Regularities of the high-temperature transformation of poly-2-methyl-5-vinyltetrazole and solid fuel compositions based on it in the nitrogen atmosphere

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Abstract. Macrokinetic regularities of high-temperature transformations of energy compositions based on poly-2-methyl-5-vinyltetrazole as an active binder have been studied. It has been shown that, in contrast to synthetic rubber, which is currently used in solid rocket fuel, poly-2-methyl-5-vinyltetrazole when added to the energy compositions based on high-nitrogen heterocycles leads to an increase in the burning rate of the fuel. The synergetic effect of the interaction between a binder and dispersant, manifested in an increase in the burning rate of the high-energy composition, reaches a maximum value when the mass ratio of the components in a binary mixture is 1:1.

Introduction
Due to high enthalpies of formation, thermal stability, satisfactory sensitivity to impact and friction, high-nitrogen heterocyclic compounds are widely used as high-energy components in the composition of solid rocket propellants, gas-generating and explosive compositions [1-4].

In recent years, the concept of creating molecules that represent a combination of several heterocycles is widely used. This approach enables one to obtain compounds with new properties that expand the field of their application [2]. For example, theoretical and experimental data are available that show that creation of a new generation of ramjet engines solid fuels based on poly-nuclear heterocyclic compounds represented by a system of furazan, furoxan and azipine (seven-membered heterocycle with one nitrogen atom) cycles is possible [3-4]. Due to the high enthalpy of formation these chemical compounds are capable, after exposure to an initiating heat impulse, of a rapid chemical transformation accompanied by the release of a large amount of heat and gases. Thus, they can serve as dispersants for other fuel components, providing gasification and removal of the formed gases from the gas-generator together with the dispersed solid particles of the fuel and transfer of gasification products to the rocket afterburner [3].

The present work is devoted to the study of macrokinetic regularities of high-temperature transformations of solid fuel compositions, based on 1,1'-dioxide-7,7'-bis(tris(1,2,5)oxadisolo)[3,4-
It should be noted that high energy characteristics, relatively high thermal stability, low toxicity and formation of a large amount of neutral gas during decomposition allows one to consider vinyl tetrazole polymers as promising components of explosive compositions and jet fuels [5-9]. It is important to note that tetrazole-containing polymers, when used in fuel systems, have advantage over other polymer analogues in that they demonstrate good compatibility with components of compositions and greater safety in handling [8, 9].

1. Methods and Materials

The following substances were used as initial components of high-energy solid fuel compositions: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (octogen, β-HMX); poly-2-methyl-5-viniltetrazole (PMVT) (figure 1, compound 1) synthesized in IPCP RAS by using technique described in [5]; 1,1'-dioxide-7,7'-bis(tris([1,2,5]oxadiasolo)[3,4- b: 3',4'-d: 3'',4'-f] azepine), (Az₂(O)₂, figure 1, compound 2) synthesized in SDCB "Technolog" using technique described in [10] and synthetic rubber IR SKI-3 produced by SIBUR Togliatti LLC. The size of particles of the solid components was in the range 200-250 μm.

A standard Crawford bomb (or a constant pressure bomb) with a volume of 3·10⁻³ m³ was used to determine linear rates of thermal transformations of fuel compositions. The samples for testing, where PMVT was used as a binder, were pressed at 10 MPa into cylinders with a diameter of 8 mm and height of 8-10 mm. The samples with a poly-isoprene rubber SKI-3 as a binder were manufactured by carefully mixing the dispersant with the rubber dissolved in toluene, followed by distillation of the toluene at room temperature. The samples prepared this way were coated on the lateral surface with epoxy adhesive to provide the linear propagation of the combustion front and placed into the bomb in an asbestos-cement cup of the same internal size. Measurements were performed at a nitrogen pressure of 2 MPa.

Thermal initiation of the process was carried out from the open side of the cup with a nichrome spiral to which alternating current of 8 V was applied. The initiation time was 2 sec; the temperature did not exceed 1500 K. Temperature measurements were performed with the help of a thermocouple mounted at a distance of 4 mm from the open side of a cup. The thermocouple was in contact with the side surface of the sample, which was pressed into this cup. The pressure in the system was monitored by using inductive pressure sensors DD-10 and ID-21.

The average time of the process \( t \) was determined from experimental dependencies of pressure on the process time where the latter was defined as the interval between the time of beginning of growth of pressure and the time of pressure drop. The average linear rate of the process \( U \) was defined as \( U = \frac{h}{t} \), where \( h \) is the height of the cylindrical sample. The resulting accuracy of the burning rate measurements was 6%.
2. Results and discussion

The high-temperature transformation of two series of samples of high-energy fuel compositions were studied, with PMVT being used as a polymer binder and Az$_2$(O)$_2$ or HMX (for comparison) being chosen as dispersants. Each series consisted of samples with different concentrations of components.

