Kinetics of thermal decomposition of hexanitrohexaazaisowurtzitane

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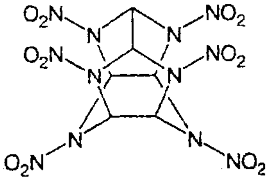
Thermal decomposition of hexanitrohexaazaisowurtzitane (HNIW) in the solid state and in solution was studied by thermogravimetry, manometry, optical microscopy, and IR spectroscopy. The kinetics of the reaction in the solid state is described by the first-order equation of autocatalysis. The rate constants and activation parameters of HNIW thermal decomposition in the solid state and solution were determined. The content of N_2 amounts to approximately half of the gaseous products of HNIW thermolysis. The thermolysis of HNIW and its burning are accompanied by the formation of a condensed residue. During these processes, five of six nitro groups of the HNIW molecule are removed, and one NO_2 group remains in the residue, which contains amino groups and no C—H bonds.

Key words: nitramines, hexanitrohexaazaisowurtzitane, thermal decomposition, solid state reactions, kinetics.

Hexanitrohexaazaisowurtzitane (HNIW) possesses several interesting properties. Therefore, the study of its thermal decomposition is of great interest despite numerous works devoted to thermolysis of *N*-nitro compounds.[1] Since HNIW is a powerful explosive,[2] it is important from the practical viewpoint to know its thermal stability. Unlike other explosive cyclic nitramines, the HNIW molecule contains six NNO_2 groups and has a polycyclic structure; both these factors can affect the regularities of thermolysis. HNIW has a number of crystalline modifications,[3] and it is a convenient object for studying the influence of the crystal structure on the reactivity of molecular crystals.

In the first study of the thermal decomposition of HNIW,[4] the kinetics of the process based on the weight loss in the 190—204 °C temperature interval has been investigated. The reaction proceeds with an almost unchanged rate up to ~50% conversion. The kinetic curves were processed using the first-order equation. As a result, the following activation parameters were found: $E_a = 151.7$ kJ mol^{-1}, $A = 10^{13.6}$ s^{-1}. By contrast, the authors of Ref. 5 studied the thermal decomposition of the ε-form of HNIW in the 160—180 °C temperature range. They found that the reaction proceeds with a pronounced autoacceleration and its rates can be described by the first-order kinetic equation of autocatalysis. For noncatalytic process, the activation parameters E_a and A are equal to 172±26 kJ mol^{-1} and $10^{13.8\pm3}$ s^{-1}, and for the catalytic process, they are 185±7 kJ mol^{-1} and $10^{18.0\pm0.8}$ s^{-1}, respectively. Thermal decomposition of HNIW was also studied in a 1% solution in acetone at 146—226 °C.[6] The kinetics of the reaction, as well as that of decomposition of 12 nitramines studied in the cited work, obeys the first-order equation. The activation parameters E_a and A are equal to 177 kJ mol^{-1} and $4 \cdot 10^{17}$ s^{-1}, respectively.



Data on heat release under the conditions of programmed heating also provide information on the thermal decomposition of HNIW. Temperatures corresponding to the beginning of heat release can depend on various factors, such as the heating rate, the amount of a sample, and others. In the case of the ε-modification of HNIW, this temperature is equal to 210 °C (at a heating rate of 10 °C min^{-1}),[7] 220 °C (10 °C min^{-1}),[2] and 218.91 °C (2 °C min^{-1}).[5]

The composition of gaseous products of HNIW thermolysis has been studied in several works.[4—6] For example, at 240 °C, 1 mole of HNIW gives 9.61 moles of gaseous products with the following composition (the number of moles of the corresponding composition is indicated in parentheses): N_2 (4.29), N_2O (0.82), CO_2 (3.30), and CO (1.20).[6] The reaction in acetone affords the same substances but in a different ratio: 0.97, 0.07, 0.20, and 0.19, respectively; as a whole, 1 mole of HNIW gives 1.43 moles of gaseous products. At 250—400 °C, NO_2 (~50%) and NO (~25%) are the main gaseous products of decomposition.[4] CO, HCN, N_2O, and CO_2 are formed in lower amounts. Under the conditions of nonisothermal decomposition up to

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270 °C, CO_2, N_2O, NO_2, and HCN are the main gaseous products; NO and CO traces were also observed.[5]

