Thermochimica Acta, 168 (1990) 211-221
Elsevier Science Publishers B.V., Amsterdam

THERMAL DECOMPOSITION OF TETRAZOLE-CONTAINING POLYMERS. I. POLY-5-VINYLTETRAZOLE THERMOLYSIS

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(Received 21 February 1990)

ABSTRACT

Thermal decomposition of poly-5-vinyltetrazole has been investigated by the methods of chemical and complex thermal analyses under isothermal and nonisothermal conditions, infrared spectroscopy and gas chromatography. Activation parameters of the decomposition process have been evaluated by various methods. The analysis of the obtained data leads to the conclusion that, depending on the conditions of the experiment, decomposition of polymer tetrazole cycles may proceed in two parallel ways: either destruction of the tetrazole rings with elimination of hydrogen azide, or their tautomeric isomerization into the respective azidoazomethine, from which a nitrogen molecule is then 'chipped off'.

INTRODUCTION

The thermal decomposition of tetrazole is accompanied by its vaporization [1]. The mechanism and kinetic parameters of this process depend on the experimental conditions, i.e. on the fact of how far one manages to either retard, or increase the rate of a substance transition to a gaseous phase. Massive substituents in the 1,5 or 2,5 positions, for example aryl moieties [2], generally make it possible to carry out the thermolysis in the condensed phase, but in this case the mechanism of tetrazole ring destruction in many respects is determined by conjugation of the tetrazole and aryl π-electron systems. Fixing of tetrazole fragments on the polymer carbon chain makes it possible to eliminate decomposition from the gaseous phase. The tetrazole heterocycle is substantially less thermostable than the polymeric chain, and this enables one to carry out thermal decomposition of fixed tetrazole rings in the condensed phase. References 3-6, which are devoted to the study of thermal destruction of polymers with tetrazole substituents, contain data on the mechanism and kinetic regularities of thermolysis of the tetrazole fragments and polymeric matrix. The present work has been carried out with the aim of a more detailed study of regularities of thermal decomposition of

0040-6031/90/$03.50

tetrazole heterocycles in the simplest carbon chain tetrazole-containing polymer—poly-5-vinyltetrazole (PVT).

EXPERIMENTAL

The polymer PVT(I) was obtained by the interaction of polyacrylonitrile (characteristic viscosity $[\eta] = 1.1$ dl g^{-1}, DMF, 293 K) with sodium azide and ammonium chloride [7], and was purified by repeated precipitation from the dimethylformamide solution by trifluoroacetic acid. The degree of conversion of nitrile groups to tetrazole rings found by direct titration of PVT(I) in DMF by an alcoholic solution of KOH was 89%. The elementary analysis of the original polymer and that subjected to thermal decomposition was carried out on a Hewlett-Packard 1080 analyser. The residual sodium content was determined on a Flaphokol atomic absorption spectrometer, and did not exceed 0.4 wt.% PVT(II) was obtained by homopolymerization of 5-vinyltetrazole in degassed water in the presence of ammonium persulphate (0.5 mol%) in an argon atmosphere. The synthesized polymer has a characteristic viscosity $[\eta] = 0.88$ dl g^{-1} (DMF with addition of 5% $LiNO_3$, 293 K).

The thermal decomposition of PVT was studied by complex thermal analysis methods on a derivatograph (MOM, Budapest), as well as by means of the DAGV-70-2M gas volumeter. On the derivatograph the experiments were carried out in air using a platinum holder, with a heating rate of 5 K min^{-1}. For the volumetric experiments glass ampoules were used and the experiments were carried out in a static argon inert atmosphere with heating rates of 0.63, 1.25, 2.5, 5, 10 and 20 K min^{-1}, as well as under isothermal conditions within the temperature range $T = 478$–503 K. The sample mass was 10 mg. A CPM-2 gas chromatograph was used to check the released gas composition. The quantitative content of hydrogen azide in the thermolysis products was determined photometrically in the form of a complex with Fe^{III} on a Spekol-21M instrument at a wavelength of 462 nm. The IR spectra of the initial polymers and those experiencing thermal decomposition in an inert atmosphere were obtained by means of the Specord 75 IR spectrometer.

RESULTS AND DISCUSSION

The obtained samples of PVT(I) and PVT(II) were white friable powders composed of filiform particles. The polymers are hygroscopic. According to the thermogravimetric data, the water content in PVT(I) and PVT(II) reaches 10%, which approximately corresponds to monohydration of each tetrazole ring.

