

THERMAL DECOMPOSITION OF TETRAZOLE. PART III. ANALYSIS OF DECOMPOSITION PRODUCTS

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ABSTRACT

By means of methods of IR and ^1H NMR spectroscopy, mass spectrometry, chromatography, elemental and chemical analyses it could be stated that tetrazole thermolysis, both in a melt and in the gaseous state, proceeds mainly through elimination of a nitrogen molecule, but in the melt the nitrogen is eliminated predominantly from the azide structure and in the gaseous state it eliminates from the cyclic 2*H*-form. When carrying out the process in a melt, ca. 5% of the tetrazole decomposes with hydrogen azide evolution. The intermediates (nitrene or *C,N*-nitrilimine respectively) are unstable and, depending on the experimental conditions, they are capable of either decomposing, with formation of HCN, N_2 and H_2 , or participation in reactions leading to formation of cyanamide polymers.

INTRODUCTION

In the previous papers of the series [1,2], the kinetics of thermal decomposition of tetrazole in conditions of programmed heating were studied and the kinetic scheme of this complex process proceeding in a melt and in the gaseous phase by different mechanisms was validated. The present, third, part of the work is devoted to the study of tetrazole thermolysis products with the aims of obtaining experimental verification of the previously advanced assumptions and acquiring additional data on the tetrazole thermolysis mechanism. The decomposition conditions were selected in such a way that the process proceeded predominantly in only one of the above phases.

EXPERIMENTAL

With the aim of localizing the decomposition process predominantly in the melt, thermolysis was carried out in a medium of purified Vaseline oil, which is stable at the experimental temperatures and does not dissolve the

tetrazole. The gaseous decomposition products were passed through an alkali or Fe^{3+} salt aqueous solution and analysed by the methods of mass spectrometry (Varian MAT 311) and chromatography. The alkali solution was qualitatively analysed for its content of cyanide ions {by the reaction of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ formation}, and the Fe^{3+} salt solution was analysed for its content of azide ions (by the photolorimetric method on a Specol-21-M instrument using a 0.2% aqueous solution of FeCl_3 as comparison solution). The condensed product was identified by the methods of elemental analysis (Hewlett-Packard 1080 analyser), IR (Specord-75-IR, pellets with KBr) and ^1H NMR spectroscopy (JNM PS-100; deuteriodimethyl sulphoxide solution with hexamethyldisiloxane as internal reference).

The gaseous tetrazole decomposition products were studied in both a self-generating and a flowing atmosphere. In the first case the tetrazole sample was sealed in a vacuum ampoule purged with argon. The sample mass was so selected that at the end of the experiment, the pressure of vapour and decomposition products at the experimental temperatures did not exceed atmospheric. The decomposition was carried out by complete immersion of the ampoule into a liquid heat carrier (Wood's alloy) heated to the experimental temperature. In the case of incomplete immersion the tetrazole was transferred to the cold part of the ampoule without decomposition. The thermolysis was carried out at temperatures derived from the DSC data [1]: 433 K (just after the tetrazole melts); 493 K (corresponds to beginning of the decomposition exo-effect) and 553 K (corresponds to the end of the decomposition exo-effect). In all cases the decomposition time amounted to 15 min. The decomposition products were analysed mass spectrometrically.

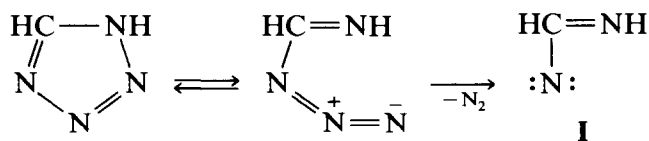
When investigating tetrazole thermolysis in a flowing atmosphere, the experiments were carried out in a quartz tube placed in a tube furnace in the argon carrier flow. The tetrazole sample mass was placed in the zone where the temperature reached 405 K. Under these conditions tetrazole does not decompose, but the equilibrium pressure of its vapour is fairly high [3]. The gas carrier flow carried the tetrazole vapours into the heating zone, where decomposition took place. The decomposition products were analysed by mass spectrometry, chromatography, IR and ^1H NMR spectroscopy as described above.

