Thermal decomposition of *C*-iodotetrazoles

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Thermal decomposition of 1-substituted *C*-iodotetrazoles in melt and solutions has been investigated. Thermal stabilities, kinetic and activation parameters, and compositions of products of thermolysis of *C*-iodotetrazoles depend on the substituent nature. The scheme of thermolysis of *C*-iodotetrazoles has been suggested.

Key words: *C*-iodotetrazole, thermolysis; kinetics; mass spectrometry; IR spectroscopy.

The previous study[1] of the kinetics of thermal decomposition of 5-iodo-1-ethyltetrazole (**1**) in melt and in solutions made it possible to suggest that this reaction occurs *via* a stage of isomerization of the initial tetrazole to the corresponding azidoazomethine form followed by homolytic cleavage of the C—I bond. It is known[1,2] that electron-donating substituents at the N atom in position 1 of the heterocycle hinder rearrangements of 1,5-disubstituted tetrazoles into azidoazomethines, due to an increase in the energy of conjugation of the cyclic system. On the contrary, electron-accepting substituents decrease the tendency of tetrazole to open the cycle, *i.e.*, facilitate this rearrangement. In continuation of these studies, the thermal decompositions of 5-iodo-1-methyltetrazole (**2**), 5-iodo-1-phenyltetrazole (**3**), and 1,2-bis(5-iodotetrazolyl)ethane (**4**) are studied in this work.

Experimental

Samples **2**, **3**, and **4** were synthesized at the Institute of Physicochemical Problems of Belorussian University. The melting points of compounds **2** and **3** are 95 and 140 °C, respectively. Compound **4** decomposes even in the solid state. Kinetic measurements were performed by manometric, volumetric, and thermogravimetric methods (see Ref. 1). Volatile products of the thermolysis of compound **3** were analyzed on a MI1201-V mass spectrometer provided with a quartz pyrolytic cell with a fixed volume. The total pressure of gaseous thermolysis products in the cell was determined by a mechanotron (2 % accuracy). Fused products of the thermal decomposition of tetrazole **3** were studied on a Specord-75 IR spectrophotometer (as pellets with KBr) within the 400 to 4000 cm^{-1} frequency range.

Results and Discussion

In thermogravimetric experiments, the thermal decomposition of compound **3** in the solid state at 80—130 °C was accompanied by spalling of individual crystals and ejection of a portion of the sample from the reaction vessel, which made kinetic measurements difficult and introduced large errors into the values of the measured parameters.

In *m*-dinitrobenzene and dimethylphthalate solutions the kinetics of thermal decomposition of compound **3** up to 80 % conversion obeys a first-order law (Fig. 1, Table 1). The thermal decomposition of tetrazole **3** in solutions is described by the Arrhenius equation:

$$k_{DNB} = 10^{15.5\pm1.2} \cdot \exp\,[(-133800\pm6500)/(RT)],$$

$$k_{DMP} = 10^{14.1\pm0.9} \cdot \exp\,[(-122600\pm5500)/(RT)],$$

where k_{DNB}/s^{-1} and k_{DMP}/s^{-1} are the thermolysis rate constants in *m*-dinitrobenzene and dimethylphthalate solutions, respectively.

Mass-spectral analysis showed that N_2 is the only product of the thermal decomposition of **3** that remains

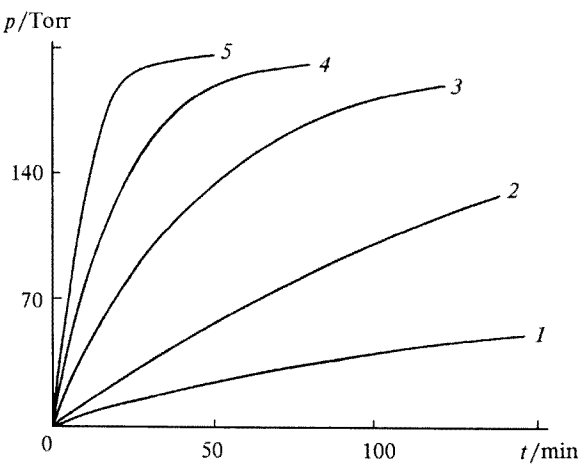

Fig. 1. Kinetics of thermal decomposition of tetrazole **3** in the *m*-dinitrobenzene solution in a vacuum; the initial weighed sample is 3.0 mg, the volume of the reaction vessel is 4.0 mL. Curves: *1*, 80 °C; *2*, 90 °C; *3*, 100 °C; *4*, 105 °C; *5*, 110 °C.