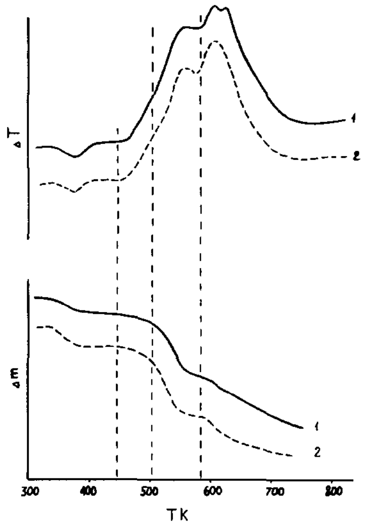


Fig. 1. DTA and TG curves of thermal decomposition of poly-5-vinyltetrazole: 1, PVT(I); 2, PVT(II).

Figure 1 presents DTA and TG curves for PVT(I) and PVT(II) obtained by means of the derivatograph. Within the range 320–390 K water is removed and then chemical conversion of the PVT proceeds without polymer melting. For both PVT(I) and PVT(II) an insignificant mass loss not related to water removal starts as low as 450 K. Decomposition of the PVT(II) homopolymer is accompanied by two exothermic peaks. The first one ($T_{max} = 564$ K) should evidently be attributed to decomposition of the tetrazole ring, and the second ($T_{max} = 615$ K) to thermooxidative destruction of the polymeric residue [5]. In the PVT(I) polymeric matrix which remains after decomposition of the tetrazole rings, fragments with different thermal stability probably exist, as evidenced by splitting of the second exothermic maximum. Because of the absence of major differences in PVT(I) and PVT(II) thermolysis, basically at the stage of tetrazole ring decomposition, the PVT(I) sample was studied further.

With the heating rate increase, gas-release curves are regularly shifted towards the low-temperature region (Fig. 2), and when the heating rate is 40 K min^{-1} an explosion-like decomposition of the substance takes place. Attention is attracted by the fact that, at low heating rates only (0.63 K min^{-1}), the released gas volume corresponds to elimination of one gas molecule from each heterocycle. In the other cases this volume is higher, and naturally it grows with the heating rate increase. Gas chromatographic analysis with a heating rate of 5 K min^{-1} has shown that the main gaseous product of the PVT thermal decomposition was nitrogen, which conforms to the data of ref. 5. However, along with nitrogen we have observed the release of hydrogen azide (HN_3) and trace quantities of methane (CH_4). Quantita-

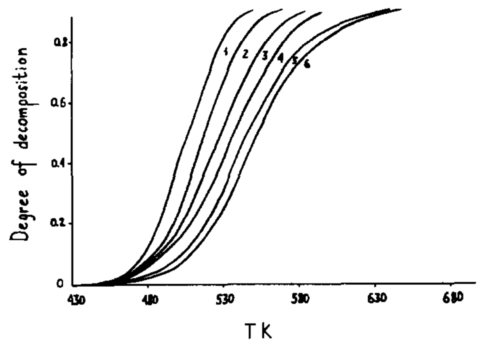


Fig. 2. Kinetic curves of PVT thermal decomposition under nonisothermal conditions at various heating rates (K min^{-1}): 1, 0.63; 2, 1.25; 3, 2.5; 4, 5; 5, 10; 6, 20.

tive measurements under the conditions of our experiments have shown that the HN_3 mole fraction in the thermolysis products depends on the heating rate and is 2.4% at 2.5 K min^{-1}, 3.4% at 5 K min^{-1} and 4.15% at 20 K min^{-1}.

The dependence of the activation energy (E) of PVT thermolysis on the degree of decomposition, found by the Ozawa method [8], is presented in Fig. 3. The activation energy increases up to a decomposition degree $\alpha = 0.15$ and reaches the value of 215 kJ mol^{-1}, which points to a complex character of the PVT thermolysis and, in particular, to its proceeding at least in two parallel ways with different activation energies. After $\alpha = 0.2$, the character of dependence of E on α changes radically, which may be due to a change of the limiting stage of the process. Within the range $\alpha = 0.2$–0.8 the activation energy continuously decreases and reaches the value of 135 kJ mol^{-1}. Further more abrupt decrease of E is probably correlated with transition of the process to the diffusionally controlled region.

