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Thermal Decomposition of 2,4,6-Triazidopyridine

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Abstract—The thermal decomposition of 2,4,6-triazidopyridine in the melt is studied using thermogravimetry, manometry, mass spectrometry, and IR spectroscopy. In the temperature range of 120–160°C, the process obeys the first-order kinetic law, being described by the Arrhenius equation k [s^{-1}] $= 10^{12.8 \pm 0.4}\exp[-(31200 \pm 1500)]/RT$ with values of the parameters typical of the thermal decomposition of aromatic and heterocyclic azides. The reaction produces nitrogen, as the only gaseous product. Unlike the other heterocyclic azides, the decomposition of which is characterized by anomalously high values of the Arrhenius parameters, the thermal decomposition of 2,4,6-triazidopyridine yields a condensed product having a system of polyconjugated bonds with higher force characteristics. It is concluded that the decomposition of 2,4,6-triazidopyridine proceeds by a mechanism in which the rate-limiting step is the dissociation of the nitrogen molecule from the azide group to form a nitrene.

Keywords: azides, heterocyclic compounds, kinetics, thermal decomposition, thermogravimetry, manometry, mass spectrometry, infrared spectroscopy, reaction products

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INTRODUCTION

In recent years, due to the increased interest in nanomaterials, polyazides based on nitrogen heterocycles are considered as intermediates for producing carbon−nitrogen nanostructures [1−4]. The latter are synthesized using the photolysis or thermal decomposition of heterocyclic polyazides [4−7]. Furthermore, polyazides are deemed as potential initiating explosives and molecular nitrogen generators. It is known [8−12] that heterocyclic polyazides are extremely sensitive to mechanical and thermal influences. This fact was taken into account when carrying out the experimental part of this work, which is devoted to studying the kinetics, products (both gaseous and condensed), and mechanism of the thermal decomposition of 2,4,6-triazidopyridine

I
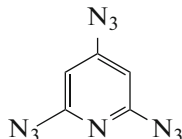
EXPERIMENTAL

Compound **I** was synthesized by triazidation of 2,4,6-trifluoropyridine with sodium azide in dimethyl sulfoxide according to the known procedure [13]. Melting points, IR spectra, and ^{1}H, ^{13}C, and ^{15}N NMR spectra of **I** corresponded to the literature data [14]. Before the experiments, **I** was recrystallized from ethanol. The purity of **I** was confirmed by elemental analysis; measured: 1.12 wt % H, 29.84 wt % C, and 69.07 wt % N; calculated: 1.00 wt % H, 29.71 wt % C, and 69.29 wt % N.

Preliminary thermogravimetric experiments were conducted in an open reactor system (quartz beaker suspended from the arm of an ATV-14M thermobalance [15] on a platinum wire) in dry argon (1 atm) at a sample heating rate of 4°C/min. The kinetics of the thermal decomposition of **I** in the melt was studied under isothermal conditions by using a Bourdon glass gauge [16].