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Table 1. First-order rate constants (k) of thermal decomposition of tetrazole **3** in solutions (vacuum, m/V = 0.75 mg mL^{-1})

Solvent	$k \cdot 10^4/s^{-1}$				
	80 °C	90 °C	100 °C	105 °C	110 °C
Dimethylphthalate	0.90±0.12	2.6±0.2	7.65±0.35	11.7±0.5	22.5±0.80
m-Dinitrobenzene	0.40±0.07	1.5±0.2	6.80±0.45	13±2	26±2

in the gas phase at room temperature. The volumetric measurements showed that the complete decomposition of 1 g of compound **3** results in the formation of 125 mL of gases that are not condensed at 22 °C. N_2 comprises 93 % of the total volume of gases, which is confirmed by the method of freezing the products by liquid nitrogen (−196 °C). Thus, the complete decomposition of 1 mol of tetrazole results in the formation of 1.4 mol of N_2. These results are confirmed by the data of quantitative mass spectrometry of thermolysis products of compound **3** in the pyrolytic cell, using the mechanotron.

The second identified product of the thermal decomposition of tetrazole **3** is I_2. It is condensed on the reaction vessel walls. The formation of I_2 is confirmed by its qualitative reaction with chloroform.

The IR spectrum of initial compound **3** (Fig. 2, curve *1*) contains several narrow ($\Delta\nu \leq 1$ cm^{-1}), symmetric, and sufficiently intense bands, which indicates the absence of a noticeable exchange of the vibrational energy between molecules in crystal **3** and the absence of tensions in the crystal lattice.[4] The lines in the range of 1200—1500 cm^{-1} are assigned to stretching vibrations of C—N bonds of the tetrazole cycle. The spectrum of the completely decomposed sample (see Fig. 2, curve *2*) contains an intense absorption band at 2230 cm^{-1} that corresponds to stretching vibrations of the nitrile —C≡N group. The bands assigned to the conjugated systems of C—N and N—N bonds are retained, but their frequencies and intensities change, and peak widths increase by tens times. This testifies that the structure of the solid product of thermolysis of compound **3** is amorphous. At the same time, the intensity of the absorption band at 1010 cm^{-1} decreases, which is caused by the thermal decomposition of the tetrazolic cycle.

The IR spectrum of sample **3** kept for 20 min at 120 °C in a vacuum (which corresponds approximately to the 16 % depth of decomposition) is the superposition of the IR spectra of initial and completely decomposed tetrazole **3**. The comparison of the IR spectra of initial and partially decomposed compound **3** testifies that no changes in defects of the crystal lattice occur and microtensions appear in it, but an increase in the reflection coefficient is observed, which is maximum in the solid product of the complete decomposition of **3**. The IR spectrum of the solid product of the thermal decomposition of tetrazole **3** contains absorption bands at 3080 cm^{-1} characteristic of the conjugated —CH=CH— bonds, and at 1460 and 1550 cm^{-1}, which indicate the presence of phenyl groups. The ratio of intensities of the absorption bands of —C≡N groups and the conjugated system of —CH=CH— bonds is close to that in the IR spectrum of benzonitrile. The absorption band at 820 cm^{-1} can be assigned to the bending vibration of the triazine cycle.[5] A diffuse series of bands characteristic of stretching vibrations of N—H bonds is observed in the 2800—3500 cm^{-1} range in the IR spectrum of the final product of thermal decomposition of tetrazole **3**.

The following scheme of chemical reactions during thermolysis of 5-iodo-1-phenyltetrazole **3** can be supposed on the basis of the comparative analysis of the data of kinetic measurements, volumetry, mass spec-

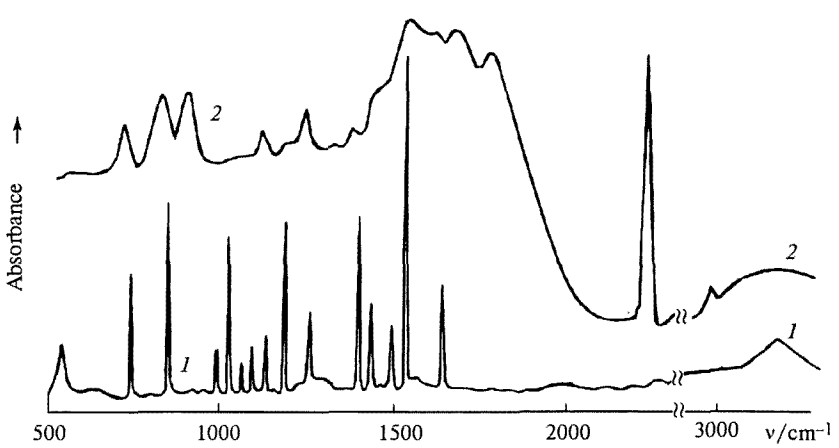
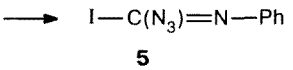
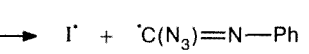