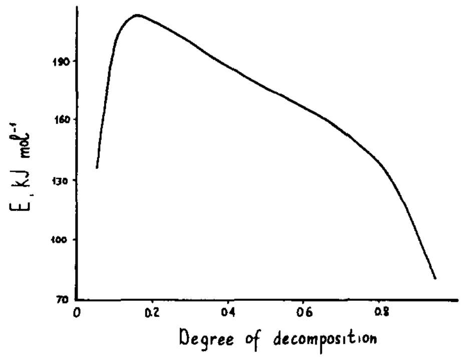


Fig. 3. Dependence of activation energy of PVT thermolysis on the degree of its decomposition found by the Ozawa method.

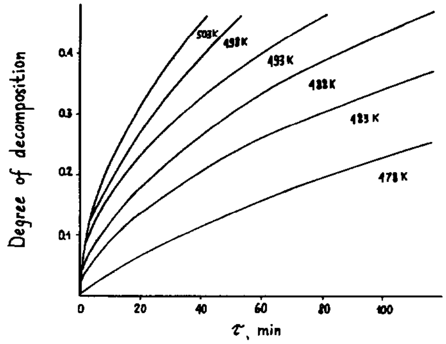


Fig. 4. Kinetic curves of PVT thermal decomposition under isothermal conditions.

Under isothermal conditions at $T > 505$ K, the PVT decomposes explosively just after location of a sample in the heating zone, whereas at $T < 478$ K the decomposition proceeds very slowly. Because of this we studied the isothermal decomposition of PVT within a comparatively narrow temperature range. On all kinetic curves, except that obtained at $T = 478$ K, one can distinguish two sections: a first one with comparatively rapid reaction proceeding, which increases with the temperature rise, and a second, which is characterized by slower gas release. The chromatographic analysis of the released gas (for $T = 488$ K) has shown that in the initial states of thermolysis, along with nitrogen, HN_3 and CH_4 are released as under nonisothermal conditions; but the peaks related to HN_3 and CH_4 rapidly disappear. Step-by-step temperature rises in the reaction cell by 4–5 K, with simultaneous sampling to the chromatograph, make it possible to record renewed release of these gases.

In order to obtain linear transformations of isothermal kinetic curves we have tested more than 20 kinetic functions, which are those most frequently used in topochemistry, but none of these allowed linearization of the whole kinetic curve. For this reason, estimation of the kinetic parameters was made by the isoconversional method [9], making it possible to evaluate the effective value of the activation energy without any assumptions as to the kinetic function of the process. Figure 4 presents the dependence of the activation energy on the degree of conversion of PVT under isothermal conditions. It is obvious that, in the initial stages up to $\alpha = 0.4$, the process is a complex one, since gradual decrease of the efficient value of the activation energy is observed. After reaching half-transformation the curve comes to a plateau with $E = 140$ kJ mol^{-1}.

In ref. 5 the activation energy of the thermal decomposition of PVT(II) under isothermal conditions has been found also. Within the range $\alpha = 0$–0.8 it is 164 ± 7 kJ mol^{-1} when the thermolysis is assumed to proceed by the first order equation. In our opinion such a value of the activation energy is an average one, since the estimation was done within the range of transfor-

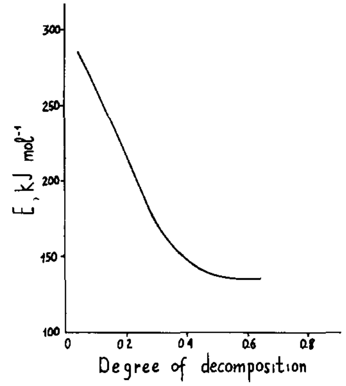


Fig. 5. Dependence of activation energy on degree of PVT conversion under isothermal conditions.

mation degrees covering the transition region from a complex to an essentially one-stage process (Fig. 5).

