



Study of the Thermal Decomposition and Combustion of Guanidinium 5,5'-Azotetrazole Salt

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Abstract: The thermal decomposition and combustion of guanidinium 5,5'-azotetrazole salt (Gu_2AzT) have been investigated. Temperature profiles in the Gu_2AzT combustion wave were measured using thin tungsten-rhenium micro thermocouples. It was shown that combustion of the salt obeys the condensed-phase mechanism. The high burning rate of Gu_2AzT is connected with the high decomposition rate in the melt. The kinetic parameters of the controlling chemical reaction have been estimated, and a detailed combustion mechanism for Gu_2AzT has been proposed.

Keywords: salt of 5,5'-azotetrazole with guanidine, burning rate, temperature profiles, thermal decomposition, combustion mechanism

Introduction

Salts of 5,5'-azotetrazole (H_2AzT) with organic bases, including guanidine (Gu_2AzT), have been considered as potential components for some gunpowders [1], gas-generating compositions [2-4], and 'green' (HCl – free exhaust gases) double-base [1, 5] and composite propellants [2, 4]. Gu_2AzT is of special interest because of its high nitrogen content, low burning temperature and the low molecular weight of its combustion products. It has been also offered as a gas generating agent for automobile airbag systems in mixtures with different oxidizers (e.g. potassium nitrate [3] and copper(II) oxide [6]). According to

literature data Gu_2AzT has a high enthalpy of formation ($\Delta H_f^\circ = 410$ [7] or 452 [8] kJ/mol), as well as a low sensitivity to mechanical stimuli [7].

Literature data exist for the thermal decomposition of 5,5'-azotetrazole salts under non-isothermal conditions [5, 7, 8]. The burning behaviour and combustion mechanism of compositions of 5,5'-azotetrazole salts with oxidants have been studied in model engines [6]. The burning rate, laser ignition and flash pyrolysis characteristics of triaminoguanidinium azotetrazolate have been determined [9]. However, a systematic study of the combustion and thermal decomposition, as well as a study of the combustion mechanism of 5,5'-azotetrazole salts, were not conducted.

The goal of the present work was to study Gu_2AzT combustion behaviour, its combustion wave structure and to determine the location and chemical nature of the leading reaction of combustion.

Experimental part

Preparation

The disodium salt of 5,5'-azotetrazole pentahydrate ($\text{Na}_2\text{AzT}\cdot 5\text{H}_2\text{O}$) is the most readily accessible azotetrazolate described in the literature and can be synthesized by oxidation of 5-amino-1*H*-tetrazole with potassium permanganate in sodium hydroxide solution. $\text{Na}_2\text{AzT}\cdot 5\text{H}_2\text{O}$ (2.1 g, 7.0 mmol) was dissolved in hot water (20 mL), yielding a clear bright yellow solution, and a solution of guanidinium nitrate (1.7 g, 14.0 mmol) in hot water (10 mL) was added in small portions. An immediate precipitation of the product was observed as the reaction mixture cooled. The resulting mixture was stored in a refrigerator for 2 h. After this time, the yellow powder was filtered off and washed with cold water (10 mL), and then isopropyl alcohol (30 mL). The product was left to air-dry (1.87 g, 94%).

Decomposition study

The thermal studies were carried out using differential scanning calorimetry (DSC). A sample (2-3 mg) was pressed in aluminium caps and heated at different rates. Manometric experiments were carried out in thin-walled glass manometers of the compensation type (glass Bourdon gauge). A sample of Gu_2AzT (10-15 mg) was loaded into a vial of 12-15 cm³ volume. The vial was evacuated to 0.1 mm Hg, sealed, and immersed in a thermostat containing Wood's metal. The temperature in the thermostat was maintained constant with an accuracy of ± 0.5 °C. The pressure of the gases evolved during the course of

the experiments (the accuracy of the pressure measurements was ± 0.5 mm Hg) was recalculated to the volume of the gases under normal conditions, and the rate of gas evolution was then evaluated. The rate constant was calculated as the current gas evolution rate to the final volume of the evolved gases.

Combustion Study

The burning rates were measured in the pressure interval 0.1-20 MPa in a constant-pressure bomb of 1.5 L volume equipped with windows. Samples for testing were prepared as pressed cylinders at 0.82-0.84 TMD (1.538 g/cm^3 [7]) confined in transparent acrylic tubes of 4 mm i.d. A video camera was used to determine the character of the combustion process as well as the burning rates.

