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The thermal decomposition of tetrazoles

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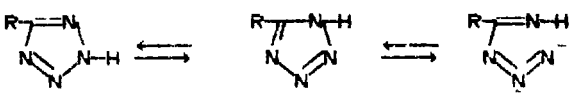
Abstract

A brief review of the literature on the thermal decomposition of chemical compounds containing a tetrazole heterocycle is given. It is shown that there are two radically different pathways of the tetrazole cycle fragmentation connected with the formation of a molecule of nitrogen or azides. The elimination of nitrogen from 2,5-disubstituted tetrazoles results in a nitrilimine The elimination of nitrogen from 1,5-disubstituted tetrazoles leads to the formation of a nitrene The stabilization of active intermediate products depends on the chemical properties of the substituents and the conditions under which the process is carried out, and leads to a wide spectrum of final products for the thermal decomposition of tetrazoles Kinetic studies of the thermolysis of tetrazoles show that the mechanism of heterocycle fragmentation can vary with varying temperature. The elimination of nitrogen from tetrazoles is preceded by a high-polarity transition state.

INTRODUCTION

Tetrazole and its derivatives were first obtained more than a century ago [1] when the study of the thermal decomposition of tetrazoles began [2], owing to the suprisingly high thermostability of these compounds that have four nitrogen atoms in the heterocycle. Further systematic studies of tetrazole thermolysis, which began in the 1950s, included both purely scientific and applied problems. The similarities in the thermolysis reactions and mass-spectrometric fragmentation of tetrazoles were reviewed by Shurukhin et al. [3].

For tetrazole and its 5-substituted derivatives, tautomeric and ring–chain isomerisms are known [4]



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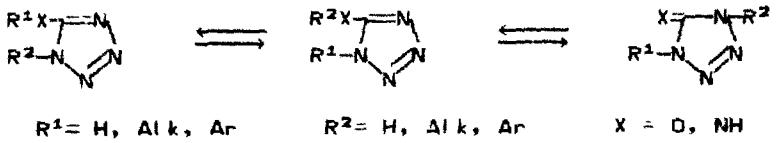
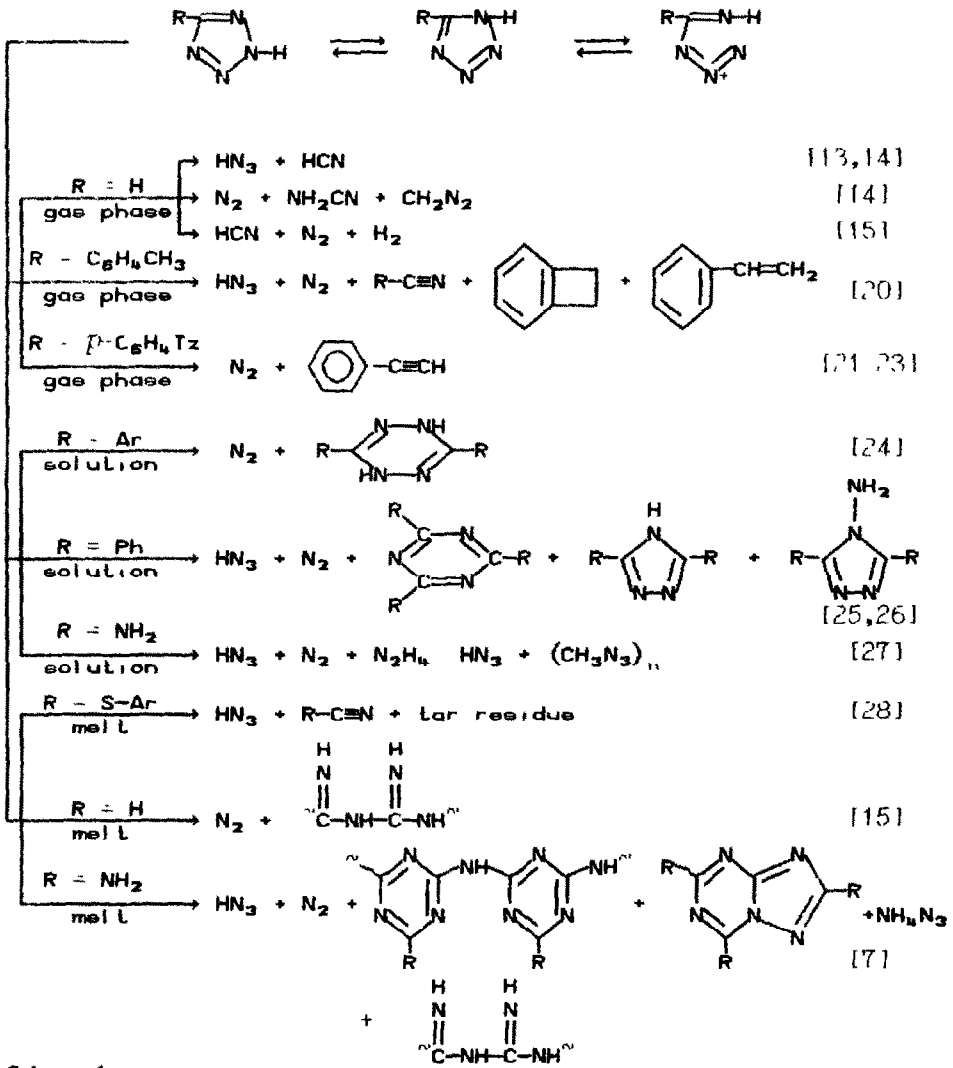
5-aminotetrazoles [5–7] as well as 5-alkoxytetrazoles [8,9] readily undergo sigmatropic rearrangement, and not only protons but also alkyl substituents can change their position [8–12].