Spectral investigations (Fig. 6) have revealed no significant differences in the IR spectra of PVT(II) and PVT(I), except for the redistribution of intensities of some absorption bands. Both polymers show the 1040 cm^{-1} absorption band which characterizes stretching deformation vibrations of the tetrazole ring [10]. The bands at 1135 and 1190 cm^{-1} can probably be attributed to vibrations of C–H bonds of the carbon skeleton [11]. The stretching vibrations $\nu_{(C-N)}$, $\nu_{(N-N)}$, $\nu_{(C=N)}$ and $\nu_{(N=N)}$ of the tetrazole ring are to be found in the region from 1200–1600 cm^{-1} [12]. The intense band with its maximum at 1645 cm^{-1} is probably attributable to absorption caused by deformation vibrations of the N–H bond, the long-wave shift of which is due to the donor–acceptor interaction of a hydrogen atom with tetrazole rings of adjacent macromolecules. The stretching vibrations of

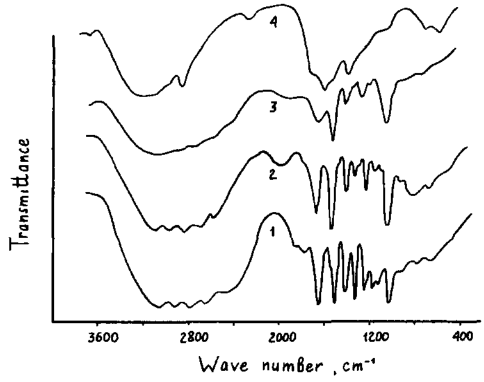


Fig. 6. IR spectra: 1, PVT(I); 2, PVT(II); 3, PVT(I) subjected to thermal decomposition up to $\alpha = 0.2$; 4, residue of PVT(I) thermal decomposition.

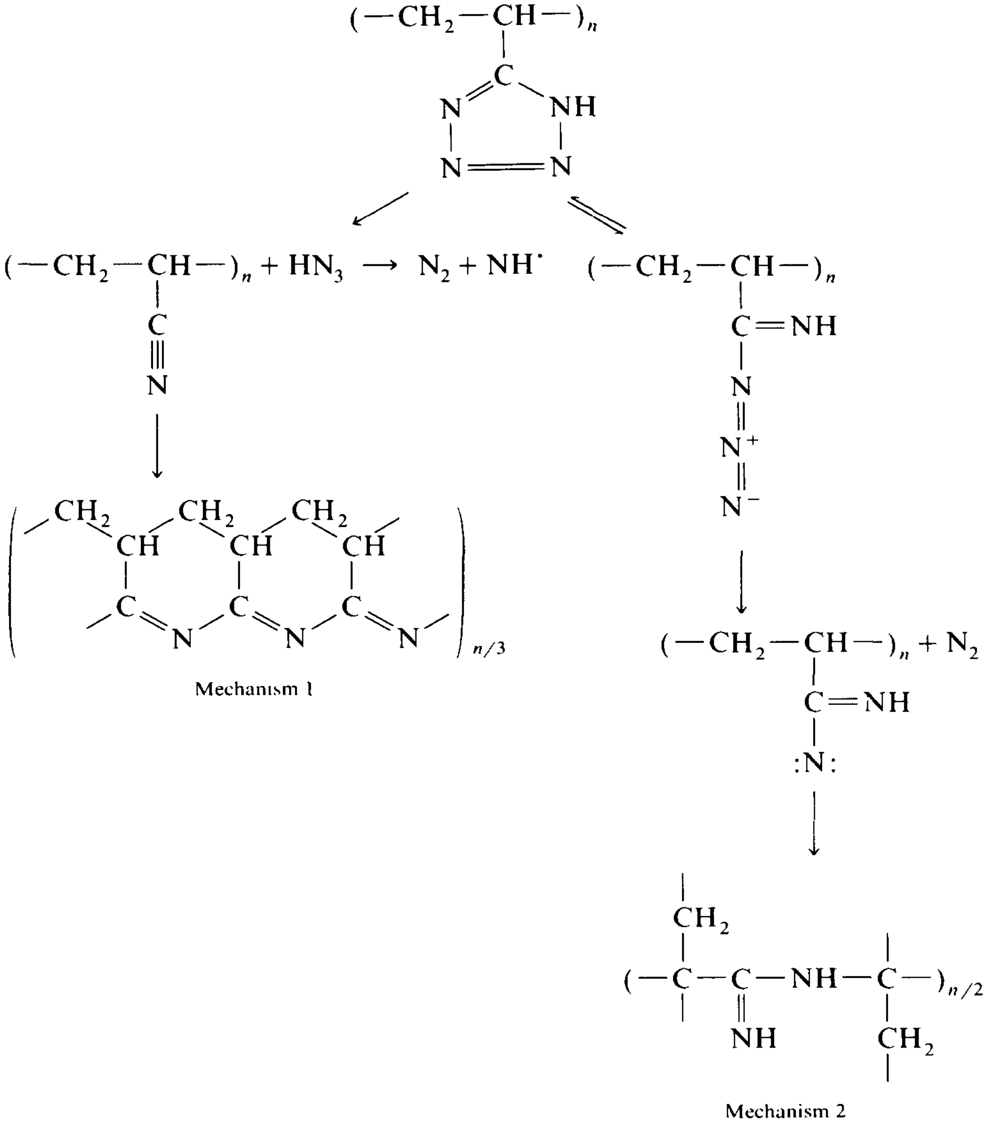
$-CH_2$ and $-CH-$ groups of the polymer matrix provide a wide band within the range 2800–3000 cm^{-1}, which is followed by a structured band from 3000–3200 cm^{-1}. This is related to the stretching vibrations of N–H bonds of the tetrazole ring, which participate in the formation of hydrogen bonds between the heterocycles [5,13].