The temperature profiles in the combustion wave were measured using fine thermocouples. The thermocouples were welded from 80%W + 20%Re and 95%W + 5%Re wires 25 μm thick, followed by rolling into bands 5-7 μm thick. The thermocouple was embedded in the center of the sample so that the section with the junction was parallel to the combustion front. The thermocouple signal was recorded with a Pico ADC 216 digital oscilloscope. Thermodynamic calculations were performed using the 'REAL' computer simulation of chemical equilibrium code [10].

Results and Discussion

Initial screening of the Gu_2AzT was performed using differential scanning calorimetry. DSC reveals that Gu_2AzT has only one exothermic peak at 262 $^\circ\text{C}$ (10 K/min), with an energy release of 200-300 cal/g. Kinetic data for the thermal decomposition of Gu_2AzT under non-isothermal conditions were calculated with help of Kissinger's equation [11], suggesting a first order reaction:

$$\ln \frac{\phi}{T_m^2} = \ln \frac{AR}{E} - \frac{E}{RT_m}$$

where: ϕ is the heating rate, $^\circ\text{C/s}$, E is the activation energy, A is the pre-exponential factor, and T_m is the maximal temperature of the exotherm. The rate constants for Gu_2AzT decomposition, according to the DSC data, fall on a straight line ($\ln k$ vs $1/T$), with a rather high activation energy of 46.3 kcal/mol.

Curves of the gas release in the experiments on the isothermal decomposition in glass manometers have a typical saturated shape, the final gas volume increasing with increasing temperature from 365 to 465 cm^3/g (4.6 to 5.9 mol/mol) (Figure 1). The gaseous decomposition products which

condensed upon cooling to room temperature were about 5%. Cooling the remaining gases, after decomposition at 226.5 °C, to low temperatures (to -33 °C), resulted in the condensation of ~1 mol gases that might be connected with the condensation of low volatility HCN, NH₂CN and so on. The remaining 1.9 mol of condensable gas (from -33 °C to -195 °C) are most likely ammonia, and the non-condensable gas is evidently nitrogen. Complete decomposition of Gu₂AzT leads to the formation of a condensed, light-brown residue, which according to IR spectroscopy has C=N bonds and its elemental content is close to that of melamine and melem (2,6,10-triaminoheptazine), a product of cyanamide polymerization. IR-spectroscopic analysis of the gaseous products of the flash pyrolysis of the analogous compound triaminoguanidinium azotetrazolate also showed the presence of ammonia, HCN, nitrogen and cyanamide [9].

In the temperature range of 200-226.5 °C, the decomposition of Gu₂AzT is described by a first-order reaction with autocatalysis to a high degree of decomposition: $k_1 = 5.0 \times 10^{14} \cdot \exp(-42260/RT)$, $k_2 = 4.2 \times 10^{17} \cdot \exp(-46340/RT)$, c⁻¹. Therefore, the kinetics calculated from the data obtained under non-isothermal conditions in the DSC experiments is formal, since it is the averaged kinetic parameters of the process with the autocatalytic stage (Figure 2). For comparison, data on the thermal decomposition of tetrazole [12] are presented in Figure 2. The comparison shows that the direct reaction (k_1), as well as the autocatalytic stage (k_2), of Gu₂AzT decomposition is slower than the decomposition of tetrazole.

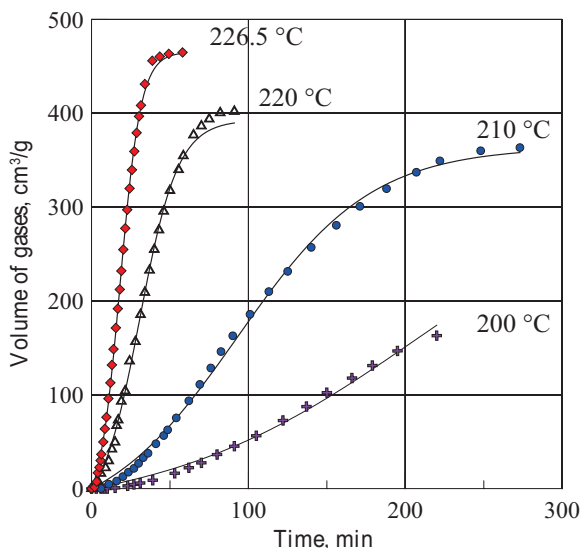


Figure 1. Curves of gas release during decomposition of Gu₂AzT at $m/V = 9\text{-}13$ mg/cc and different temperatures.