RESULTS AND DISCUSSION

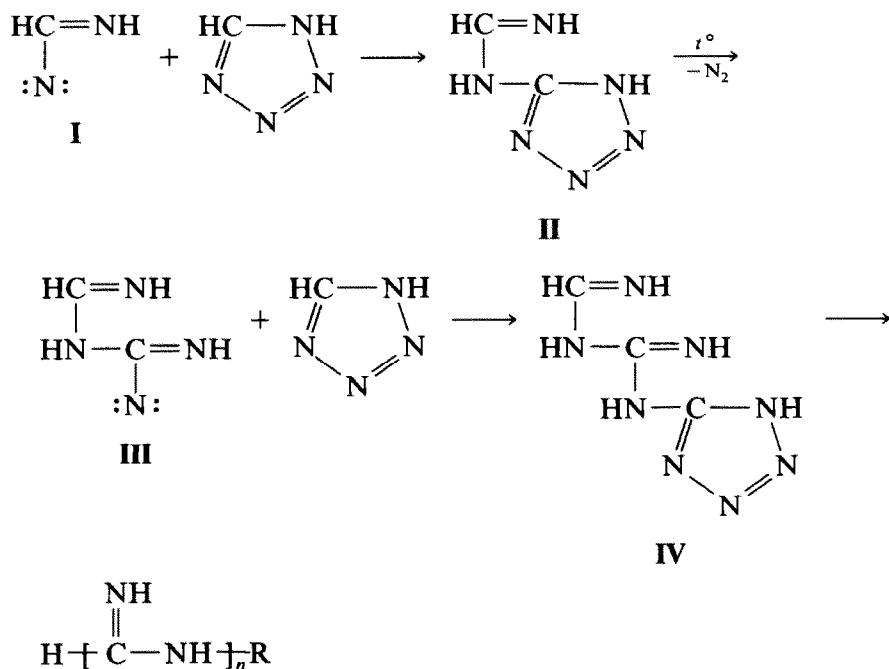
When the tetrazole thermolysis is carried out in a melt, the gaseous decomposition products are nitrogen and hydrogen azide, the content of HN_3 in the gaseous mixture being found to correspond to decomposition of $5 \pm 1\%$ of the tetrazole molecules under the assumption that one molecule of substrate produces one molecule of HN_3 . The resulting condensed product,

after careful washing from the Vaseline oil by hexane and extraction of the non-decomposed part of the tetrazole by methanol, is a yellow-brown highly dispersed thermostable powder (according to complex thermal analysis data, the product starts to decompose at 670 K under a static air atmosphere), and is partially soluble only in dimethyl sulphoxide from among the well-known solvents. It is interesting to note that the elemental composition of the soluble part of the condensed thermolysis product is identical to that for the insoluble residue, and corresponds to the empirical formula H_2CN_2 . The IR spectra of both portions are very similar, and contain two groups of structured bands in the regions of $1570\text{--}1600\text{ cm}^{-1}$ (deformation vibrations of N-H bonds) and $2900\text{--}3600\text{ cm}^{-1}$ (vibrations of associated N-H bonds). The NMR spectrum of the soluble portion contains a single broadened intense signal with its maximum at 3.83 ppm (protons of N-H group). In the mass spectrum of the soluble part of the product there are groups of signals with m/e values of 42 and its multiples, i.e. 84 and 126. Heating of the soluble portion of the product to 390 K leads to loss of solubility; despite this the elemental composition after heating remains unchanged.

The obtained data make it possible to assume that the condensed substance, which is formed during tetrazole decomposition in the melt, is a product of cyanamide polymerization. Together with the data of refs. 1 and 2 these results allow one to suppose that, during tetrazole thermolysis in the melt, nitrogen is evolved as a result of breakdown of the azido-form originating from the initial stage of the process



Since the condensed product formed has an elemental composition identical to that of the nitrene **I**, one may suppose that it is formed as a result of isomerization of the nitrene to cyanamide, which is polymerized under the thermolysis conditions. Evidently such a mechanism is partially realized in the thermolysis of 1-trimethylsilyltetrazole [4], as a result of which polycyanamide is formed, among other products. Probably, also, other processes leading to formation of polycyanamide may proceed in the melt during tetrazole thermolysis. Attachment at a C-H bond and hydrogen atom elimination are known to be basic reactions of nitrenes [5]. One may suppose that under the conditions where the thermolysis process is localized in the tetrazole melt the two above reactions take place with the participation of **I** and tetrazole molecules. With implantation of nitrene **I** by the C-H bond of the tetrazole a 5-substituted derivative (**II**) is probably formed, which decomposes to form a nitrene of more complex structure (**III**). In its turn the latter interacts with tetrazole, and so on. Thus, a peculiar polycondensation

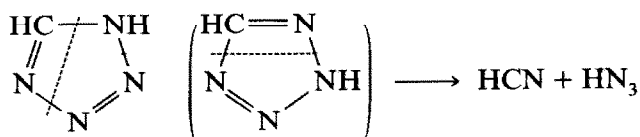


Scheme A. (R is probably H).

with a nitrogen molecule chip-off evidently takes place, which leads to polycyanamide formation by scheme A.