The IR spectrum of the PVT subject to thermal decomposition up to a degree of $\alpha = 0.2$ (Fig. 6) preserves the basic bands which are characteristic both of the stretching and the stretching deformation vibrations of the tetrazole ring. However, already at this decomposition stage the polymer is practically insoluble in dimethylformamide and other solvents in which the initial PVT is soluble.

In the IR spectrum of the residue from thermal decomposition of the PVT, tetrazole ring bands are missing and three continuous absorption regions are observed. Within the range 550–700 cm^{-1} there is a broad maximum, which may be due to the formation of conjugated structures [1]. A faint band at 730–740 cm^{-1} is probably due to rocking vibrations of $-\overset{|}{C}H-$ and $=NH$ [8,14]. The maximum at 1595 cm^{-1} may be caused by stretching vibrations of $C=N$, and that at 1420 cm^{-1} is caused by deformation vibrations of $-\overset{|}{C}H-$ [14]. The stretching vibrations of $=NH$ groups reveal themselves in the form of a broad band at 3300–3450 cm^{-1}. We can explain the absorption at 2910 cm^{-1}, with its shoulder at 2840 cm^{-1}, by the C–H stretching vibrations of the carbon chain, and the absorption maximum with weak intensity (2220 cm^{-1}) is a characteristic absorption band of the $-C\equiv N$ groups [14].

Analysis of the whole set of kinetic and spectroscopic data made it possible to reveal such details of the thermal decomposition of PVT which for their explanation require the assumption that the thermal decomposition proceeds in at least two parallel reactions, the contribution of which to the total decomposition process depends on the experimental procedure. Their existence may probably be explained by the ring–chain tautomerism for the tetrazole rings. During decomposition of poly-1-methyl-5-vinyltetrazole [4] and the unsubstituted tetrazole in the condensed phase [1], it was assumed that tetrazole ring decyclization preceded via nitrogen molecule elimination. In ref. 5 a similar scheme is proposed also for PVT. The data from our work, however, allow another mode of decomposition of the tetrazole rings to be considered, which involves breaking of two bonds with HN_3 molecule release. As a result, the PVT decomposition may be represented as shown in Scheme 1.

The hydrogen azide is unstable and at the experimental temperatures it is partially decomposed with active radical, $NH^{\cdot}$, release [15]. Being a strong reducing agent, the latter probably can reduce carbon to methane in the absence of oxygen. This explains the appearance of methane on the chromatograms simultaneously with HN_3. When mechanism 1 takes place the



Scheme 1. Decomposition of PVT.

solid residue of the thermolysis is polyacrylonitrile, which at elevated temperatures is inclined to form polycyclic structures [16] if their are also several $-C{\equiv}N$ groups present. We find confirmation of the existence of polymers of such structure in the IR spectrum of the solid residue from PVT thermolysis.

