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KINETICS AND MECHANISM OF CHEMICAL REACTIONS. CATALYSIS

Kinetics of the Thermal Decomposition of 2,4,6-Triazido-3,5-Difluoropyridine

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Abstract—The kinetics and products of the thermal decomposition of 2,4,6-triazido-3,5-difluoropyridine in melt at temperatures of 120–160°C have been studied using pressure measurements, differential thermal analysis, and IR spectroscopy. The reaction occurs in two macroscopic steps, each described by a first-order kinetic equation. In the first, the activation energy and the common logarithm of the pre-exponential factor are 35.6 ± 1.2 kcal/mol and 15.1 ± 0.6 s^{-1}, respectively. For the studied compound (and certain other heterocyclic azides, such as 2,4,6-triazido-1,3,5-triazine and 2,4,6-triazidopyrimidine), the pre-exponential factor is anomalously high. This is due to the fact that the 2,4,6-triazido-3,5-difluoropyridine molecule contains no hydrogen atoms. For such azides, the usual decomposition mechanism (cleavage of the azide group with subsequent attack of nitrene on a hydrogen atom of a neighboring molecule) is impossible, which favors the stability of the formed nitrene. In this case, the reaction occurs through a complex chain polymerization mechanism, which leads to the formation of specific condensed products: packs of planar polyconjugate carbon–nitrogen networks with a porphyrin-like structure.

Keywords: 2,4,6-triazido-3,5-difluoropyridine, heterocyclic compounds, kinetics, thermal decomposition, differential thermal analysis, pressure measurements, IR spectroscopy, reaction products

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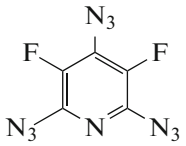
INTRODUCTION

The thermal decomposition of aromatic and heterocyclic azides is of interest in a wide variety of contexts, and there is significant interest in the kinetics of the reaction examined here [1]. The vast body of experimental data that has accumulated to date enables the following general conclusions concerning the features of thermolysis of the said compounds to be drawn. The first step of the reaction is the decomposition of the azide group to form nitrogen and the corresponding nitrene. Although the studied substances are quite diverse, the activation parameters of the decomposition of aromatic and heterocyclic azides fall within quite a narrow range: the activation energy is usually 34–35 kcal/mol, and the pre-exponential factor is 10^{13}–10^{14} s^{-1}. However, in recent years, it has been found that the characteristics of the decomposition of a number of heterocyclic azides are outside these ranges. In particular, for the decomposition of 2,4,6-triazidopyrimidine [2] and cyanuric triazide [3] in the liquid phase, the Arrhenius parameters—both the activation energies and the pre-exponential factors—exceed those indicated above. In our previous work [3], we discussed the nature of this anomaly, but many details thereof remain unclear.

In view of the above, in this work, we studied the kinetics of the thermal decomposition of 3,5-difluoro-2,4,6-triazidopyridine (**I**) in melt.



I

This object was chosen because, unlike the previously [4] studied 2,4,6-triazidopyrimidine, molecule **I** at positions 3 and 5 contains fluorine instead of hydrogen, atoms. This allowed the effects of the nature of substituents at these positions on the kinetics and mechanism of the reaction to be determined.

EXPERIMENTAL

Compound **I** was synthesized from pentafluoropyridine and sodium azide and characterized by UV, IR, and NMR spectroscopy [5]. The melting point was