The gaseous products of thermal decomposition of **I**, noncondensable under normal conditions, were analyzed on a MI-1201V mass spectrometer (ionizing electron energy, 70 eV; accelerating voltage, 5000 V). The structure of the solid residue was analyzed by infrared spectroscopy on an ALPHA FTIR spectrometer (Bruker Optics).
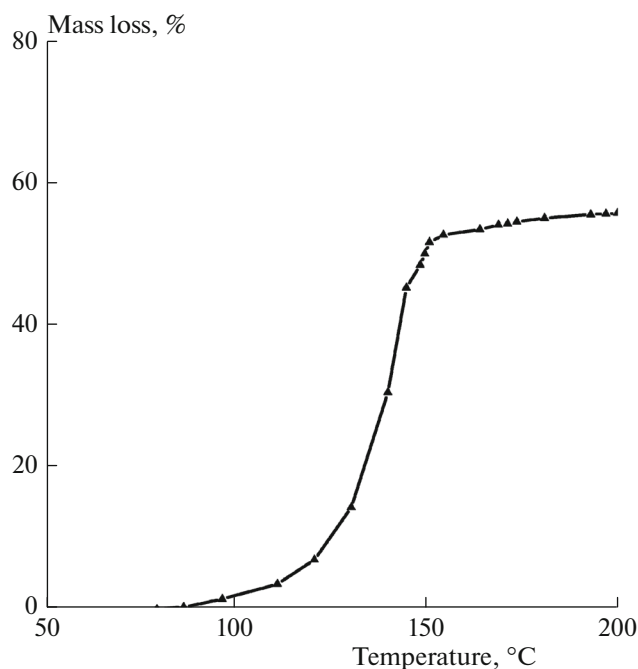
Fig. 1. Nonisothermal kinetics of the thermolysis of compound **I** in an argon atmosphere (1 atm.). The linear heating rate, 4°C/min; the sample weight, 6.1–6.2 mg.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows how **I** decomposes in an nonisothermal mode. It can be seen that, under these conditions, the reaction proceeds in a temperature range of 90 to 160°C, resulting in a weight loss of up to 60%.
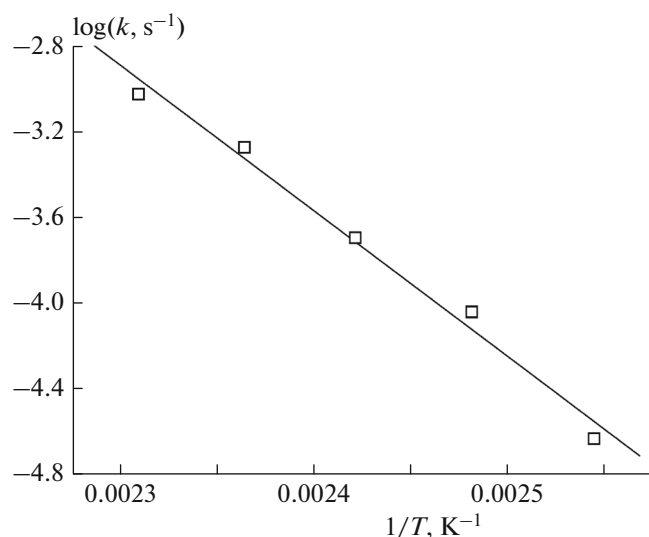
The thermal decomposition of **I** in the melt obeys the first order kinetic law up to a 80% conversion. At higher degrees of conversion, the first-order kinetic equation does hold, apparently due to the occurrence of secondary processes. The values of reaction rate constant versus the temperature are listed in the table. This dependence is linear in the Arrhenius coordinates (Fig. 2), given by

$$k(\mathbf{I}) = 10^{12.8 \pm 0.4}\exp[-(31200 \pm 1500)]/RT,$$
$$\text{s}^{-1} \ (r = 0.993),$$

where $R = 1.987$ cal mol^{-1} K^{-1}.

Mass-spectral analysis of the data (Fig. 3) shows that nitrogen is the only gaseous product of the thermal decomposition of **I** in the temperature range covered. Note that the purity of the resulting nitrogen is close to 100%.

IR spectroscopic examination of the solid product of the thermal decomposition of **I** in the melt revealed that it is a compound having polyconjugated bonds between C and N atoms (Fig. 4). Along with stretching (1200–1600 cm^{-1}) and bending (500–820 cm^{-1}) vibrations of the system of conjugated bonds, the IR spectra of the thermal decomposition products of **I** exhibit bands within 2120–2160 cm^{-1}, belonging to residual azide groups stabilized by the inhibitory effect of the solid matrix of the product [12]. The 2210–2260-cm^{-1} weak bands belong to C≡N triple bonds [17], present in small amounts.

The above data indicate that, in its kinetic behavior, **I** differs significantly from similar compounds, such as 2,4,6-triazido-1,3,5-triazine and 2,4,6-triazidopyrimidine. The thermal decomposition of the latter two compounds is characterized by anomalously high values of the preexponential factor, a feature that
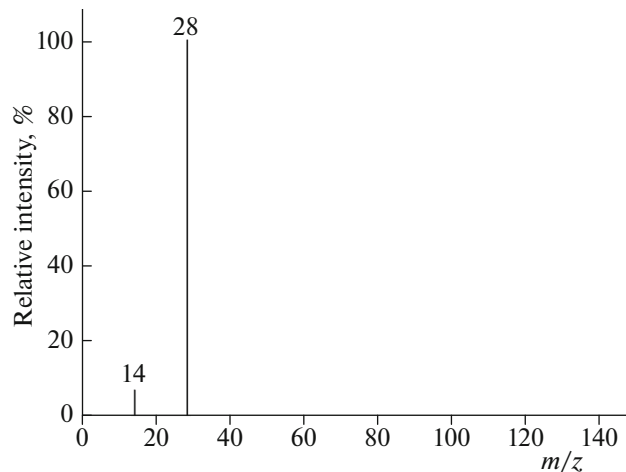

Fig. 2. Arrhenius dependence of the rate constants for the thermal decomposition of compound **I** in the melt.