Fig. 2. IR spectrum of initial tetrazole **3** (*1*) and solid residue after complete thermal decomposition of compound **3** (*2*).

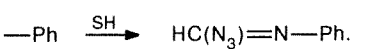
trometry, and IR spectroscopy. As the majority of 1,5-disubstituted tetrazoles,[6,7] compound **3** undergoes thermal rearrangement to form azidomethine form **5**.



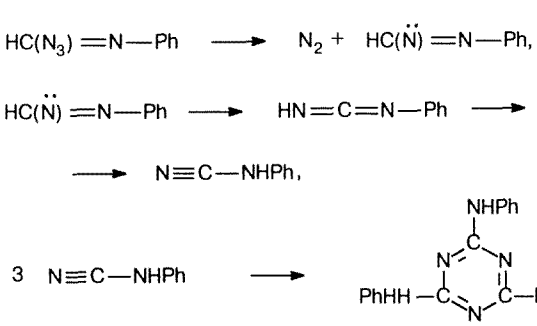
The electron-accepting Ph-substituent in position 1 of the heterocycle of the molecule of **3** facilitates the formation of the reactive form of azidoazomethine **5** (see Refs. 2 and 3) compared to the similar rearrangement of tetrazole **1**. Therefore, comparable rates of thermal decomposition of compounds **3** and **1** (see Ref. 1) are observed at 80—110 °C and 130—160 °C, respectively. Then, as in the case of thermolysis of **1**, the homolytic cleavage of the I—C bond occurs.



The recombination of I· radicals results in the formation of I_2. Subsequent thermal transformations involving ·C(N$_3$)=N—Ph radicals can be presented in the following way:

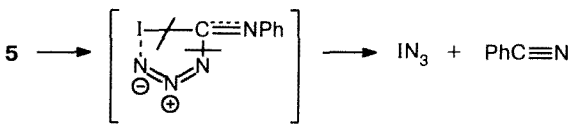


Due to the high reactivity the ·C(N$_3$)=N—Ph radical abstracts the H atom from any adjacent molecule, including a solvent molecule.

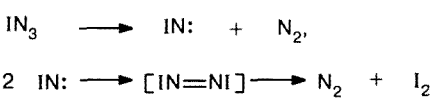


The data of IR spectroscopy, which indicate that N—H bonds, phenyl groups, and the system of conjugated C=N bonds are present in the solid product of decomposition of tetrazole **3**, testify in favor of the formation of 1,3,5-tris(phenylamino)triazine. The spectrum also contains the low-frequency absorption band at 820 cm^{-1} typical of triazines.[5]

However, the reaction scheme suggested does not explain two important experimental facts: the existence of the intense absorption band of the nitrile bond, which is likely belongs to benzonitrile, and the fact that the complete decomposition of 1 mol of compound **3** results in the formation of 1.4 mol of N_2 rather than 1 mol of N_2, as provided by the reaction scheme suggested above. Therefore, the existence of an additional competitive route of thermal decomposition of tetrazole **3** followed by the elimination of an azidoiodide molecule from compound **5** can be suggested.



Phenylisonitrile (it should give the characteristic absorption at 2100—2180 cm^{-1})[8] is not present in the solid residue after decomposition and cannot be an intermediate reaction product, because its isomerization to benzonitrile requires high temperatures.[9] It can be supposed that the elimination of azidoiodine is accompanied by the migration of the phenyl group to the C atom, which is typical of the Wolf rearrangement.[10,11] Intermediate azidoiodine decomposes to iodine and nitrogen.



According to this scheme, the complete decomposition of 1 mol of tetrazole **3** should result in the formation of 1.5 mol of N_2. Since, according to the volumetric data, the complete decomposition of 1 mol of compound **3** is accompanied by the release of 1.4 mol of N_2, the contribution of this route of decomposition (*via* intermediate azidoiodine) is 80 %.