The equilibrium concentration in a mixture of isomers changes, as a rule, on passing from a crystalline state into a melt or gas phase, and depends on



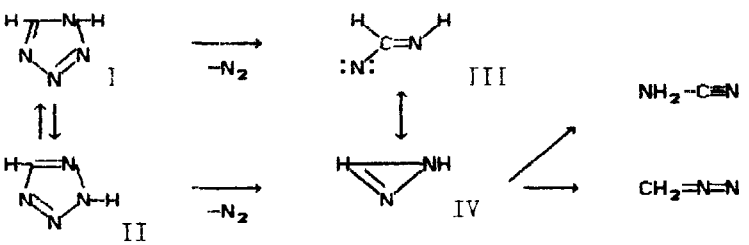
Scheme 1

the temperature and polarity of the solvent in solutions. Sometimes the above equilibrium transformations make it impossible to propose an unambiguous scheme for the thermolysis of the tetrazoles, but they do permit an investigation of the influence of structural factors on the stability of the tetrazole cycle.

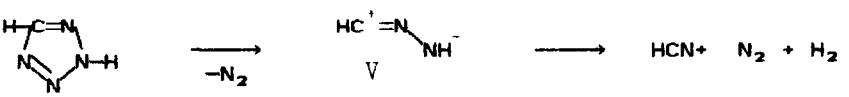
The authors of the present review are not attempting a detailed analysis of the literature concerned with the thermal decomposition of tetrazoles. We have analysed some literature data as well as our own papers, which can clarify the most general pathways of the thermal decomposition of tetrazole-containing compounds with substituents in various positions of the heterocycle. Primary consideration was given to the influence of the medium (temperature, aggregate state) and of the chemical structure of the compounds on the mechanism of tetrazole thermolysis. The data of the kinetic studies of thermal decomposition of tetrazole-containing compounds have also been surveyed.

THERMAL DECOMPOSITION OF TETRAZOLE AND ITS 5-SUBSTITUTED DERIVATIVES

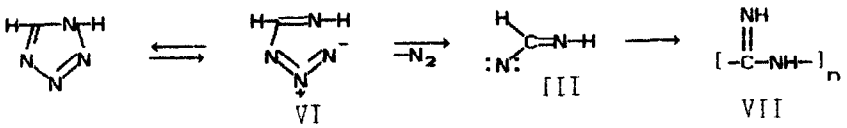
The thermal decomposition of tetrazole has been studied in the gas phase [13–15] and in a melt [15,16]. With slow heating the tetrazole vapour slowly decomposes from $T = 225°C$, into hydrogen azide and hydrogen cyanide [13] (Scheme 1). At a higher temperature, $T = 280°C$, an alternative thermolysis pathway [15] takes place, with elimination of the nitrogen molecule from the tetrazole cycle. Under flash-thermolysis conditions (800°C), elimination of nitrogen molecules predominates [14]. Because tetrazole mainly exists in the 2-H form (**II**) in vapours [17,18], then, as the quantum-mechanical calculation has shown [14], the decomposition can involve a metastable intermediate of isodiaziridine (**IV**). With decomposition of the 1-H form, formation of nitrene (**III**) precedes that of isodiaziridine (**IV**)



In ref. 15, it is assumed that the intermediate product of tetrazole decomposition is nitrilimine (**V**)



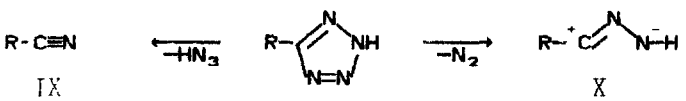
In a melt, tetrazole is less thermally stable than in a vapour and begins to decompose at 170°C [15]. It is assumed [15,19] that the 1-H form of tetrazole is in equilibrium with its azide form (**VI**) from which a nitrogen molecule splits off



VI III VII

In this case, in a condensed phase, the polycyanamide (**VII**) formed as the result of nitrene implantation in the C–H bond of tetrazole [15] is accumulated.