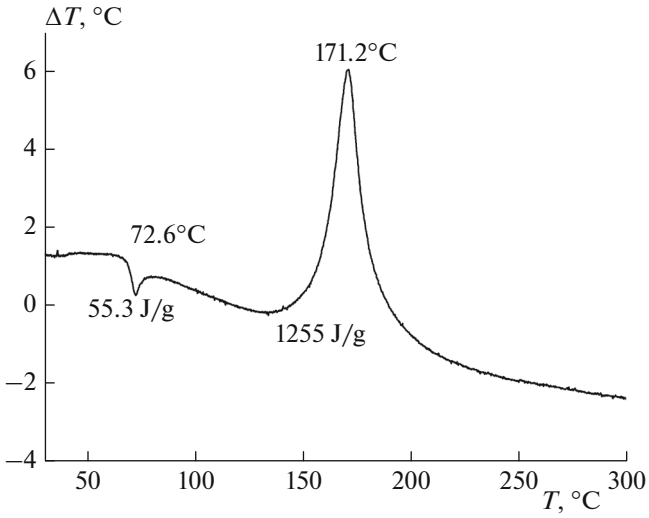


Fig. 1. Differential thermal analysis curve of melting and thermal decomposition of 3,5-difluoro-2,4,6-triazidopyridine (ΔT is the temperature difference between the test sample and the reference sample).

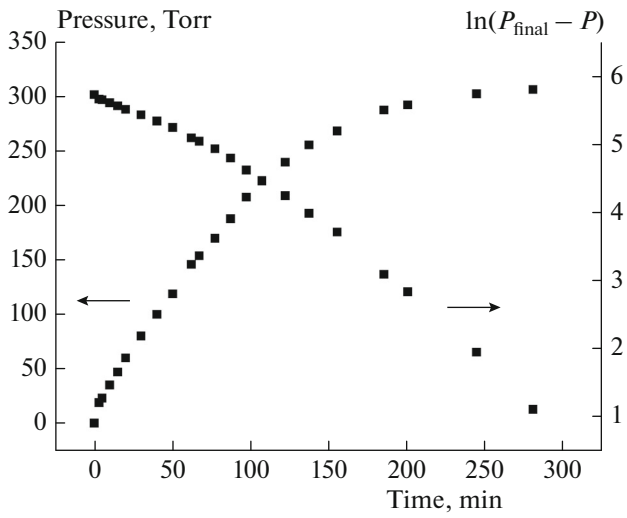


Fig. 2. Kinetics of the thermal decomposition of 3,5-difluoro-2,4,6-triazidopyridine at 140°C.

75–76°C. The purity of **I** was confirmed by elemental analysis. Analytically calculated wt %: C, 25.22; N, 58.82. Found wt %: C, 25.48; N, 58.74.

A differential thermal analysis of the thermal decomposition of **I** was performed with a Thermoscan-2 instrument (Russia) within the temperature range 25–300°C at a rate of 5.0°C/min in an air atmosphere.

The kinetics of the thermal decomposition of **I** in melt was studied by measuring the pressure with Bourdon glass-diaphragm pressure gages.

The IR spectra of the condensed products of the decomposition of **I** were recorded using an ALPHA FTIR spectrometer (Bruker Optics, Germany). The IR-absorption spectra of samples compacted into pellets with KBr were recorded at a resolution of 4 cm^{-1}, using 16 scans.

RESULTS AND DISCUSSION

Early in this study, we performed a differential thermal analysis of **I**. The curve of this analysis (Fig. 1) had an endothermic peak (T_{min} = 72.6°C), which represented the melting of **I**, and an exothermic peak (T_{max} = 171.2°C), which corresponded to the thermal decomposition of **I**. The heat of melting of **I** was found to be –(16.6 ± 1.3) kJ/mol. The heat of decomposition of **I** within the studied temperature range was found to be 298 ± 29 kJ/mol.

Pressure measurements showed that, in the isothermal decomposition of a melt of **I** within the temperature range 120–160°C, from one mole of 3,5-difluoro-2,4,6-triazidopyridine, ~2.8 moles of gas is released (under the assumption that the formed gas is an ideal gas). When the gas was cooled to room temperature, as follows from the results of checking using the ideal gas law, the gaseous products did not condense. Therefore, it was natural to assume that the only gaseous product of the reaction was molecular nitrogen.

The data on the reaction kinetics suggest that, unlike most organic azides (including 2,4,6-triazidopyrimidine, which has a similar structure), the thermal decomposition of **I** is not described by a first-order equation. In Fig. 2, the kinetic data obtained at 140°C are plotted in semilog coordinates. Instead of a straight line corresponding to a first-order kinetics, the kinetic curve is convex upward. In the initial portion, the semilog anamorphosis can be represented as a straight-line segment, and the process can be characterized by rate constant k_1. The right branch of the anamorphosis can also be rather coarsely straightened, and effective rate constant k_2 can be calculated. Within the studied temperature range, the ratio k_2/k_1 is approximately 2. The higher the conversion corresponding to the completion of the first step of the reaction, the higher the experimental temperature. At a temperature of 140°C, for which the data in Fig. 2 are given, the conversion is 38%.