The kinetic curves of the formation of gas-phase products of the thermal decomposition of tetrazole **2** in melt are presented in Fig. 3. As in the case of thermolysis of compound **1**,[1] a portion of forming volatile products (~5 vol. %) goes from the gaseous to condensed phase due to secondary reactions; this is indicated by the pressure drop at high degrees of conversion. We assume that the condensation of volatile products of thermolysis of tetrazole **2** is continuous and parallel to the main process of thermal decomposition. However, it appears only after a considerable decrease in the rate of thermal decomposition due to a decrease in the concentration of the initial (decomposed) substance. The decomposition of compound **2** obeys the first-order law up to ≥80 % conversion. The rate constants at 120, 130, 140, and 150 °C are equal to $(3.0\pm0.2)\cdot10^{-5}$, $(11.5\pm0.4)\cdot10^{-5}$, $(41\pm3)\cdot10^{-5}$, and $(146\pm8)\cdot10^{-5}$ s^{-1}, respectively. The process is described by the Arrhenius equation:

$$k_{melt} = 10^{19.3\pm0.6}\cdot\exp[(-178000\pm9000)/(RT)].$$

The kinetic and activation parameters of the thermal decomposition of tetrazole **2** are close to those previously obtained[1] for the thermal decomposition of com-

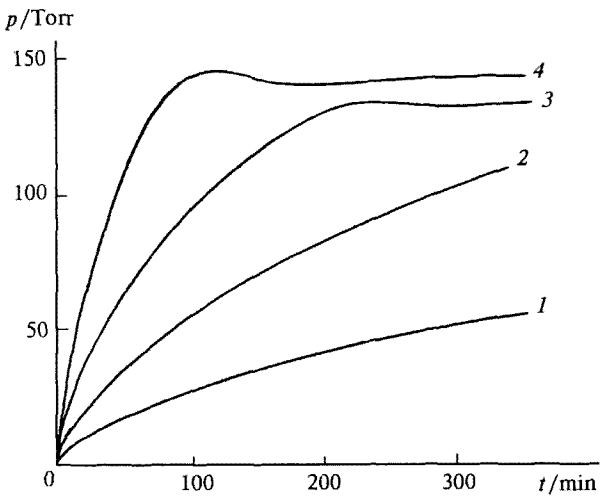


Fig. 3. Kinetics of thermal decomposition of tetrazole **2** in melt in a vacuum; the initial weighed sample is 3.0 mg, the volume of the reaction vessel is 4.0 mL. Curves: *1*, 120 °C; *2*, 130 °C; *3*, 140 °C; *4*, 150 °C.

Table 2. Activation energy (E_a) and logarithms of pre-exponential factors (k_0) of Arrhenius equations of thermal decomposition of *C*-iodotetrazoles in *m*-dinitrobenzene solutions

Compound	E_a/J mol^{-1}	logk_0
5-Iodo-1-ethyltetrazole (**1**)	174000±9000	18.2±1.2
5-Iodo-1-methyltetrazole (**2**)	167700±8500	17.6±1.8
1,2-Bis(5-iodotetrazolyl)ethane (**4**)	149000±11000	15.1±1.2
5-Iodo-1-phenyltetrazole (**3**)	133800±6500	15.5±1.2

pound **1**. In a *m*-dinitrobenzene solution the decomposition is described by the Arrhenius equation:

$$k_{DNB} = 10^{17.6\pm1.8} \cdot \exp[(-167700\pm8500)/(RT)].$$

The kinetics of thermal decomposition of compound **4** was studied by the manometric method in a *m*-dinitrobenzene solution at 110—150 °C. The process obeys a first-order kinetic law. The rate constants at 110, 120, 130, 140, and 150 °C are equal to $(2.4\pm0.3)\cdot10^{-5}$, $(6.5\pm0.5)\cdot10^{-5}$, $(22.0\pm1.5)\cdot10^{-5}$, $(78\pm5)\cdot10^{-5}$, and $(250\pm14)\cdot10^{-5}$ s^{-1}, respectively. The process is described by the Arrhenius equation:

$$k_{DNB} = 10^{15.1\pm1.2} \cdot \exp[(-149000\pm11000)/(RT)].$$

One can judge the thermal stabilities of compounds **2**, **4**, and **3** at 110 °C on the basis of the rate constants of their thermal decomposition, equal to $7\cdot10^{-6}$, $2.4\cdot10^{-5}$, and $2.6\cdot10^{-3}$ s^{-1}, respectively. The Arrhenius parameters of thermal decomposition of *C*-iodotetrazoles in dinitrobenzene are presented in Table 2.

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