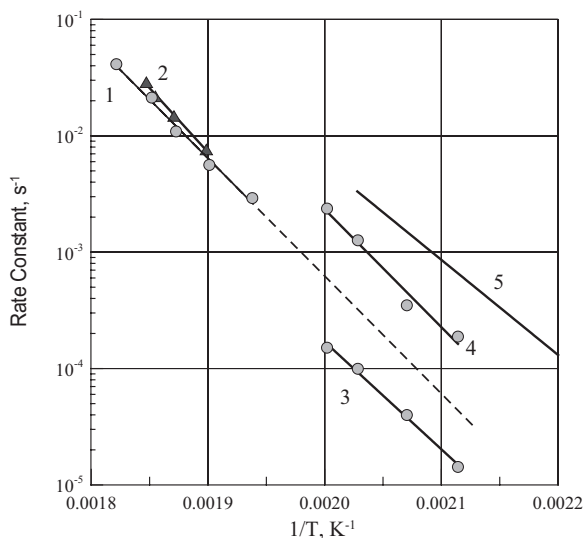


Figure 2. Comparison of the decomposition rate constants of solid Gu_2AzT , measured under non-isothermal (1 and 2 [7]) and isothermal conditions (3 is direct reaction, 4 is self-acceleration). 5 is the decomposition rate constants of tetrazole.

Gu_2AzT in the form of samples pressed into 4-mm acrylic tubes can sustain burning at a pressure of 0.2 MPa and shows stable burning above 0.6 MPa. The burning is flameless at all pressures studied and accompanied by the formation of copious white smoke and a solid residue inside the tubes. The burning rate of Gu_2AzT at 10 MPa was 25.6 mm/s, which is 1.5 times faster than HMX (Figure 3). The Gu_2AzT burning rate-pressure dependence is expressed as $b_r = 0.69p^{0.78}$, mm/s for the pressure interval 0.2-20 MPa.

The temperature profiles in the Gu_2AzT combustion wave were obtained at pressures of 0.7, 1.1, 2.0, and 10 MPa with the help of thin tungsten-rhenium thermocouples. A phenomenon of flameless combustion was observed at all pressures studied (Figure 4), which is typical for combustion governed by reactions in the condensed phase. The characteristic temperatures in the combustion wave of Gu_2AzT , the surface temperature (T_s) and the maximum temperature (T_f), were measured.

The experimental Gu_2AzT surface temperature data, in coordinates $\ln p$ vs. $1/T_s$, fall satisfactorily on a straight line, $\ln p = -13066/T + 20.26$ (Figure 5). The slope of the line yielded the enthalpy of the salt evaporation as 77.9 kcal/mol. This value is close to the Gu_2AzT salt dissociation ΔH_{diss} (73 kcal/mol), calculated according to the following scheme:

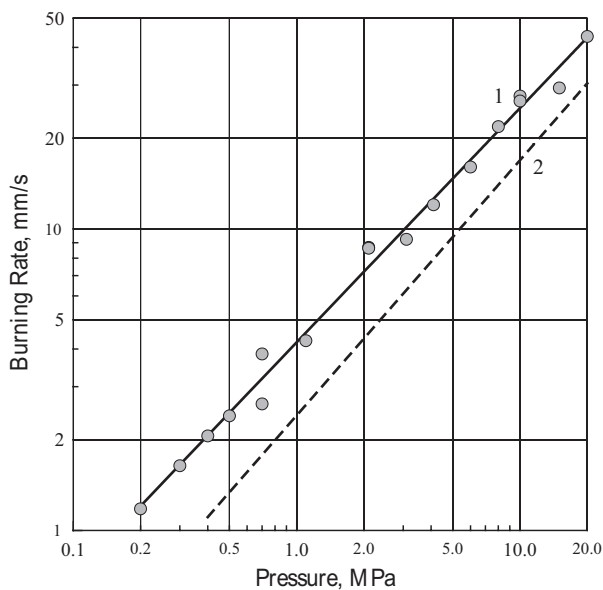


Figure 3. Comparison of burning rates of Gu₂AzT (1) and HMX (2).