Table 1 presents the rate constants for the first step of the reaction. The common logarithm of the preexponential factor and the activation energy were found by the Arrhenius equation (r = 0.998) and are 15.1 ± 0.6 s^{-1} and 35.6 ± 1.2 kcal/mol, respectively.

The k_2 values are determined at low accuracy. The corresponding portions of the semilog anamorphoses can only approximately be considered linear (see Fig. 2). Moreover, at high temperatures, the second step occurring at the rate constant k_2 begins at high conversions (e.g., at 160°C, this happens when 80% conver-

sion is reached). Therefore, the temperature dependence of the rate constant k_2 was not investigated.

Figure 3 shows the IR spectrum of the condensed product of the thermal decomposition of 3,5-difluoro-2,4,6-triazidopyridine. For comparison, Fig. 2 also presents the IR spectra of the products of the decomposition of the previously studied 2,4,6-triazidopyridine [4], 2,4,6-triazidopyrimidine [2], and 2,4,6-triazido-1,3,5-triazine (cyanuric triazide) [3].

IR spectroscopy and electron microscopy showed [6] that the condensed products of the thermal decomposition of 2,4,6-triazidopyrimidine and 2,4,6-triazido-1,3,5-triazine are structurally similar: their structures rest on packs of flat layers constituted by polyconjugate bonds C–N. The strongest bands (Fig. 2) have absorption maxima at 1346–1347 and 1540–1555 cm^{-1}, which suggests that these materials contain C–N bonds of different orders (about 1.5 and much higher than 1.5) and are located in aromatic cycles and diazene bridges, respectively.

The IR spectra of **I** and 2,4,6-triazidopyridine also have series of intense bands within the range 1200–1600 cm^{-1}, which characterize polyconjugate C–N bonds, but these spectra significantly differ both from each other and from the IR spectra of 2,4,6-triazido-1,3,5-triazine and 2,4,6-triazidopyrimidine (Fig. 3). The most intense bands, at 1405 and 1446 cm^{-1}, in the IR spectrum of **I** characterize C–N bonds of similar orders, and a relatively narrow band, at 1213 cm^{-1}, may receive a partial contribution from C–F stretching vibrations [7]. The IR spectra of the products of the decomposition of **I**, 2,4,6-triazidopyrimidine, and 2,4,6-triazido-1,3,5-triazine are characterized by close values of the weighted average frequency within the range of the stretching vibrations of C–N bonds (at 1405, 1415, and 1425 cm^{-1}, respectively), whereas the corresponding value for the product of the decom-

Table 1. Rate constants for the first step of the thermal decomposition of **I**

Temperature, °C	Rate constant, s^{-1}
120	1.8×10^{-5}
130	5.2×10^{-5}
140	1.5×10^{-4}
150	5.2×10^{-4}
160	1.1×10^{-3}

