Thermal decomposition of 1-ethyl-5-iodotetrazole

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The thermal decomposition of 1-ethyl-5-iodotetrazole in a melt and in solutions was studied using thermogravimetry, manometry, pyrolytic mass spectrometry, and IR spectroscopy. The kinetic and activation parameters of the process and the nature of the decomposition products were determined. The reaction mechanism is assumed to involve equilibrium tautomeric rearrangement of the tetrazole to azidoazomethine form followed by homolytic cleavage of the C—I bond.

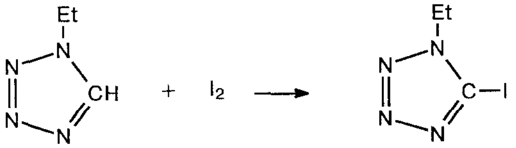
Key words: kinetics, mechanism, thermolysis, 1-ethyl-5-iodotetrazole, mass spectrometry.

Tetrazoles possess a combination of unique properties (considerable thermal stability along with high enthalpy of formation, physiological activity, high reactivity in complexing with metals, sensitivity to photochemical transformations) and are believed to be promising compounds for practical applications.[1—3] For these reasons, it is of interest to synthesize new tetrazole derivatives, including polymers, from vinyl-substituted tetrazoles.[4] Tetrazoles are strained energy-rich heterocycles, which allows us to include them among explosive compounds. In view of this, it is necessary to study the thermal transformations of tetrazoles.

An analysis of literature data on the thermal decomposition of 1,5-disubstituted tetrazoles shows that this process typically starts with rearrangement with ring opening to give the corresponding azidoazomethines.[5—7] To date, the thermal decomposition of a series of 1,5-disubstituted tetrazoles, mostly the alkyl-, amino-, nitro-, and phenyl derivatives and that of a polymer derived from 5-vinyl-1-methyltetrazole, has been studied.[7] In the present work we studied 1-ethyl-5-iodotetrazole (EIT). We assumed that the presence of a I—C bond can alter the behavior of the tetrazole concerning thermal decomposition.

Experimental

1-Ethyl-5-iodotetrazole, m.p. ~82 °C, was synthesized by treating 1-ethyltetrazole with iodine in acetic acid containing the $KMnO_4—H_2SO_4$ oxidating system:



The product was characterized by elemental analysis and IR and mass spectra. Kinetic measurements were carried out on an ATV-14M automatic electronic thermobalance designed and assembled at the Institute of Chemical Physics in Chernogolovka of the RAS[8] and by the manometric method using glass membrane Burdon manometers. Mass spectra were obtained on an MI 1201-V mass spectrometer equipped with a modified ion source and a pyrolytic cell.[9] The procedure permits valid identification of primary decomposition products, including labile compounds. The mass spectrometric analyses were performed under the following conditions: ionization energy, 70 eV; accelerating voltage, 4 kV; pressure in the ion source, 10^{-5} Pa. The mass spectrum of EIT was first recorded without heating of the pyrolyzer and then with heating.

IR spectra were recorded on a Specord 75-IR spectrophotometer (the spectrum of EIT was recorded in KBr pellets, and that of the condensed thermolysis product was measured in a film deposited from acetone).

Results and Discussion

The mode of fragmentation of EIT under electron impact is demonstrated by the data in Table 1. The mass spectrum of EIT also contains a low-intensity (~7 %) peak with m/z 254, which indicates the presence of an I_2 admixture not exceeding 0.5 mass. % (as estimated taking into account the volatility of I_2 and the low intensity of the $[I_2]^+$ molecular ion).

To assess the thermal stability, we recorded the kinetics of EIT mass loss with programmed heating of the sample at a rate of 0.5 deg min^{-1} in air. Intense mass loss by EIT is observed in the temperature range of 130—170 °C. *In vacuo*, the compound sublimes rapidly and reprecipitates onto the cold walls of the reaction vessel. For this reason, all subsequent thermogravimetric experiments were carried out in krypton or air at atmospheric pressure.