Fig. 3. Mass spectrum of the gaseous products of thermal decomposition of compound **I** (140°C, 3 h).
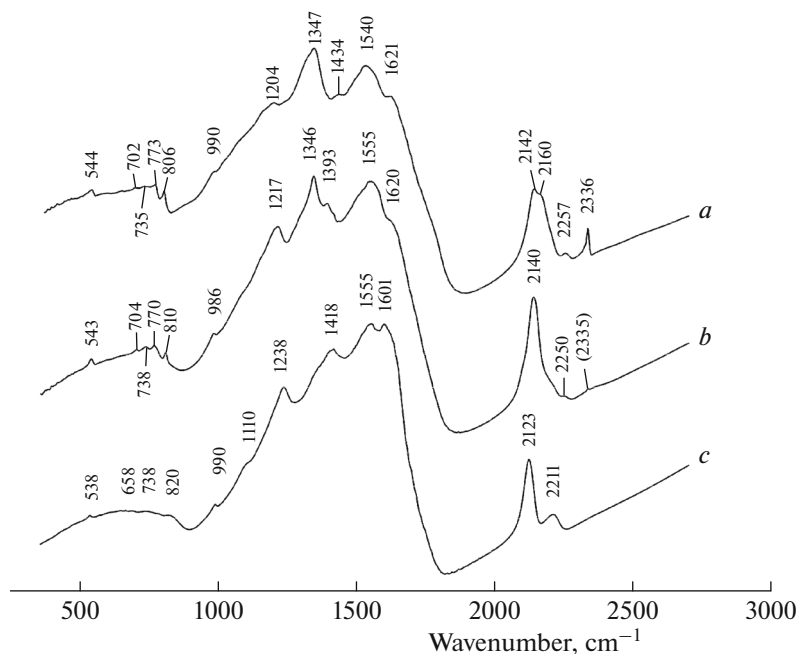
Fig. 4. IR spectra of the thermal decomposition products of (*a*) 2,4,6-triazidopyrimidine, (*b*) 2,4,6-triazido-1,3,5-triazine, and (*c*) compound **I**.

was attributed to the process being limited by polymerization (polycondensation), accompanied by the formation of two-dimensional carbon–nitrogen networks [1]. This abnormality is apparently due to the fact that the 2,4,6-triazido-1,3,5-triazine molecule does not contain hydrogen, a factor that makes unfeasible the reaction of abstraction of a hydrogen atom from a neighboring molecule by the nitrene formed in the first event of decomposition of the azide group, a reaction typical of the thermal decomposition of organic azides. The 2,4,6-triazidopyrimidine molecule contains only one hydrogen atom, so the aforementioned polymerization (condensation) reaction remains predominant [12]. The **I** molecule contains two hydrogen atoms, which allows it to decompose by the traditional mechanism, in which the rate-limiting step is the decomposition of the azide group to the nitrogen and nitrene [18–21].

This difference in the mechanisms of dissociation of heterocyclic azides affects the composition of the condensed decomposition products. By comparing

First-order rate constants for the thermal decomposition of compound **I** in the melt (Bourdon gauge, $m/v = 0.9$–1.0 mg/cm^3)

Temperature, °C	Rate constant, s^{-1}
160	$(9.4 \pm 1.0) \times 10^{-4}$
150	$(5.3 \pm 0.5) \times 10^{-4}$
140	$(2.0 \pm 0.1) \times 10^{-4}$
130	$(9.0 \pm 0.8) \times 10^{-5}$
120	$(2.3 \pm 0.2) \times 10^{-5}$

the IR spectra of the thermal decomposition products of 2,4,6-triazido-1,3,5-triazine and 2,4,6-triazidopyrimidine (Fig. 4) in the region of stretching vibrations, it is easy to see that, in the case of **I**, the corresponding bands are shifted to shorter wavelengths, which can be explained by a greater content of carbon in the decomposition products of **I** as compared to 2,4,6-triazidopyrimidine.

The possible scheme of the decomposition of **I** is given below:

$$\text{(scheme)} \qquad + \ N_2, \qquad (1)$$

(2)

(3)