5-Substituted tetrazole derivatives (**VIII**) decompose by two alternative mechanisms with formation of nitrogen or hydrogen azide



IX VIII X

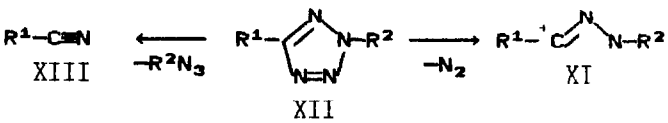
Depending on the character of the substituent R and the conditions of thermolysis, either one or both of the above-mentioned pathways are followed. The variety of products accumulated in the residue (Scheme 1) is determined by nitrile (**IX**) cyclotrimerization or by nitrilimine (**X**) stabilization.

If thermolysis of **VIII** is carried out in a melt, then the nitrile formed as a result of HN_3 loss is capable of cyclotrimerization. In the mesithylene solution (164°C), the benzonitrile formed by the decomposition of 5-phenyltetrazole trimerizes [25,26]. The decomposition of 5-mercaptotetrazoles in a melt [8] is accompanied exclusively by the formation of HN_3; in this case, thiocyanates and a slightly soluble tar residue, perhaps the product of polymerization of the latter, are formed.

If a nitrogen atom is eliminated from the heterocycle of 5-substituted tetrazoles, the nitrilimine (**X**) is observed independently of whether the thermolysis proceeds in the gas phase or in solution. However, their further transformation depends on the experimental conditions. During the pyrolysis of 5-substituted tetrazoles in the gas phase [21–23], the nitrilimine decomposes, as a rule, with the formation of very active particles, in particular carbenes, whose stabilization leads to many reaction products [20]. In a solution, the nitrilimine is stabilized by cyclization due to interaction of two molecules [24], or it reacts with nitriles with formation of 1,2,4-triazoles [25,26].

THERMAL DECOMPOSITION OF 2,5-SUBSTITUTED DERIVATIVES OF TETRAZOLE

As with the 5-substituted tetrazole derivatives, there are two alternative pathways of decomposition of 2,5-substituted tetrazoles (**XII**)

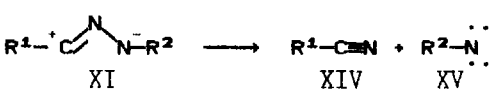


The splitting-off of azide is quite rare in the thermolysis of thermally stable 2,5-disubstituted tetrazoles. For instance, the formation of methylazide and benzonitrile which undergo trimerization are observed during the thermal decomposition of 5-phenyl-2-methyltetrazole at 220°C in a melt (Scheme 2) [26].