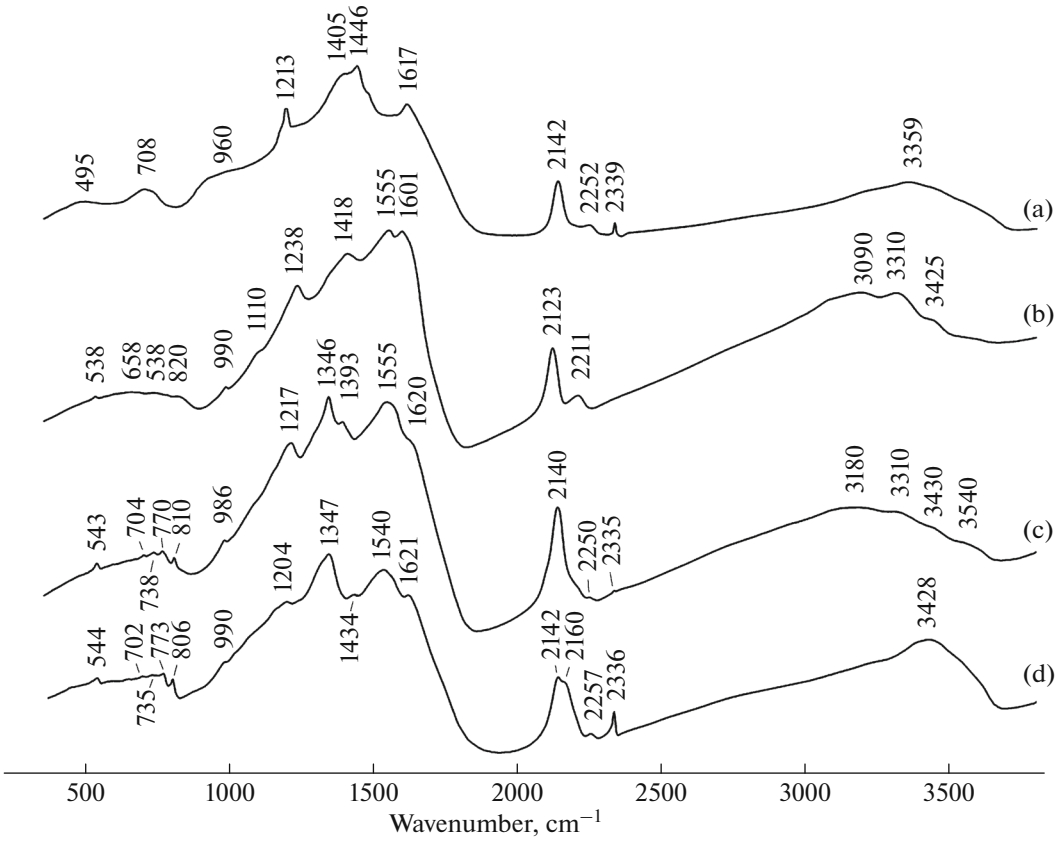


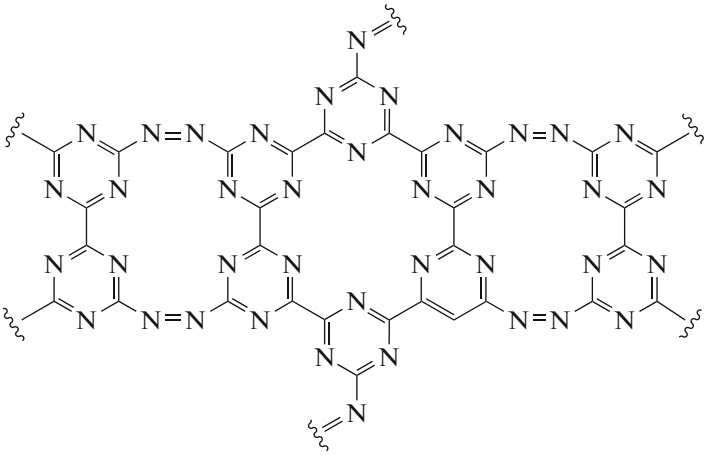
Fig. 3. IR spectra of the products of the thermal transformations of (a) 2,4,6-triazido-3,5-difluoropyridine at 150°C, (b) 2,4,6-triazidopyridine at 150°C, (c) 2,4,6-triazidopyrimidine at 160°C, and (d) 2,4,6-triazido-1,3,5-triazine at 170°C. In all the cases, reaction time was 2 h.

position of 2,4,6-triazidopyridine is about 1500 cm^{-1}. This implies that the thermal transformations of **I** give rise to networks of polyconjugate bonds, which are similar to the networks underlying the structure of the products of the thermolysis of 2,4,6-triazidopyrimidine and 2,4,6-triazido-1,3,5-triazine but are formed by C–N bonds with closer degrees of conjugation. The last conclusion follows from the fact that the stretching vibrations of C–N bonds in the product of the thermolysis of **I** manifest themselves within a relatively narrow frequency range (1300–1500 cm^{-1}), whereas for the products of the thermal transformations of 2,4,6-triazido-1,3,5-triazine and 2,4,6-triazidopyrimidine, the range is 1230–1600 cm^{-1}.