According to the published data,[8] the thermal decomposition of HNIW at 205 °C is accompanied by the formation of an amorphous[4] solid residue (17% of the weight of the starting sample) with the molecular formulas $H_3C_3N_2O_2$ [4] and $C_6H_5N_5O_2$.[8] It has been shown by IR spectroscopy that the condensed residue contains the C=O, C=N, N—H, and amide groups. According to the results of Ref. 5, the residue contains the amide and carbonyl groups, C=N, C—C, C=C, NO, and polymeric fragments of the azine and melone types. At higher temperatures, the condensed residue undergoes decomposition and NO_2 was found among the gaseous products of this process.[8] This suggests that the condensed product of HNIW thermolysis contains the nitro groups.

Based on the data presented above, the predominant role of homolysis of the $N-NO_2$ bond at the first stages of HNIW decomposition was suggested.

In this work, we studied in detail the kinetics of thermal decomposition of HNIW. Since HNIW is close to HMX in explosion properties, the parameters of decomposition of these two substances were compared in several cases.

Experimental

Samples of the ε-modification of HNIW (Thiokol Corporation, Brigham City, Utah, USA) were used. Observations by an MBI-15-2 optical microscope showed that the samples consist of transparent well formed crystals with mainly orthorhombic and pseudo-hexagonal habitus. The crystals have an average size of 150 μm and are characterized by a narrow size distribution.

The kinetics of thermal decomposition of HNIW was studied by two methods. An ATV-14M automated electronic thermobalance designed at the Institute of Problems of Chemical Physics of the RAS (Chernogolovka) was used for thermogravimetric measurements. Samples with a weight of 8—10 mg were placed in quartz glasses with an inner diameter of 6 mm and a height of 10—12 mm. In addition, the kinetics of thermal decomposition of HNIW was studied by the manometric method for 3% solutions in *m*-dinitrobenzene, which dissolves nitro compounds well and has a low vapor density under the measurement conditions. Manometric experiments were carried out by the compensation method using glass membrane Bourdon gages in the 150—195 °C temperature range.

IR spectra were recorded on a Specord 75-IR spectrophotometer with a spectral width of the gap of ≤3 cm^{-1} in the interval of 400—2000 cm^{-1}.

Results and Discussion

The IR spectra of ε-HNIW samples molded with KBr (Fig. 1) coincide with the published data.[3,5] It is remarkable that all lines in the spectrum of HNIW are narrow. This indicates that the fragmentary mobility in the HNIW crystal is absent. Prior to measurements, the HNIW samples were dried on a thermobalance to constant weight. However, as shown by the IR spectra (bands at 3415 and 3515 cm^{-1} in Fig. 1), a minor amount of water (most likely, water of intracrystallization) remains in the substance.

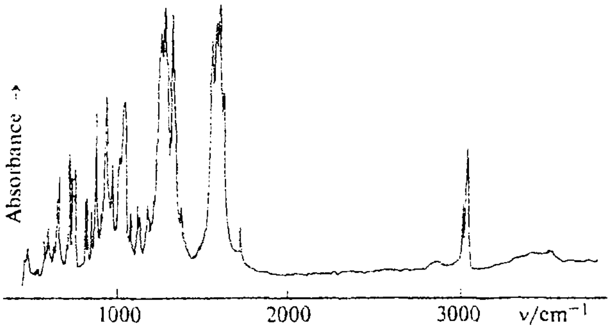

Fig. 1. IR spectrum of ε-HNIW.

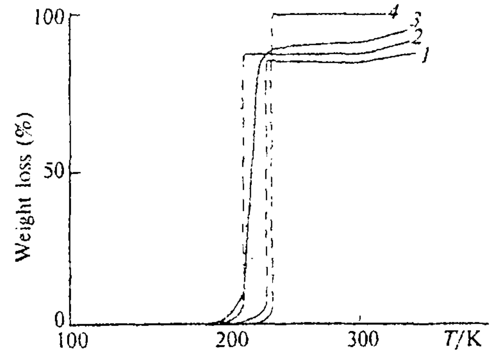

Fig. 2. Thermal decomposition of HNIW (*1—3*) and HMX (*4*): *1* and *4*, in air; *2*, in argon; and *3*, under continuous evacuation (weighed sample 10 mg, heating rate 4 °C min^{-1}).