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Table 1. Fragmentation of EIT under electron impact

m/z*	Formula of the ion	I_{OTH} (%)	m/z	Formula of the ion	I_{rel} (%)
224 (M+)	$C_3H_5N_4J$	65	43	C_2H_5N	22
196	$C_3H_5N_2I$	3	42	C_2H_4N	23
181	CN_3I	7	41	C_2H_3N	21
167	CN_2I	77	40	C_2H_2N	9
140	CHI	56	29	C_2H_5	47
139	CI	45	28	N_2,C_2H_4	49
128	HI	18	27	HCN	80
127	I	100	26	CN	10
97	$C_3H_5N_4$	12	15	CH_3	18
57	$C_2H_5N_2$	28			

* Peaks with intensities below 1 % are not listed.

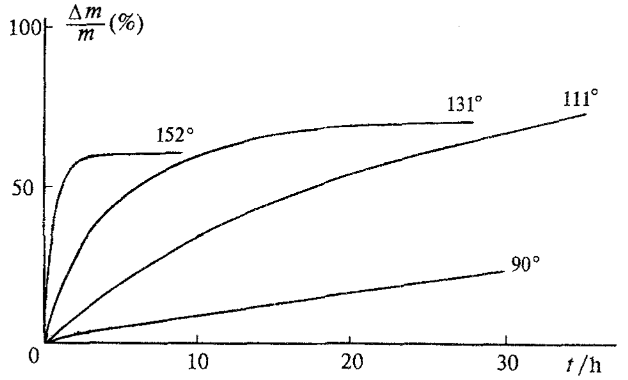


Fig. 1. Kinetics of the thermolysis of EIT in air. Weight of samples 15—17 mg.

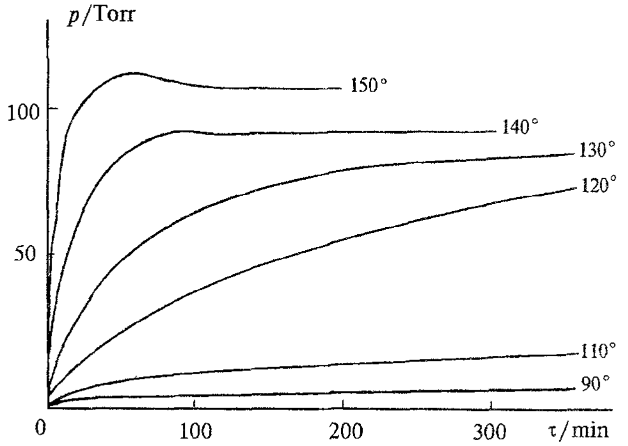


Fig. 2. Kinetics of the thermal decomposition of melted EIT *in vacuo*. Weight of samples 3 mg, volume of the reaction vessel 4 mL.

The kinetic curves of EIT thermolysis under isothermal conditions are presented in Fig. 1. We should note the complexity of the kinetics of this process. A decrease in temperature results in an increase in the fraction of products that are volatile under thermolysis conditions. Since the maximum extent of EIT decomposition, as estimated from the relative amount of the products (or the fraction of the condensed residue), is a function of temperature, the effective activation energy of the process was calculated from the dependence of the initial rate of mass loss on the temperature. The initial rates of EIT thermolysis in krypton at 90, 110, 120, 131, and 152 °C are 1.3±0.1; 4.8±0.3; 10.9±0.9; 21±2, and 170±12 % min^{-1}, respectively. It should be noted that the initial rates of thermolysis in air are almost the same (1.2±0.1, 4.8±0.2, 10.5±0.8, and 20±3 % min^{-1} at 90, 110, 120, and 130 °C, respectively).

The dependences of the logarithms of the initial rates of EIT thermolysis on the inverse temperature imply that the process does not obey the Arrhenius equation. In this case, the effective activation energy (E_{ef}) is temperature-dependent. Calculations show that E_{ef} changes from 40 to 175 kJ mol^{-1} in the temperature range from 90 to 150 °C. We shall demonstrate below that E_{ef} = 174 kJ mol^{-1} for the thermal decomposition of EIT in a closed reaction system. When thermolysis of EIT is carried out in an open system, in the low-temperature range EIT predominantly undergoes evaporation followed by condensation on the vessel walls (as identified by the IR spectrum). An increase in the temperature results in an increase in the contribution of thermal decomposition, which has a much higher thermal coefficient than evaporation. The estimate made demonstrates that the initial rate of thermal decomposition at 150 °C is 30—40 times higher than the initial rate of evaporation of the sample. A brown compound, which condenses on heating the sample at 150 °C, turned out to be crystalline iodine.

