calculated from DSC peak maximum temperature *vs.* heating rate relationship [18].

Initial decomposition steps of TKX-50 were predicted with the help of molecular dynamics simulations on the periodic TKX-50 crystal [19]. The authors showed that continuous heating of this periodic system eventually led to decomposition of the protonated or diprotonated bistetrazole to release N_2 and N_2O. The reaction barrier for release of N_2 and N_2O was calculated with help of finite cluster quantum mechanics studies (B3LYP). The author found that transferring one proton to the bistetrazole dianion decreased the reaction barriers. It is a striking result of work [19] that very unstable hydroxylamine, decomposing as it melts near 32 °C, did not undergo any changes upon virtual heating.

The purpose of the present work is to study burning regularities and combustion mechanism of TKX-50 as well as to obtain its thermochemical properties such as thermal stability and enthalpy of formation.

2. Experimental

2.1. Preparation

TKX-50 was prepared by a modified method published elsewhere [4] via the reaction of dichloroglyoxime with sodium azide in *N*-methylpyrrolidone. TKX-50 was crystallized from mother solution, isolated by suction filtration, and air dried. The obtained TKX-50 has been characterized by ^{1}H and ^{13}C NMR spectroscopy.

2.2. Decomposition study

Experiments on TKX-50 decomposition were carried out in thin-walled glass manometers of the compensation type (the glass Bourdon gauge) at 170–200 °C. A 10 to 15 mg sample was loaded into a glass manometer of 12–15 cm^3 volume. The device was vacuumized to 0.1 mm Hg, sealed, and immersed in a thermostat with the Wood's alloy. The temperature in the thermostat was maintained with an accuracy of ±0.5 °C. Pressure of gases evolved in the experiments (the accuracy of pressure measurements was ±1 mm Hg) was monitored, and the rate constant was calculated as stated below.

2.3. Combustion study

Burning rates of TKX-50 were measured in a window constant-pressure bomb of 1.5-liter volume in the 0.1–10 MPa pressure interval. Samples to test were prepared as pressed cylinders of 0.93–0.95 TMD confined in transparent acrylic tubes of 4 mm i.d. For some of combustion experiments, crystals of TKX-50 were covered with 3% of fluorocarbon-based synthetic rubber (Viton A analog) to provide for better compressibility and combustion stability of pressed samples.

Temperature profiles in the combustion wave were measured using fine tungsten–rhenium thermocouples. The thermocouples were welded from 80%W + 20%Re and 95%W + 5%Re wires 25 μm thick followed by rolling in bands 5–7 μm thick. The thermocouple was embedded into the center of the sample. The method of preparation of the strands used in burning rate determinations and temperature profile measurements was described in detail in [20]. The thermocouple signal was recorded with a Pico ADC 216 digital oscilloscope.

2.4. Calorimetric measurements

The calorimetric measurements were carried out using a standard bomb calorimeter B-08 M equipped with a modified oxygen bomb of 210.5 mL volume, which was capable of withstanding an explosion of 2 g of a powerful explosive. Distilled water was added to the calorimetric bucket to reach a total mass of 4587 ± 0.1 g; the temperature of the filled calorimetric bucket was brought to 298 ± 0.05 K. The increase in temperature was measured with a temperature measuring instruments "Testo 735" to the nearest 10^{-3} K, providing an accuracy of measurements less than 1%. The calorimeter was calibrated using thermochemical grade benzoic acid with a quoted internal energy of combustion $\Delta_c U = -26434.32 \pm 0.61\ J\ g^{-1}$ [21,22]. The heat equivalent of the calorimeter was measured as $\varepsilon = 14{,}675 \pm 3\ J\ K^{-1}$.

Samples of pure TKX-50 (~0.5 g) were placed into NiCr stainless steel crucibles and burned at oxygen pressure of 2–2.5 MPa. Ignition of all samples was performed using electrically heated steel firing wires of about 9 cm length with a quoted internal energy of combustion $\Delta_c U = 6694\ J\ g^{-1}$ [21]. A contribution of the combustion energy from the ignition wire (along with the Joule heat) was accounted for by measuring the mass of unburned wire fragments and calculating the combustion energy of the burned wire. All the experiments were carried out in nitrogen-free oxygen of 99.95% purity. In order to remove the air, the bomb was purged with oxygen at 1 MPa prior to final pressurization. Considering nitrogen atoms being present in the TKX-50 molecule, the formation of nitric acid during combustion was checked by potentiometry. The accuracy of measurements was 0.0005 °C for temperature and 0.1÷0.2% for the heat of combustion.

Thermodynamic calculations were performed with the "REAL" computer code for simulation of the chemical equilibrium [23].

3. Results and discussion

3.1. Bomb calorimetric measurements

When ignited in the calorimetric bomb at oxygen pressure of 2 MPa, pressed samples of pure TKX-50 were burned completely