The results of studying the thermal decomposition of HNIW in the nonisothermal regime at a heating rate of 4 °C min^{-1} are presented in Fig. 2. The data on HMX decomposition in air are also presented for comparison. In air and argon, HNIW thermolysis is accompanied by ignition at 243 and 224 °C, respectively. HMX is ignited at 248 °C. The dotted lines in Fig. 2 characterize the weight loss during ignition. When HMX burns, complete gasification occurs, whereas in the case of HNIW burning in air and argon, ~16% condensed residue are formed. This residue is stable up to 300 °C, and further temperature increase results in its decomposition. Being heated to 610 °C (4 °C min^{-1}), the residue losses ~60% weight. When HNIW is heated under a dynamic vacuum, the fast weight loss (~85%) begins at 215 °C, but no ignition occurs.

In a particular experiment, HNIW sample pre-powdered in an agate mortar and heated to 80 °C was subjected to further heating to 190 °C, and its IR spectrum was recorded during heating in the region of stretching vibrations of the nitro groups. Based on the shape and intensity of spectral lines, conversion can be estimated as 5.7%, and on heating from 80 to 190 °C, the spectrum of HNIW remains unchanged, *i.e.*, no phase transition occurs. Then the sample was cooled to room temperature, and the spectrum was recorded again. The overall spectrum obtained after cooling of the sample to room temperature corresponds to the γ-form of HNIW. It follows from this that transition to the γ-form occurs in the 20—80 °C temperature region, and this is precisely the form of HNIW that undergoes thermal decomposition.

The results of studying the kinetics of thermal decomposition of HNIW obtained under isothermal conditions by the gravimetric method are presented in Fig. 3. A condensed residue whose weight is 17.3% of the weight of the starting sample is formed in the studied temperature range. The kinetic curves have a pronounced autoacceleration character and are well described by the first-order equation of autocatalysis

$$d\alpha/dt = k_1(1-\alpha) + k_2\alpha(1-\alpha), \qquad (1)$$

where $\alpha = (m_0 - m)/(m_0 - m_\infty)$, m_0 is the weight of the starting sample, m is its weight at moment t, and m_∞ is the weight of the sample at the end of experiment. The calculated rate constants are presented in Table 1. The temperature dependences of the rate constants k_1/s^{-1} and k_2/s^{-1} are described by the Arrhenius equations:

$$k_1 = 10^{20.5\pm0.8}\exp[-(53400\pm1500)/(RT)] \quad (r = 0.998),$$

$$k_2 = 10^{17.3\pm1.4}\exp[-(44700\pm2900)/(RT)] \quad (r = 0.989),$$

where R is the universal gas constant expressed in cal mol^{-1} deg^{-1}.

The reaction proceeds somewhat more rapidly in dry argon than in air. When decomposition is carried out in a dynamic vacuum (under continuous evacuation), the initial rate of the process is higher than that in air or argon. In addition, for the ~22% weight loss, a characteristic inflection appears in the kinetic curve of the reaction performed *in vacuo* (Fig. 4, *a*). In a closed system (manometric Bourdon vessel), the reaction occurs in the same way as in gravimetric experiments; however, this inflection is not observed in the kinetic curve (Fig. 4, *b*). In this case, the weight loss is somewhat lower than that for the reaction in air and amounts to 75—78%.

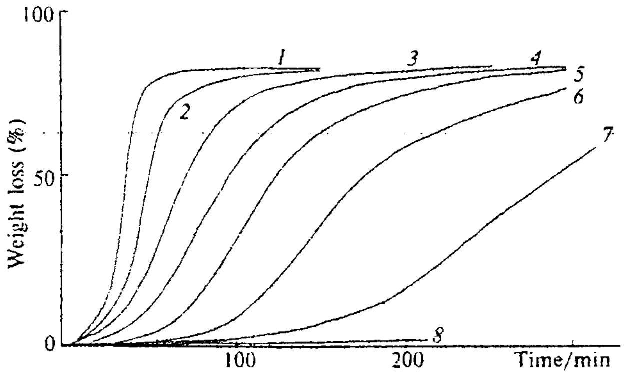

Fig. 3. Kinetics of thermal decomposition of HNIW (*1—7*) and HMX (*8*) in air: *1*, 211 °C; *2*, 206 °C; *3*, 202 °C; *4*, 196 °C; *5*, 192 °C; *6*, 187 °C; *7*, 183 °C; and *8*, 220 °C.