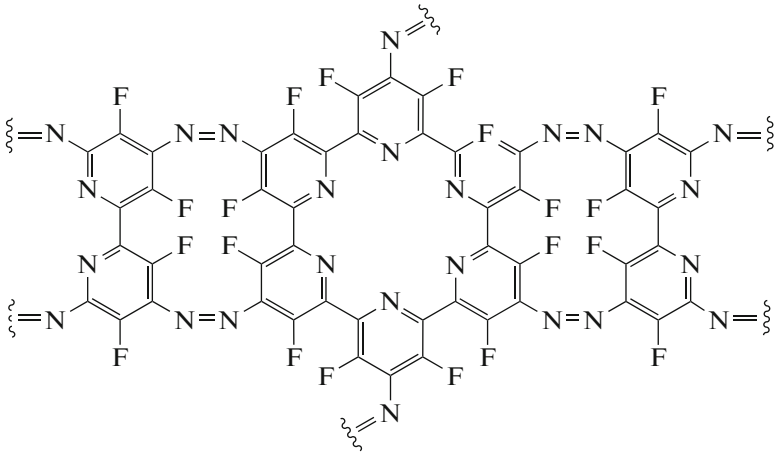
A specific feature of the IR spectra of the products of the thermolysis of the compounds (Fig. 3) is the presence of a band of residual azide groups within the frequency range 2120–2160 cm^{-1} and insignificant amounts of nitrile groups, represented by a weak band at 2210–2260 cm^{-1}.

All these materials actively absorb water in contact with atmospheric air: the bands within the range 3000–3600 cm^{-1} do so because of the stretching vibrations of H_2O molecules forming hydrogen bonds of various strengths. In addition, the products of the thermal transformations of **I**, 2,4,6-triazidopyrimidine, and 2,4,6-triazido-1,3,5-triazine sorb carbon dioxide from air (a weak narrow band at 2335–2339 cm^{-1} is assigned to the asymmetric stretching vibrations of CO_2 molecules).

IR spectroscopy data, elemental analysis, and electron microscopy, together with published data on the ^{13}C NMR spectra, led to the conclusion [6] that the structure of the product of the thermal transformations of 2,4,6-triazido-1,3,5-triazine is based on planar networks with the following structure:



Taking the above IR spectroscopy data into account, it is possible to assume that the thermolysis of **I** produces similar networks. Below, a possible structure of one such network is shown:



This assumption, namely, that porphyrin-type cycles are present, matches the ability of the products of the thermolysis of **I** and 2,4,6-triazido-1,3,5-triazine to sorb atmospheric carbon dioxide. In this con-

text, the fact that the product of the thermal transformations of 2,4,6-triazidopyridine, which was reported [6] to be a linear oligomer, has no such ability, is important. The product of the thermolysis of 2,4,6-triazidopyrimidine, which is a mixture of planar networks and linear structures, sorbs only small amounts of CO_2.

As noted in the Introduction, the kinetics of the thermal decomposition of some heterocyclic azides (in particular, 2,4,6-triazido-1,3,5-triazine) is anomalous: while the activation energies of these reactions more or less coincide with the activation energies of the decomposition of other aromatic and heterocyclic azides, the pre-exponential factor values are noticeably overestimated. Compound **I**, studied in this work, also decomposes anomalously. This is all the more surprising because the activation parameters of the decomposition of 2,4,6-triazidopyridine, the structure of which is similar to that of **I**, are characteristic of aromatic and heterocyclic azides. It is also remarkable that a clear correlation of the kinetics of the thermal decomposition with the composition of the formed condensed products exists: the end products of the thermolysis of anomalously decomposing azides are packs of planar polyconjugate networks, whereas for azides characterized by normal values of activation parameters (e.g., 2,4,6-triazidopyridine), the products of thermal decomposition are linear oligomers.