Thus, evaporation and thermal decomposition of the sample occur simultaneously in an open reaction system. For this reason, the subsequent kinetic study of the thermal decomposition of EIT was carried out in a closed vessel that had no temperature gradient over the volume. When thermolysis was carried out in Burdon manometers, we found the kinetic parameters of the process to depend on the ratio of the sample weight and the volume of the reaction vessel. Therefore, all subsequent experiments were conducted in reaction vessels of the same volume (4 mL) using samples of the same weight (3 mg), *i.e.*, at m/V = 0.75 mg mL^{-1}. Figure 2 shows kinetic curves of the thermal decomposition of an EIT melt *in vacuo* at 90—150 °C. The initial jumps on the kinetic curves (5—10 Torr) originate from the emergence of H_2O, I_2, and the original EIT into the gas phase (mass spectrometric data). We estimate that the fraction of EIT in the gaseous phase ranges from 3 to 7 %, depending on the temperature. At high degrees of conversion the pressure decreases, which indicates that some of the volatile thermolysis products are transferred to the condensed phase due to secondary reactions. The thermal decomposition of EIT obeys a first-order kinetic equation up to an extent of the reaction above 80 %. The rate constants of the thermal decomposition of melted EIT at temperatures of 90, 110, 120, 130, 140, and 150 °C are $(8.2\pm0.8)\cdot10^{-7}$; $(1.2\pm0.3)\cdot10^{-5}$; $(4.2\pm0.4)\cdot10^{-5}$; $(1.8\pm0.4)\cdot10^{-4}$; $(6.9\pm0.8)\cdot10^{-4}$, and $(2.2\pm0.2)\cdot10^{-3}$ s^{-1}, respectively.

The reaction studied obeys the Arrhenius equation

$$k = 10^{(18.8\pm2.2)}\exp[(-173900\pm8900)/RT]\ \mathrm{s}^{-1}.$$

The activation parameters of the thermal decomposition of EIT differ markedly from those of 1,5-disubstituted tetrazoles containing phenyl and alkyl substituents[6,7] (these compounds are characterized by activation energies of 188—206 kJ mol^{-1} and pre-exponential factors of 10^{15}—10^{16} s^{-1}). We studied the thermal decomposition of EIT in solution using as solvents polypropylene glycol-1000, glycerol, dimethyl phthalate (DMP), and *m*-dinitrobenzene (*m*-DNB), in which EIT is soluble. Only DMP and *m*-DNB turned out to be suitable (polypropylene glycol-1000 and glycerol are chemically incompatible with EIT and react rather quickly with dissolved iodine, which is one of the products of thermal decomposition of EIT, under thermolysis conditions). The thermal decomposition of EIT in DMP and *m*-DNB was carried out *in vacuo* at temperatures of 130—160 °C. As in a melt, the kinetic order of the process equals one. The rate constants of the thermal decomposition of EIT in DMP and *m*-DNB are listed in Table 2.

The thermal decomposition in both solvents obeys Arrhenius-type equations:

$$k_{(\mathrm{DMP})} = 10^{(17.2\pm1.3)}\exp[(-167300\pm8500)/RT]\ \mathrm{s}^{-1}$$

$$k_{(m\text{-DNB})} = 10^{(18.2\pm1.2)}\exp[(-174000\pm9000)/RT]\ \mathrm{s}^{-1}$$

An analysis of data from pyrolytic mass spectrometry (Fig. 3) makes it possible to hypothesize on the composition of the products that are volatile under pyrolysis conditions (160 °C, 10^{-5} Pa). These are (in order of increasing molecular weight): N_2 (28), $CH_2{=}CHNHC{\equiv}N$ (68), $CH_3CH_2NHC{\equiv}N$ (70), HI (128), CH_3I (142), CH_3CH_2I (156), and I_2 (254). The fraction of N_2 in gaseous products that do not undergo condensation at 25 °C is close to 82 %. The thermal decomposition of EIT in a melt is accompanied by formation of a condensed residue, which is soluble in polar compounds (*e.g.*, acetone). It should be noted that the IR spectra of the condensed products of thermal decomposition of EIT in air and *in vacuo* coincide, which implies that oxygen is not chemically bound during thermolysis of EIT in air. A comparison of the IR spectrum of the original EIT with that of the condensed residue indicates that the bands at 1460 and 1380 cm^{-1} disappear due to thermal decomposition of the tetrazole rings. The IR spectra of the condensed products of thermolysis of EIT contain bands at 3310 (NH), 1585—1605 (C=N), and 1135 and 1070 cm^{-1} (C—N), as well as a band at 2245 cm^{-1} attributable to stretching vibrations of —C≡N and/or =C=N— groups. Low-temperature thermolysis of EIT gives rise to a new band in the IR spectrum (770 cm^{-1}), which can be attributed to deformation vibrations of the substituted isotriazine ring.[10]