Table 1. Rate constants of thermal decomposition of HNIW solution in air

Temperature/°C	$k_1 \cdot 10^6$	$k_2 \cdot 10^5$
	s^{-1}	
183	6.9±0.5	9.3±0.5
187	11±1	13±2
192	22±1	19±2
196	39±2	31±3
202	86±4	47±5
206	110±8	83±5
211	195±11	180±12

It follows from manometric measurements that the complete decomposition of 1 g of HNIW gives 570 cm^3 (standard conditions) of gaseous products. This implies that the decomposition of 1 mole of HNIW is accompanied by the evolution of ~11 moles of gases. Cooling of

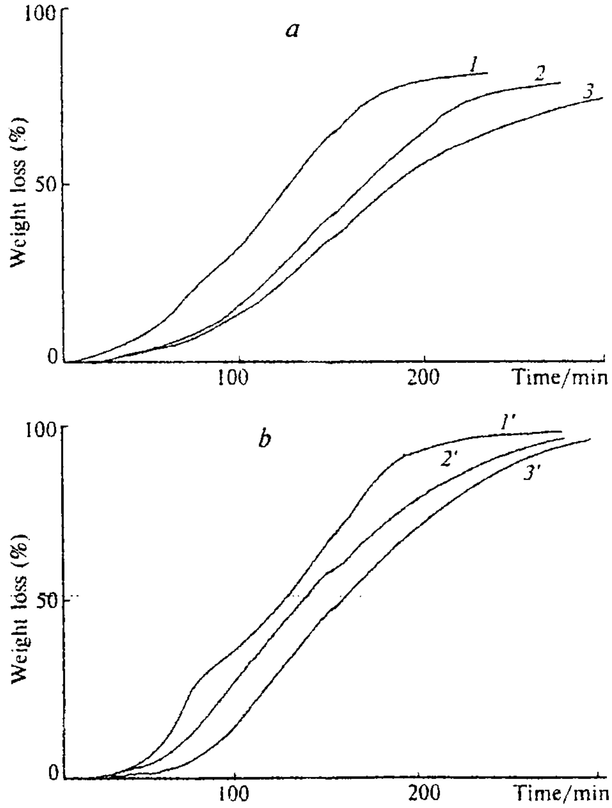

Fig. 4. Kinetics of thermal decomposition of HNIW at 196 °C (*a*) and 202 °C (*b*): *1* and *1'*, in a dynamic vacuum; *2*, in argon (1 atm); *2'*, in a Bourdon gauge; and *3*, *3'*, in air (1 atm) (weighed sample 10 mg).

the reaction system to −196 °C after complete decomposition made it possible to determine the content of N_2 in the formed gases, because only nitrogen is not condensed at this temperature. It was established that gas formed due to decomposition contained 47 vol.% N_2, *i.e.*, 5.2 moles of N_2 are formed from 1 mole of HNIW. Comparison of the volume of evolved gases with the mass loss during decomposition showed that the average molecular weight of the gaseous reaction products is equal to ~33.5.

The condensed product formed upon the thermal decomposition of HNIW in air is dark-brown. If the reaction is performed under a dynamic vacuum, the quite black residue is formed. This distinction is due to the morphological peculiarities of the residue rather than its chemical composition: after grinding for spectral measurements in molded pellets with KBr, both products gain a dark-brown color.

The IR spectrum of the condensed product of HNIW decomposition in air at 202 °C is presented in Fig. 5. The spectrum contains absorption bands of the amino groups that form hydrogen bonds (3100—3210 cm^{-1}), carbonyl groups (1753 cm^{-1}), and the nitro groups (1625, 1390 cm^{-1}). These are characteristically the same nitramine groups as those in the starting HNIW. The spectrum of the product of HNIW decomposition *in vacuo* at the same temperature has a similar shape and differs from the aforementioned spectrum mainly by a lower intensity of the band of stretching vibrations of the carbonyl group. The IR spectrum of the residue obtained by burning resembles that presented in Fig. 5 but differs by a lower intensity of the bands corresponding to the carbonyl and nitro groups. The intensity of the band attributed to CO is still lower than that in the case of HNIW thermolysis under a dynamic vacuum. By contrast, when thermal HNIW decomposition proceeds in argon, the intensity of the band corresponding to the CO group in the spectrum of the residue is higher than that for the reaction in air. Thus, the concentration of carbonyl groups in the residue decreases in the following order: argon, air, dynamic vacuum, flash. The thermolysis products have diffuse IR spectra characteristic of amorphous samples. The spectrum contains no bands of C—H vibrations.