The chemistry of high-temperature reactions of polycyclic azoles has not yet been investigated. In contrast, the mechanism of decomposition and combustion of tetrazoles derivatives has been well studied [2, 5-8, 11-12]. It has been shown that tetrazoles demonstrate self-propagating high-temperature decomposition [11]. This process is considered to be a form of combustion with no significant gas-phase reactions, although, in contrast to conventional self-propagating high-temperature synthesis (SHS), it is accompanied by formation of gas [12]. The linear rate of high-temperature transformations of the studied compositions will further on be referred to as the burning rate.

As it can be seen from Figure 2, after the action of the heat impulse on the prepared capsules with individual reagents and their composition, a self-propagating process is initiated, accompanied by heat and gas release. Moreover, the increase in pressure resulting from the release of gases is linear in time, which indicates that the process is stationary.

![Figure 2. Relative pressure increase during combustion of the binary composition with equal fractions of azepine Az$_2$(O)$_2$ and energy binder PMVT (curve 1); azepine Az$_2$(O)$_2$ (curve 2) and PMVT (curve 3) at initial nitrogen pressure of 2 MPa.](image)

Note that the rate of thermal transformation of the polymer is several times lower than the burning rate of the dispersant Az$_2$(O)$_2$ (Figure 2, curve 2 and 3). What is somewhat unexpected is that the burning rate of a binary mixture of these components exceeds the burning rate of individual substances. Indeed, increasing of the PMVT content to 50 mass % results in the burning rate growth, as presented in Figure 2 (curve 1-3) and Figure 3 (curve 1). With a further increase in the binder content of up to 80 mass %, the burning rate of the composition, although starting to fall, nevertheless remains higher than that of the individual dispersant Az$_2$(O)$_2$ (Figure 3, curve 1).

It is obvious that the maximum burning rate of a binary mixture with equal content of energy components corresponds to some optimal experimental conditions that promote the appearance of a synergistic effect. The reason for this effect can be interactions between the components of the fuel at the chemical or molecular level, change in the thermo-physical properties of the binary mixture. Elucidation of the nature and the mechanism of the observed synergistic interaction between the Az$_2$(O)$_2$ and PMVT requires additional research.

For example, in [13-14] synergism was observed when measuring the rates of combustion of charges consisting of different fractions of HMX and ammonium perchlorate AP. It was found that mutual influence of reagents occurs not only at the chemical, but also at the physical level of the process. The influence of the size and degree of contact between the particles were analyzed. The
specific surface of AP was shown to play a key role in the manifestation of the synergistic effect in combustion [13].

![Figure 3. Burning rate dependency on the polymer binder content in fuel compositions based on PMVT and Az$_2$(O)$_2$ (1); synthetic rubber SKI-3 and Az$_2$(O)$_2$ (1'); PMVT and HMX (2); synthetic rubber SKI-3 and HMX (2'). Initial nitrogen pressure P = 2 MPa.](image)

It should be noted that the interaction of HMX with the PMVT binder did not lead to an increase in the burning rate of their binary mixtures, whereas the dependence of the burning rate on the quantitative content of the composition had complicated character (Figure 3, curve 2). Attention should also be paid to the fact that the burning rate of the HMX-PMVT binary mixtures exceeds the combustion rate of HMX compositions with a synthetic rubber (these compositions are widely used in modern solid propellants). In contrast, the HMX-PMVT composition burns at a noticeable rate even at high content of the binder (Figure 3, curve 2), whereas the combustion rate of the HMX-SKI fuel decreases quickly with an increase in the proportion of SKI (Figure 3, curve 2').

As for the Az$_2$(O)$_2$-PMVT mixture, it can be seen from Figure 3 that the increase in the SKI content to 20 mass % results in slight growth of the burning rate. However, more experiments are needed to confirm the extreme burning rate dependence on the binder concentration.

It remains to note that in the range of higher concentrations of the binder, the burning rates of the Az$_2$(O)$_2$-PMVT mixtures significantly exceed the burning rates of the Az$_2$(O)$_2$-SKI compositions (Figure 3, curve 1 and 1').

3. Conclusion

Macrokinetic regularities of high-temperature transformations of energy compositions based on poly-2-methyl-5-vinyltetrazole as an active binder have been studied. It has been shown that, in contrast to synthetic rubber, which is currently used in solid rocket fuel, poly-2-methyl-5-vinyltetrazole (PMVT), when added to energy compositions based on the 1,1'-dioxide-7,7'-bis(tris([1,2,5]oxadiasolo) [3,4- b: 3',4'-d: 3''4'-f]azepine (Az$_2$(O)$_2$), leads to an increase in the burning rate of the fuel.

The synergistic interaction between the components of the high-energy composition, manifested in an increase of the burning rate, is at the maximum value when their mass ratio in a binary mixture is 1:1. In the range of the high concentrations of the binder, the burning rates of the Az$_2$(O)$_2$-PMVT mixtures significantly exceed the burning rates of the Az$_2$(O)$_2$-SKI and HMX-SKI compositions.

Obtained results need further investigations to get deeper insight into the nature of observed synergistic interaction between high nitrogen heterocyclic compounds like Az$_2$(O)$_2$ and PMVT.

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