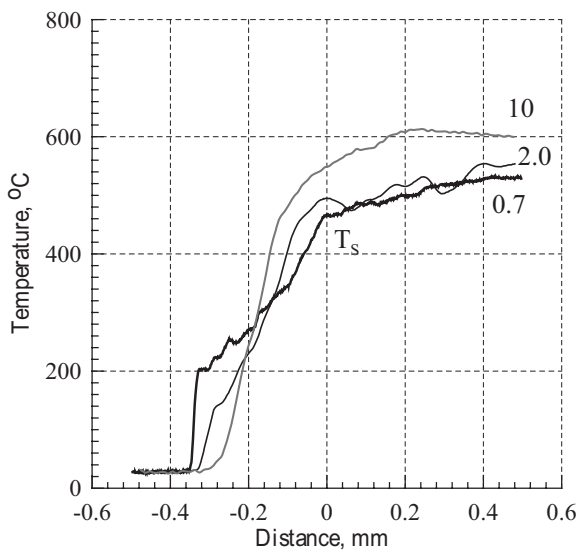


Figure 4. Typical temperature profiles for Gu₂AzT recorded at 0.7, 2 and 10 MPa.



Thus, it may be concluded that the surface temperature during Gu_2AzT combustion is controlled by the dissociation process, as in the cases of many other salts. It should be noted that the Gu_2AzT surface temperature is close to T_s for ammonium nitrate [13] (Figure 5).

The maximal flame temperature reaches $600\text{ }^\circ\text{C}$. This is much lower than the calculated adiabatic temperature ($1070\text{ }^\circ\text{C}$). It was shown earlier [14] that the incompleteness of heat release in combustion of endothermic energetic materials in the absence of oxygen was caused by the formation of high-energy thermostable nitrile derivatives in the combustion products. If one fixes 2 moles of HCN and 2 moles of ammonia in the combustion products in the calculation, the calculated adiabatic combustion temperature will be $750\text{ }^\circ\text{C}$, which is close to the measured temperatures.

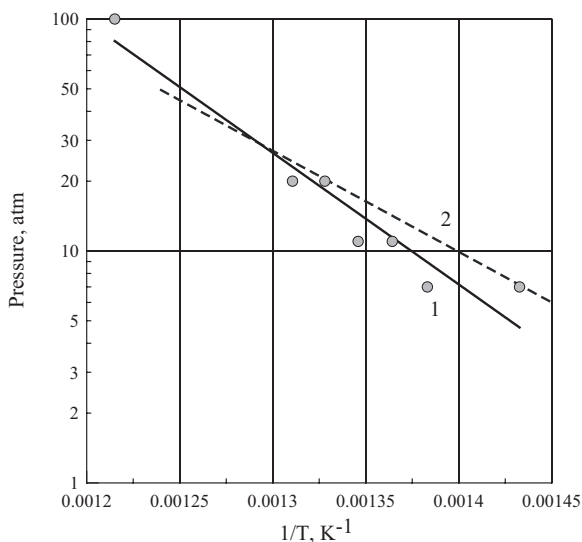
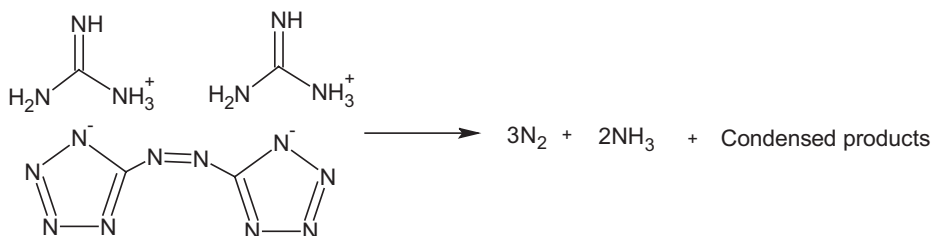


Figure 5. Vapor pressure as a function of reciprocal surface temperature for Gu_2AzT (1) and ammonium nitrate [13] (2).