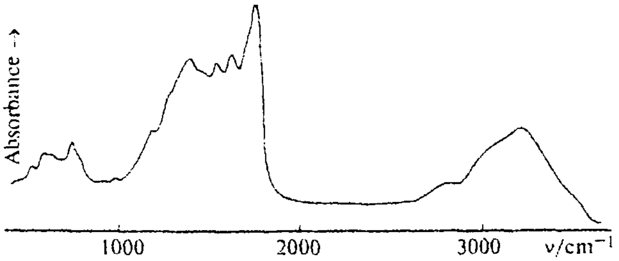

Fig. 5. IR spectrum of the condensed product of thermal decomposition of HNIW. Decomposition temperature 202 °C.

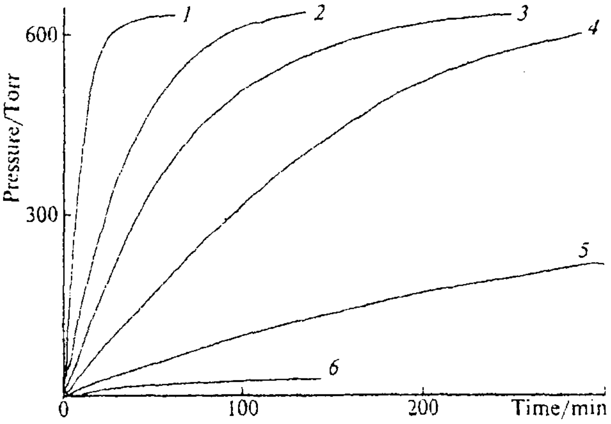

Fig. 6. Kinetics of thermal decomposition of HNIW (*1*—*5*) and octogen (*6*) solutions in *m*-dinitrobenzene: *1*, 195 °C; *2*, 180 °C; *3*, 170 °C; *4*, 160 °C; *5*, 150 °C; and *6*, 180 °C (weighed sample of HNIW (or octogen) 3 mg, weighed sample of *m*-dinitrobenzene 97 mg, volume of the reaction vessel 3.6 mL).

Microscopic observations of the condensed residue formed in the HNIW thermolysis in air or dynamic vacuum show that this residue consists of irregular particles (nearly lamellar), nonporous, brown, transparent, acute-angled, with a size of 50—70 μm (for decomposition in air) or 60—100 μm (for decomposition in a dynamic vacuum). The particles are united to form compact subparallel aggregates with a characteristic size of ~150 μm. Some aggregates retain shapes, although distorted, of the starting crystals: orthorhombic and pseudo-hexagonal.

Typical kinetic curves obtained in the experiments on the thermal HNIW decomposition in *m*-dinitrobenzene are presented in Fig. 6. In this case, the strong autoacceleration characteristic of solid phase decomposition is absent, and the reaction, except for the initial region, is satisfactorily described by the first-order kinetic equation. The rate constants are presented in Table 2. The corresponding Arrhenius equation has the form

$$k = 10^{18.6\pm0.4}\exp[-(45300\pm900)/(RT)] \quad (r = 0.999),$$

where k is expressed in s^{-1}, and R is expressed in cal mol^{-1} deg^{-1}.

Table 2. Rate constants of thermal decomposition of HNIW in *m*-dinitrobenzene (concentration of the solution 3%, m/V = 0.85 g L^{-1})

Temperature/°C	$k \cdot 10^5$	$k_0 \cdot 10^5$
	s^{-1}	
140	—	0.38±0.02
150	1.5±0.2	0.96±0.05
160	5.0±0.4	3.8±0.2
170	16±2	12.0±0.5
180	47±5	34.5±1.6
195	280±20	110±4

The initial region also obeys the first-order equation but with different constants. These constants (k_0/s^{-1}) are described by the equation

$$k_0 = 10^{16.3\pm0.7}\exp[-(41000\pm1400)/(RT)] \quad (r = 0.998).$$

The amount of gaseous products of HNIW decomposition in a solution is 540—560 cm^3 g^{-1}, which corresponds to the evolution of 10.6—11.0 moles of the gaseous products per mole of HNIW. These products contain 48—49 vol.% N_2.