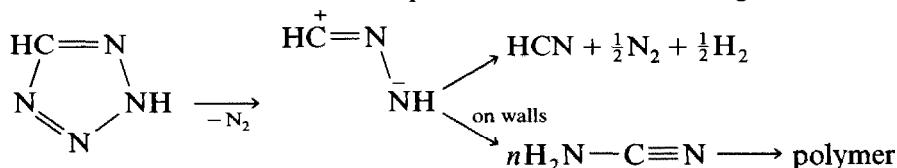
When the labile hydrogen atoms at the tetrazole N-H bond are broken off by nitrene I, probably formamidine, $\text{H}_2\text{N}-\text{CH}=\text{NH}$, is formed, which can further interact sequentially with nitrenes by way of attachment of the latter at the C-H bond with formation of a polycyanamide having terminal amino groups. One cannot rule out the possibility of breaking off a hydrogen atom from the tetrazole C-H bond or intermediate thermolysis products by nitrenes. In the final result such a process must lead to formation of ramified cross-linked polymers of cyanamide. The feasibility of such a process is indirectly proved by the insolubility, infusibility and high thermostability of a condensed product of tetrazole thermolysis.

The formation of a small quantity of hydrogen azide during tetrazole decomposition in a melt may be due to partial elimination of HN_3 from 5-substituted derivatives of II or IV type (Scheme A), or may be conditioned by the fact that 5% of the substrate molecules decompose by quite a different mechanism when the process proceeds by a route that is the reverse of synthesis

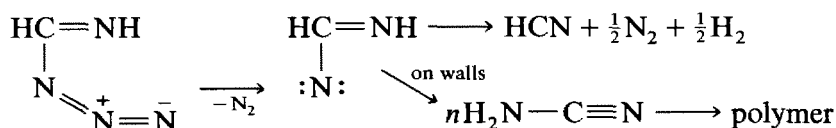


In so doing, no matter which *H*-form of the tetrazole eliminates a HN_3 molecule, hydrogen cyanide must also be eliminated, but HCN was not detected in the gaseous thermolysis products. The absence of HCN indicates that the first assumption for the mechanism is the more likely. On the other hand, one can rule out the possibility of neither polymerization of the eliminated hydrogen cyanide nor its interaction with the thermolysis products.

Which decomposition of the gaseous tetrazole in a flowing atmosphere, the process involves the formation of nitrogen, HCN and H_2 and, at the same time, a small quantity of a charred polymeric product is formed on the vessel walls. Taking into account the fact that in the gaseous phase the tetrazole exists predominantly in the form of a more volatile cyclic *2H*-form [7,8], and noting the absence of HN_3 from the products, one can assume that under the above conditions the process takes the following course



One should note that, during heating of the tetrazole in an IR gas cell [6], some bands are identified in the spectrum which are characteristic for the absorption of cyano- and azido-groups. On the basis of this fact, a conclusion was drawn on the breakdown of tetrazole in the gaseous phase to HN_3 , HCN and H_2 . In our opinion, under the described conditions [6], tetrazole can break down both in the gaseous phase and in a melt, and this composition of gaseous products probably corresponds to the total process. On the other hand the existence of an absorption band which is characteristic of an azide group [6] can be explained by the presence of the azido-form of tetrazole in the gaseous phase at high temperatures. Thus one cannot rule out the possibility of the gas-phase thermolysis proceeding with participation of the tetrazole azido-form



When tetrazole decomposes in a self-generating atmosphere, nitrogen, hydrogen cyanide and hydrogen are also basic gaseous products. Figure 1 shows the mass spectra of the tetrazole decomposition products in a self-generating atmosphere at different temperatures. The conditions of spectral recording are such that, not only gaseous products, but also vapours of readily volatile condensed compounds, were detected. At 433 K the degree of decomposition of tetrazole is relatively small, and the spectrum is determined basically by the tetrazole vapour fragmentation products (peaks