In those cases when the thermal decomposition goes through the tetrazole azidoazomethine form, active nitrene groups are formed after removal of nitrogen. Nitrene introduction at the –CH– bond on the α-carbon atom of

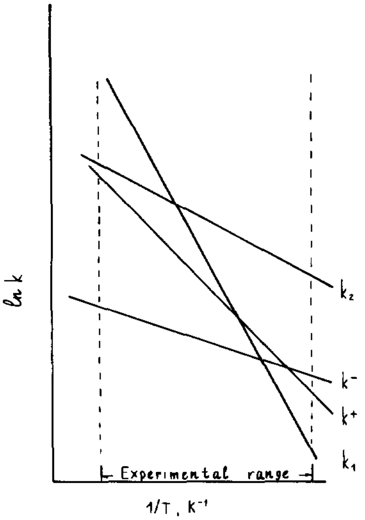


Fig. 7. Kinetic scheme of PVT thermal decomposition.

the macrochain probably leads to a polymer linkage and to practically complete loss of solubility, even in the initial stages of the thermal decomposition. The existence of =NH groups in the thermolysis products is also confirmed by IR spectroscopy.

According to Scheme 1, in the discussed case of the PVT thermal decomposition, we are dealing with a process of the following type

$$(\mathrm{I})\mathrm{G(g)} + \mathrm{D(s)} \xleftarrow{k_1} \mathrm{A(s)} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{B(s)} \xrightarrow{k_2} \mathrm{E(s)} + \mathrm{F(g)}(\mathrm{II})$$

which involves two competitive reactions, i.e. thermal decomposition of A(s) (tetrazole cyclic form) and B(s) (azidoazomethine form). In the process, the conversion of A(s) into B(s) is reversible, and the quantitative content of each of the tautomeric forms is determined by the ratio of the constants of the direct (k_+) and reverse (k_-) reactions.

Since, according to IR spectroscopic data, the initial polymer is of the PVT tetrazole form (i.e. $k_+ < k_-$; Fig. 7), the decomposition proceeding predominantly by mechanism 2 is limited by formation of the azidoazomethine form ($k_+ < k_2$). Therefore, under nonisothermal conditions, in the initial thermolysis stage low values of the effective energy of activation are observed, which probably correspond to the process of PVT conversion from the tetrazole to the azidoazomethine form. With growth of the degree of conversion (temperature) the increase of E to ≈ 215 kJ mol^{-1} takes place (intersection of Arrhenius straight lines for k_+ and k_1), which corresponds to thermal decomposition predominantly by mechanism 1. The temperature rise leads to further displacement of the tautomeric equilibrium ($k_+ > k_-$) and to depletion of the PVT cyclic form, which again reduces the contribution of mechanism 1 to the overall process of thermal decomposition, and the activation energy gradually drops to ≈ 130 kJ mol^{-1} at $\alpha = 0.8$. One should note that under nonisothermal conditions the contents of HN_3 and CH_4 in the thermolysis products also go through a maximum.

During isothermal experiments, in the initial nonisothermal stage rapid heating of a substance takes place and equilibrium between the tautomeric forms of the PVT has no time to become established. As a result, the thermal decomposition first proceeds predominantly by mechanism 1, as is proved by a high value of the activation energy (≈ 285 kJ mol^{-1}) at small degrees of conversion (Fig. 5) and by the appearance of HN_3 and CH_4 in the thermolysis products. When equilibrium at a specified temperature has become established, the effective activation energy decreases to ≈ 140 kJ mol^{-1}, which corresponds to the conversion from the cyclic to the azidoazomethine form of the PVT.

One should note that, for the process of tetrazole nonisothermal decomposition, a descending dependence of the activation energy on the degree of conversion was found [17]. The form of such a dependence was interpreted on the basis of a kinetic scheme identical with the above, but in the case of tetrazole thermolysis proceeding in the melt it was assumed that tautomeric equilibrium established rapidly, i.e. the stage of irreversible decomposition of the PVT azidoazomethine form is a limiting one. Within the framework of the proposed model of tetrazole thermolysis [17], the high value of the efficient activation energy observed at the initial stage (≈ 380 kJ mol^{-1}) is a sum of the reversible process of transition to the azidoazomethine form and the activation energy of its decomposition. With an increase in the degree of conversion (temperature) the equilibrium is displaced towards formation of the azidoazomethine form and the activation energy decreases to ≈ 150 kJ mol^{-1}, which corresponds to the irreversible decomposition of the latter form.

In conclusion it may be stated that the results of the present work, in conjunction with those from refs. 1 and 17, provide a vivid example of the way in which the mechanism and kinetic regularities of thermal decomposition reactions may depend on the phase condition of a reactant, the temperature region in which reaction proceeds and the rate of reaching this region. In this connection, comparison of the results of isothermal and nonisothermal experiments in order to reveal details of the process seems to be highly important.

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