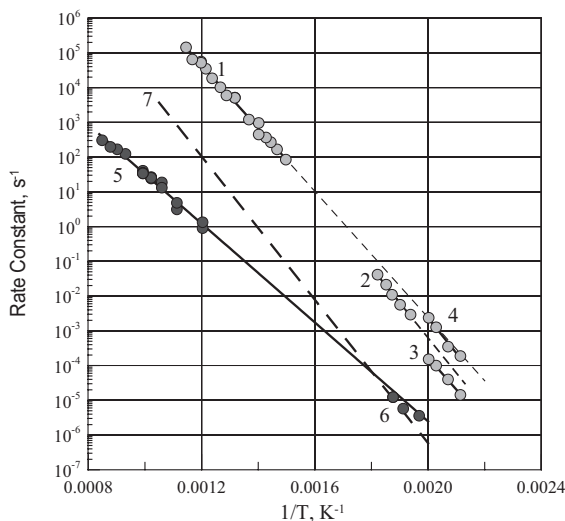


Figure 6. Comparison of the rate constants of the leading reaction in Gu_2AzT combustion (1) and the decomposition of solid Gu_2AzT , measured under non-isothermal (2) and isothermal conditions (3 is the direct reaction, 4 is self-acceleration), as well as the rate constants of the leading reaction of combustion (5) and decomposition of DAAzF (6) and ammonium nitrate (7).

As mentioned above, a phenomenon of flameless combustion was observed at all pressures studied (Figure 4), which is typical for combustions governed by reactions in the condensed phase. In previous work [15], it has been shown that for such types of energetic materials, the experimental data on burning rates and surface temperatures allows unique information on the decomposition kinetics at high temperatures to be derived. The well-known Zeldovich's model for combustion in the condensed phase [16] can be used. It was found that the kinetics of the leading reaction of combustion, $k = 3.6 \times 10^{15} \cdot \exp(-41600/RT)$, are in good agreement with the kinetic parameters for the self-acceleration of the decomposition determined under isothermal conditions at much lower temperatures (Figure 6). Since the salt is in the molten state in the combustion wave at high temperatures, this convergence suggests that the acceleration of Gu_2AzT decomposition is due to the lowering of its melting point under the influence of decomposition products and to decomposition in the liquid phase. Thus, as seen from Figure 6, the initial rate of Gu_2AzT decomposition in the solid phase (k_1) 10-16 times slower than in the liquid state (k_2). The activation energy of Gu_2AzT decomposition in the melt (41.6 kcal/mol) is higher than

the activation energy of decomposition of azofurazans (30-35 kcal/mol) [17], although the decomposition rate of, for example, diaminoazofurazan (DAAzF) is much lower (Figure 6). This difference most probably indicates that the Gu_2AzT decomposition, unlike other azocompounds, begins by decomposition of the tetrazole ring rather than the azogroup.

Conclusions

These studies show that the guanidinium salt of 5,5'-azotetrazole is quite satisfactory thermally stable. The initial rate of Gu_2AzT decomposition in the solid state is 10-16 times less than in the melt, while the activation energies are similar (42.3 and 41.6 kcal/mol, respectively). Gu_2AzT decomposition leads to the liberation of 3 moles of nitrogen, 1.9 moles of ammonia and 1 mol of readily condensable products along with the formation of a condensed residue.

In the pressure range 0.2-20 MPa, samples of Gu_2AzT pressed into 4 mm inner diameter acrylic tubes burn in the flameless regime 1.5 times faster than HMX. The surface temperature-pressure dependence ($\ln p = -13066/T + 20.26$) has been defined with the help of thin tungsten-rhenium thermocouples. It is controlled by dissociative evaporation of the salt and has a quite high value (370 °C at atmospheric pressure and 455 °C at 1 MPa), comparable to that of HMX and AN at high pressures. The measured temperature of combustion of Gu_2AzT is low (600 °C) and well below the adiabatic temperature (1070 °C), which is associated with the formation of endothermic nitrile fragments in the combustion products. It has been shown that combustion of the salt obeys the condensed-phase mechanism. The high burning rate of Gu_2AzT is connected with the high decomposition rate in the melt.

It is obvious that the presence of compounds containing the nitrile group among the Gu_2AzT combustion products does not allow Gu_2AzT to be used as a monopropellant in gas generators. The high decomposition rate of Gu_2AzT in the melt, along with a high boiling point, suggests that the addition of Gu_2AzT to ammonium nitrate-based propellants will stabilize their combustion and increase the burning rate due to faster heat release in the condensed phase.

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