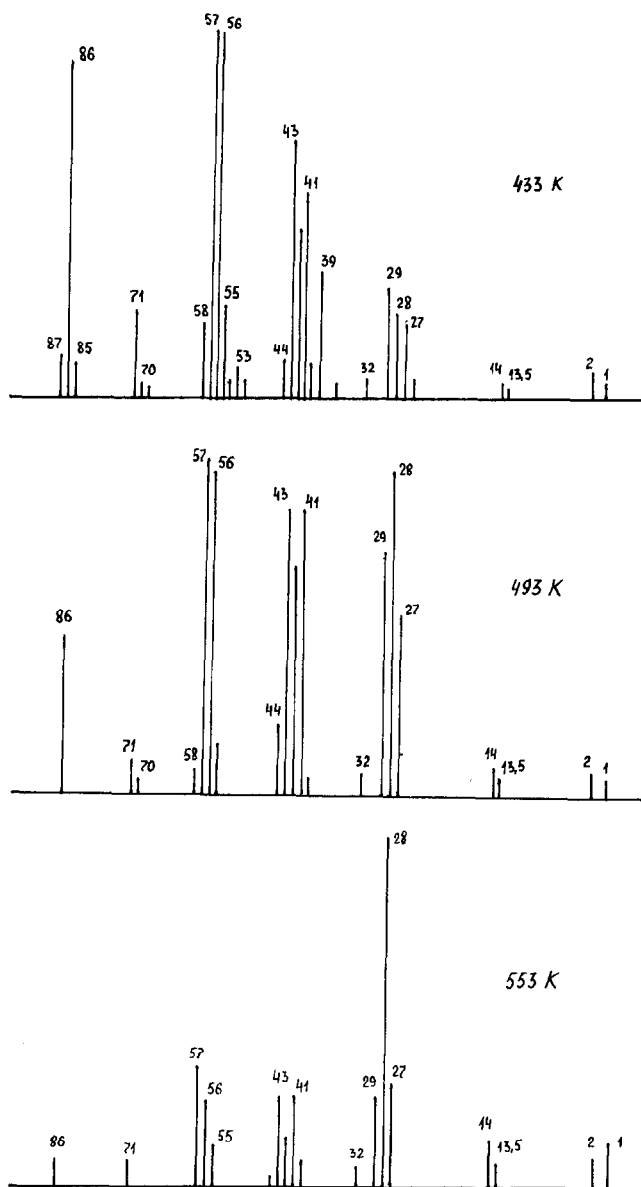


Fig. 1. Mass spectra of tetrazole thermal decomposition products.

with $m/e = 57, 56, 43$ and 42). With temperature rise the intensity of these peaks is reduced, and that of the signals with $m/e = 28, 14$ (nitrogen), 27 and 13.5 (hydrogen cyanide, two-fold ionized molecule) and 2 and 1 (hydrogen) is increased. The existence of a peak with $m/e = 86$, exceeding the mass of the parent, in the mass spectrum is interesting. One can assume that this peak relates to the product which is formed when two hydrogen atoms are

broken off the substrate by nitrene III (Scheme A), with the formation of a corresponding amine with a molecular mass of 86. These data reveal the complex nature of the tetrazole thermolysis, and indirectly confirm the possibility of polycyanamide formation by the mechanism given in Scheme A.

The obtained data show, that both in a melt and in the gaseous phase, tetrazole thermolysis proceeds mainly through elimination of a nitrogen molecule, but in the melt nitrogen is predominantly cleaved from the azide structure, and in the gaseous phase it is removed from the cyclic one. When conducting the process in a melt under the described conditions, ca. 5% of the tetrazole decomposes with elimination of HN_3 . The intermediates formed after elimination of a nitrogen molecule (nitrene or *C,N*-nitrilimine respectively) are unstable and, depending on the experimental conditions, are capable of either decomposing with the formation of gaseous HCN , N_2 and H_2 , or participation in reactions leading to the formation of cyanamide polymers. Nitrogen is the basic gaseous product of tetrazole thermolysis in a melt. When conducting the process in the gaseous phase, where the conditions for reactions of polymer formation to proceed are substantially harsher, the basic portion of an intermediate decomposes with the formation of HCN , N_2 and H_2 .

As a result of these investigations, we have obtained experimental data which confirm our previous assumptions on the mechanism of the tetrazole thermolysis process [1,2]. The composition of the tetrazole thermal decomposition products depends substantially on the experimental conditions, and can be adjusted by changing the proportion of substrate subject to thermolysis either in the melt or in the gaseous phase.

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