In a particular series of experiments, we studied the influence of the ratio of the amount of the solution to the free volume of the reaction vessel (m/V) on thermal HNIW decomposition in a solution. In these experiments, the volume of the reaction vessel was equal to 6 mL, and the amount of a 3% solution was varied so that the m/V values were 0.84, 0.42, and 0.23 g L^{-1}. The rate constants remained virtually unchanged: at 180 °C they were equal to $4.7 \cdot 10^{-6}$, $4.4 \cdot 10^{-6}$, and $4.9 \cdot 10^{-6}$ s^{-1}, respectively. The content of N_2 in the gaseous decomposition products also remained unchanged: 48, 45, and 44 vol.%, respectively.

The data in Fig. 2 show that thermal HNIW decomposition under nonisothermal conditions begins at a higher temperature than was found in the works cited above. This difference can be due to both the conditions of measurements (heating rate, amount of the substance) and the fact that phase transitions accompanied by the appearance of new crystalline modifications with different reactivities are possible during heating. In the case of octogen, both the decomposition and ignition occur at temperatures 5 °C higher than those for HNIW, whereas, according to the published data,[2] this difference is 45 °C. The reason for these divergences is, most likely, also in different experimental conditions. Although all known data indicate a lower thermal stability of HNIW as compared to HMX, the results of isothermal measurements (see below) are more accurate and reliable for quantitative comparison.

The absence of HNIW ignition on heating under a dynamic vacuum can be due to the fact that continuous evacuation provides expelling of active intermediate products (for example, NO_2) from the system, thus suppressing exothermal reactions with their participation. This assumption is confirmed by the dependence of the content of the carbonyl groups (most likely, formed due to the oxidative effect of NO_2) in the condensed residue on the reaction conditions. Argon is heavier than air, and oxidative processes in Ar have time to occur to a greater extent. By contrast, the lowest number of carbonyl groups is formed in a flash when the reaction proceeds very rapidly and oxidative processes have no time to develop. Suppression of reactions involving active intermediate particles under a dynamic vacuum makes it possible to explain the somewhat lower total mass loss under these conditions than that for decomposition in air.

It is of interest that the amount of the condensed residue formed from HNIW is almost the same during both slow isothermal decomposition and ignition. This suggests that, despite substantial differences in the temperature regimes, the same reactions occur in both cases. It is also of interest that thermolysis and subsequent HMX ignition are not accompanied by the formation of the condensed residue, but complete gasification takes place. Perhaps, this is related to the fact that the HNIW molecule contains C—C bonds, whereas they are absent in HMX. In fact, it has been shown[9] in the study of thermal decomposition of several polynitro compounds including nitramines that if the molecules of a compound contain no C—C bonds, we observe a fast sequence of transformations through the intermediate formation of high-activity species, first of all radicals, with the evolution of gaseous products. When molecules of the starting substance contain the C—C bond, it is cleaved in one of the aforementioned transformations, and a carbon-centered radical is formed, which can serve as an acceptor with respect to some atoms or functional groups. As a result, a relatively stable condensed compound is formed.

The presence of nitro groups in the condensed residue, which is indicated by its IR spectrum, agrees well with the previously found[8] formation of NO_2 during thermolysis of this residue. As mentioned above, the amount of the residue is 16—17% by weight of the starting substance, *i.e.*, 1/6 fraction of the starting weight remains. Since the HNIW molecule contains six nitro groups, we may assume that five of them are eliminated on thermolysis, and one nitro group is retained in the residue. The published data and our results indicate the complex structure of the residue formed and the presence of various functional groups in it. Therefore, the polymeric nature of this residue cannot be ruled out, although it is a loose powder rather than a resin. This conclusion is all the more probable because the volatility of the residue is very low: during continuous evacuation its amount remains the same as that in the experiments in air or argon. Therefore, it is pertinent to note that we failed to perform isothermal decomposition at the temperatures used (183—211 °C) under continuous evacuation even for such a low-volatility substance as HMX because it is sublimed and deposited on cool parts of the setup. This also indicates a much lower volatility of HNIW as compared to that of HMX, because its decomposition under the same conditions results in much lower sublimation (see below).