The results are likely explicable in terms of the kinetics and mechanisms of the thermal decomposition of organic azides. It is well known that the first step of the reaction is the cleavage of the azide group into molecular nitrogen and the corresponding nitrene. The nitrenes formed by the decomposition of azides in the ground state are triplets [1], i.e., are free radical-like particles prone to the detachment of a hydrogen atom and the formation of a corresponding amine. The rate-determining step of the reaction is the cleavage of azide group, for which the values of the activation energy and the pre-exponential factor are characteristic of aromatic and heterocyclic azides. The nitrene formed in the first step enters a chain of subsequent transformations to form a linear oligomer (or polymer). A possible scheme of such transformations, with the example of 2,4,6-triazidopyridine, has been presented earlier [4].

The decomposition of 2,4,6-triazido-1,3,5-triazine and **I** proceeds by an essentially different mechanism. The molecules of these compounds do not contain hydrogen atoms; thus, the nitrenes formed in the first step of the reaction react through another mechanism. It is difficult to characterize the mechanism of so complex a process which gives rise to packs of planar polyconjugate carbon–nitrogen networks, in detail. Certain aspects of this mechanism have been discussed previously, using the example of 2,4,6-triazido-1,3,5-triazine [3]. The decomposition of **I**, which also forms packs of polyconjugate networks, likely proceeds according to the same mechanism. It appears probable that the formation of polymer structures that are so complex occurs through a chain mechanism. The observed rate constant for a nonbranching chain reaction is determined not only by the rate constant for the chain initiation step (in our case, the cleavage of azide group) but also by the rate constants for individual steps of chain propagation and termination [8]. This may be the cause of the high values of activation energy and the pre-exponential factor.

As noted above, 2,4,6-triazidopyrimidine, which contains only one hydrogen atom, can decompose through either mechanism, i.e., by forming both packs of planar polyconjugate carbon–nitrogen networks and linear oligomers, with the former mechanism, however, dominating [6].

One more specific feature of the thermal decomposition of **I** that distinguishes it from the decomposition of other organic azides is the fact that the kinetics of the reaction is not described by a first-order equation (Fig. 2). To explain this, let us consider the following scheme of the process:

$$A \rightarrow B + C, \quad (1)$$

$$A + B \rightarrow C, \quad (2)$$

where B is the intermediate and C is the end product of the reaction. Let us designate the rate constants for reactions (1) and (2) as k_1 and k_2, respectively. Very early in the process, when the concentration of [B] is very low, the rate-determining step of the reaction is step (1), and the reaction is described by a first-order equation with the rate constant k_1. Let us assume that the reaction reaches a quasi-stationary mode, i.e., $d[B]/dt = 0$. In this case, for the studied reaction, we obtain $d[C]/dt = 2k_1[A]$. Thus, in the quasi-stationary mode, the kinetics of the reaction are described again with a first-order equation, but with a doubled rate constant.

A scheme including steps (1) and (2) was proposed for the thermal decomposition of N-nitrodimethylamine $(CH_3)_2NNO_2$ [9], where the intermediate B was nitrogen dioxide. It was shown [10] that the kinetics of this reaction is exactly described by the dependence presented in Fig. 2, with the ratio between the slopes of two portions of the semilog anamorphosis in this figure being 2. This suggests that the same kinetic scheme, in which B is intermediate nitrene and C is gaseous nitrogen (the release of which was measured to determine the kinetics of the reaction), is also applicable to the thermal decomposition of **I**. In this case, however, reactions (1) and (2) should not be regarded as unit steps. They are macroscopic steps, which occur through complex chain mechanisms but can be nonetheless described by simple kinetic equations.

According to the above considerations, the data in Fig. 2 mean that the quasi-stationary mode occurs not once the reaction begins, but after some time. In this case, one can assume that, in the decomposition of **I**, the intermediate nitrene incapable of entering the

reaction of the detachment of hydrogen has a kinetic stability that is quite high and, in the quasi-stationary mode, accumulates in noticeable amounts. An additional factor, which could inhibit the reaction at high conversions, may be the transition of some of the reacting particles in the solid state due to increases in the size of planar networks and, as a rule, decreases in their diffusion mobility.

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