(4)
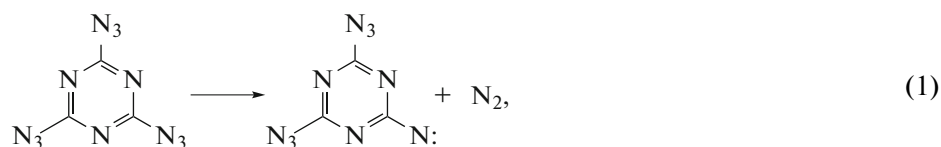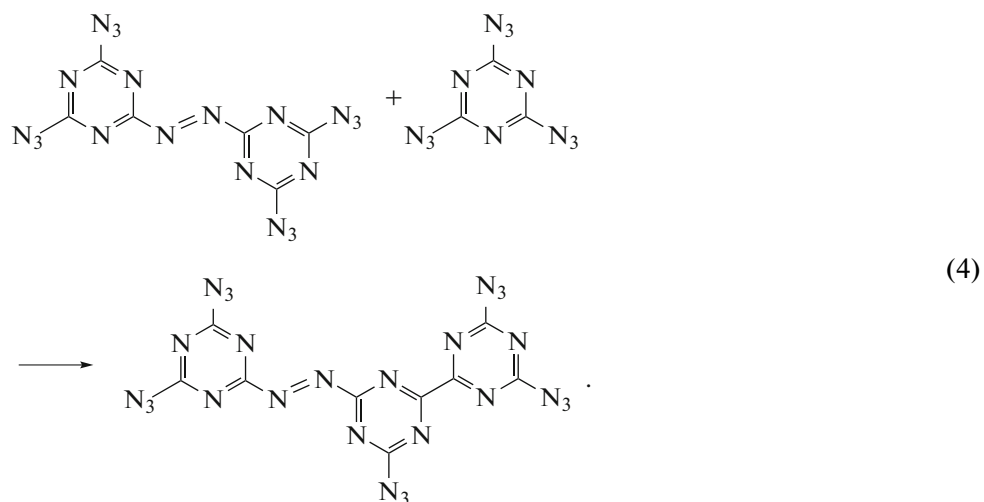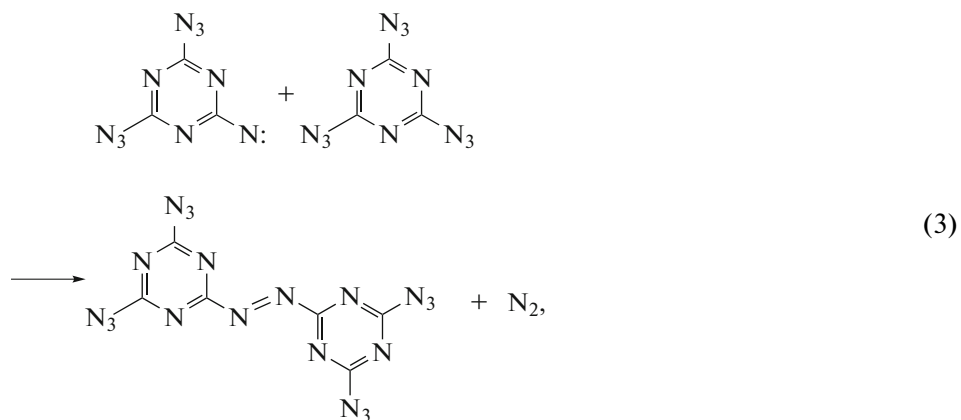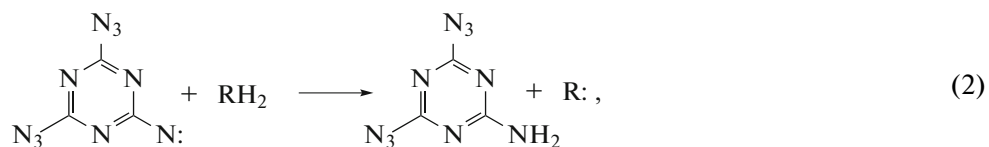
In this scheme, reaction (1), the dissociation of the azido group to form the nitrogen and the corresponding nitrene, limits the rate of the entire process, a feature typical of the thermal decomposition of organic azides. Reaction (2) is the abstraction of a hydrogen atom from any neighboring molecule by the nitrene formed to produce an amine, a reaction characteristic of nitrenes. Reactions (3) and (4) are hypothetical. They demonstrate how the aforementioned polyconjugated carbon−nitrogen bonds are formed.

The difference between the mechanisms of the thermal decomposition of the above azides affects the value of the reaction rate. A comparison of the rate constants shows that the reactivity of heterocyclic azides decreases in the series **I** > 2,4,6-triazidopyrimidine > 2,4,6-triazido-1,3,5-triazine.

Knowledge of the pressure of nitrogen released by the thermal decomposition of **I** makes it easy to calculate that, in the reaction under study, 1 mole of **I** produces 3.3 moles of nitrogen, which corresponds to a weight loss of 46% of the starting material. This value agrees well with the results of the nonisothermal experiment (Fig. 1) and indicates that, during the process, nearly all the azide groups dissociate, while the heterocycles remain unaffected.

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