The values of overall gas release and N_2 content in the gas formed due to the thermal HNIW decomposition well agree with the previous data.[6] The only noticeable distinction is that the thermal decomposition of HNIW in acetone gives a much lower amount of the gas than that formed by the decomposition of the pure substance.[6] Meanwhile, in our experiments, the amounts of gas released during HNIW decomposition in the solid phase and in *m*-dinitrobenzene were approximately equal. The reason for these distinctions remains unclear.

It is not surprising that N_2 was not observed among the gaseous decomposition products in several works[4,5]; gas analysis was carried out by IR spectroscopy, which does not detect nitrogen. As mentioned above, the thermal decomposition of one HNIW molecule gives approximately five N_2 molecules. At the same time, during thermolysis and formation of the condensed residue each HNIW molecules loses, most likely, five nitramine groups (see above). Therefore, during thermal decomposition almost all nitrogen goes to the gas phase in the form of N_2.

The kinetic data, according to which the thermal decomposition of solid HNIW occurs with pronounced autoacceleration, agree well with the previously obtained results.[5] The activation parameters determined from the temperature dependence of the rate constants k_2 coincide within the experimental error with the published data.[5] However, in the case of the temperature dependence of the k_1 constants, the agreement of the activation parameters is absent. Probably, this is related to the fact that the k_2 values greatly exceed the corresponding k_1 values (*cf.* data in Table 1 and Ref. 5). It follows from this that even at very low conversions, the second term on the right side of Eq. (1) determines, to a great extent, the reaction rate. Due to the relatively low contribution of the term containing k_1, this rate constant cannot be determined with an sufficient accuracy.

The kinetic curves of thermal HNIW decomposition obtained previously[4] have a different shape: autoacceleration is absent, and the reaction proceeds for a long time with an almost unchanged rate. Evidently, the kinetics of this topochemical process substantially depends on the morphological peculiarities of HNIW crystals. In this connection, it is significant that the authors of this work[4] obtained the γ-modification of HNIW from the β-form, whereas we used for this purpose the ε-form.

As can be seen in Fig. 4, *a*, the reaction proceeds in argon somewhat more rapidly than in air. The reason for this is not clear. Perhaps, the intermediately formed NO_2, whose oxidative effect results in the appearance of carbonyl groups, plays a noticeable role in this case. Since argon is heavier than air, it could provide a longer presence of NO_2 in the reaction zone and, as a consequence, an elevated concentration of the carbonyl groups in the condensed residue.

In the isothermal experiments, a lower thermal stability of HNIW as compared to that of HMX is clearly manifested (see Fig. 3).

The fact that HNIW decomposes more rapidly under evacuation than in air or argon suggests that the dynamic vacuum provides partial sublimation; however, its extent is much lower than that in the case of HMX, which sublimes more rapidly than has time to decompose. The sublimation rate can depend on the crystal morphology. Microscopic observations showed the morphological distinctions of the HNIW crystals. Therefore, we can assume that the HNIW crystals sublime at different rates. After the more easily sublimed crystals were removed, the rate of mass loss decreases, which is expressed as the characteristic inflection of the kinetic curves (see Fig. 4, *a* and *b*). In the closed system (Bourdon gauge), which is initially evacuated, the reaction also occurs more rapidly than in air or argon (see Fig. 4, *b*). However, in this case, unlike gravimetric experiments, the substance that goes to the vapor phase does not leave the reaction system and continues to decompose and, hence, the inflection in the manometric kinetic curve is absent.

The self-acceleration character of decomposition observed for HNIW thermolysis is known for many solid-phase processes and can be explained by at least two reasons. First, liquid products can be formed in thermal decomposition of solid explosives. If the starting substances are capable of dissolving in these products, the reaction gains a biphase character: it proceeds in both the solid phase and solution. Since thermal decomposition of explosives in the solid phase occurs, as a rule, much more slowly than in the liquid phase,[10] the reaction is accelerated due to the enrichment of the system in the liquid phase.[11] Second, the phenomenon of autoacceleration during decomposition of solids can be due to the topochemical character of the reaction that occurs not uniformly over the whole volume but heterogeneously, by the nucleation and development of reaction centers. The above results of microscopic studies, in particular, the acute-angled, not smoothed character of aggregates of the condensed decomposition product, indicate that no liquid phase is formed during the reaction and the process proceeds topochemically. The exterior of the aggregates mentioned and their coincidence in size and shape with the initial HNIW crystals assume that the initial crystals are cracked during decomposition and the fragments are disoriented and substituted by the reaction products. Since the weight of the condensed residue amounts to 16—17% by weight of the starting substance and the sizes of the aggregates formed correspond approximately to those of the starting crystals, we believe that the particles in the composition of the aggregates are microporous. The pore size should not exceed ~1000 Å, otherwise these particles would not be transparent.