Table 2. Rate constants of thermal decomposition of EIT in solutions

Solvent	$k/10^4$ s^{-1}			
	130 °C	140 °C	150 °C	160 °C
DMP	1.08±0.09	2.98±0.25	8.85±0.60	26.8±1.2
m-DNB	0.61±0.04	1.80±0.15	6.50±0.45	19.5±1.0

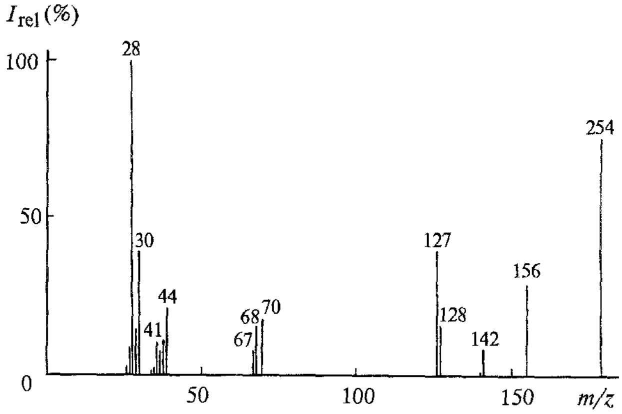
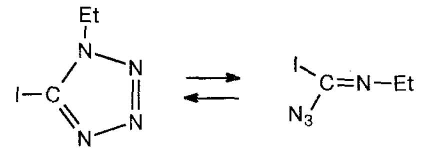
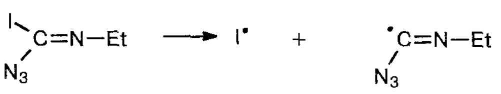


Fig. 3. Mass spectrum of the products of thermal decomposition of EIT *in vacuo* at 160 °C.

Data from pyrolytic mass spectrometry, IR spectroscopy, and kinetic measurements make it possible to assume that thermal decomposition of EIT starts with thermal tautomeric rearrangement into azidoazomethine, which is typical of 1,5-disubstituted tetrazoles.[6,7]



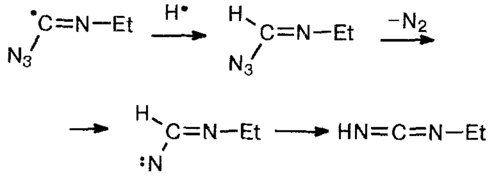
The mechanism of subsequent thermal transformations is specific and differs from the generally accepted nonradical mechanism of the thermal decomposition of tetrazoles. The thermal decomposition of $IC(N_3){=}NEt$ occurs by homolytic cleavage of the iodine—carbon bond:



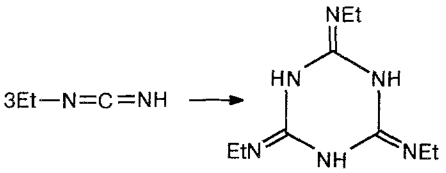
$$IC(N_3){=}N{-}Et \longrightarrow I^{\bullet} + {}^{\bullet}C(N_3){=}N{-}Et$$

The reactions involving I˙ yield I_2, EtI, MeI, and HI. One cannot rule out the possibility that alkyl iodides are also formed by direct abstraction of EtI and MeI from an $IC(N_3){=}NEt$ molecule. This pathway of decomposition is supported by pyrolytic mass spectrometry, which mainly detects primary thermolysis products.

The sequence of the thermal transformations of the $^{\cdot}\mathrm{C(N_3){=}NEt}$ radical can be represented as follows:



Carbodiimide can undergo isomerization to give ethylcyanamide, $\mathrm{EtNHC{\equiv}N}$, or cyclotrimerization into a isotriazine derivative:[11]



The formation of a cyclotrimerization product is indicated by IR spectroscopic data (see above).

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