On going to a solution, the system becomes homogeneous, no autoacceleration is observed, and the first-order kinetic equation is satisfactorily fulfilled. Other nitramines, in particular, HMX,[12] behave similarly. The activation parameters of HNIW decomposition in *m*-dinitrobenzene agree well with the published data[6] on its decomposition in acetone. Thermolysis of HMX in *m*-dinitrobenzene (ignoring the initial region of the kinetic curve) proceeds with an activation energy of 188 kJ mol^{-1} and is characterized by a pre-exponential factor of $10^{16.0}$ s^{-1}.[12] Thus, the activation energies of the decomposition of HNIW and HMX are close, whereas the pre-exponential factor in the case of HNIW is much higher, which determines the higher reactivity of this substance. Unlike the solid state and melt, in a dilute solution the interaction between molecules of the reactant is absent and, hence, the solution is very convenient for the characterization of the reactivity of the substance, ignoring the role of the condensed state. Using the activation parameters presented above, we obtain that the rate constants of thermal decomposition of HNIW and HMX in a solution at 200 °C are equal to $4.4 \cdot 10^{-3}$ and $1.6 \cdot 10^{-5}$ s^{-1}, respectively. Therefore, the reactivity of HNIW is more than two order of magnitude higher than that of HMX. This ratio is retained at other temperatures, because the activation energies of thermolysis of both substances are close. The conclusion about the higher reactivity of HNIW in a solution is clearly illustrated by the data in Fig. 6 where the kinetics of termolysis of HNIW and HMX at the same temperature are compared. The initial regions of the kinetic curves characterize, most likely, the primary act of the reaction, the cleavage of the $N-NO_2$ bond.[11] Note that the activation energy of 171 kJ mol^{-1} (found from the temperature dependence of the k_0 constant) virtually coincides with the E_a values for other reactions involving the cleavage of this bond.[11] At the same time, the pre-exponential factor is much higher than those for other nitramines, indicating the substantial role of the entropy contribution to the kinetics of this reaction.

It is of interest that the activation parameters of HNIW thermal decomposition in a solution are very close to the corresponding values calculated from the temperature dependences of the rate constants k_2 for the solid phase process. The reactions in the solid phase usually proceed more slowly than those in the liquid or gas phase due to the retarding effect of the crystalline lattice.[10] As HNIW decomposes, its crystal structure is gradually destroyed, and the product that formed is completely amorphous. The rate constant k_2 describes the occurrence of the process not at the first, but at the next stages of transformation where the ordered structure of the crystalline lattice is already distorted to a great extent and more and more amorphous phase is formed. This partially amorphized system imitates the liquid phase to some extent, due to which, most likely, the activation parameters are close. Of course, a complete analogy is not observed, and it is seen from comparison of the data in Tables 1 and 2 that the reaction rate constants in the solution are noticeably higher than k_2.

For the thermal decomposition of nitro compounds in dilute solutions, secondary reactions involving the starting substance are considerably suppressed. Therefore, it can be assumed that the rate constant of this reaction characterizes, to some extent, the primary elementary act of the process. As applied to HNIW, this is indirectly confirmed by the fact that the variation of the m/V parameters, *i.e.*, a change in the pressure of gaseous reaction products above the solution (and, hence, the concentrations of these products in the solution) has no effect on the rate constant. Based on the published data, we may assume that the homolytic cleavage of the $N-NO_2$ bond is the primary act of HNIW decomposition. In this case, the activation energy of the process rather exactly corresponds to the dissociation energy of this bond. At the same time, the value of the pre-exponential factor indicates a high positive activation entropy of the process. This can be explained by the fact that the internal rotation about the $N-NO_2$ bond is retarded, and the elongation of this bond during the formation of the transition state is accompanied by the liberation of internal rotation. However, these concepts are valid only for the fulfillment of the assumption that the rate constant of decomposition in a solution describes the primary elementary act of decomposition only.

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