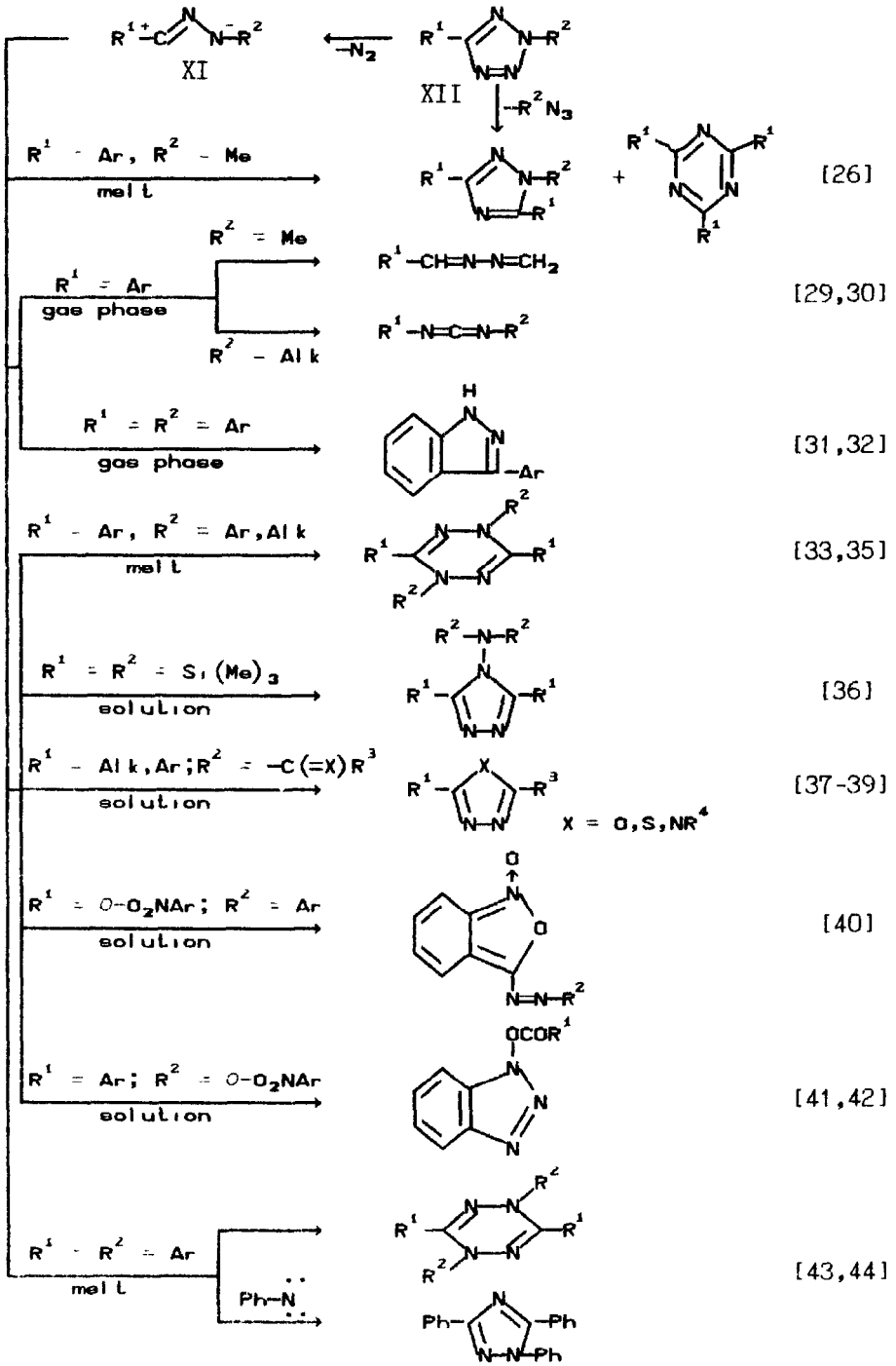
Generally, the 2,5-disubstituted tetrazoles decompose quantitatively with elimination of nitrogen and formation of the intermediate nitrilimines (**XI**). Further transformations of nitrilimines (**XI**) depend on their reactivity, as well as on the ability of the substituents R^1 and R^2 to enter into an intramolecular reaction with the nitrilimines. Under conditions of gas-phase thermolysis (400–500°C), 2,5-diaryltetrazoles transform into the corresponding indazoles [31,32]. If the cyclization to indazole is impossible, then the rearrangement to carbodiimide is observed or 1,4-migration of hydrogen occurs and azine, which undergoes further pyrolysis, is formed [29,30].

In solutions under milder conditions, in the absence of substituents with a multiple bond, nitrilimines are cyclized into derivatives of 1,4-dihydrotetrazine [33–35] which, in turn, can isomerize into 1,2,4-triazoles [36]. But if the substituent R^2 in the α position has a double bond, then intramolecular 1,5-dipolar cyclization with the formation of 1-oxa-3,4-diazole [37], 1-thia-3,4-diazole [38] or 1,2,4-triazole [39] is observed. A nitrogroup in the ortho position in both the substituent R^1 [40] and R^2 [41,42] also provides additional possibilities for intramolecular stabilization of the intermediate nitrilimine (**XI**) by closing to form five-member heterocycles: 1-aryloxibenztriazole [40] or 3-arylazoantropyloxide [41,42].

In thermolysis of 2,5-disubstituted tetrazoles in a melt, the reactions of intermediate nitrilimine (**XI**) are analogous to the reactions in a solution, but in this case the elimination of nitrene (**XV**) can be observed



Nitrile (**XIV**) interacts with nitrilimine (**XI**) and 2,3,5-substituted 1,2,4-triazoles are detected in the reaction products [43,44]. The active nitrene


XI
XII
$-N_2$
$-R^2N_3$
R^1 - Ar, R^2 - Me
melt
[26]
R^2 = Me
R^1 = Ar
gas phase
R^2 - Alk
[29,30]
R^1 = R^2 = Ar
gas phase
[31,32]
R^1 - Ar, R^2 = Ar,Alk
melt
[33,35]
R^1 = R^2 = $Si(Me)_3$
solution
[36]
R^1 - Alk,Ar; R^2 = $-C(=X)R^3$
solution
[37-39]
X = O,S,NR^4
R^1 = O-O_2NAr; R^2 = Ar
solution
[40]
R^1 = Ar; R^2 = O-O_2NAr
solution
[41,42]
R^1 - R^2 = Ar
melt
Ph-N
[43,44]

Scheme 2

(**XV**) easily implants in C–H bonds and is capable of yielding a wide spectrum of products in which amines predominate.

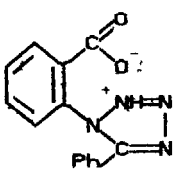
THERMAL DECOMPOSITION OF 1-SUBSTITUTED, 1,5-DISUBSTITUTED AND FUSED TETRAZOLES

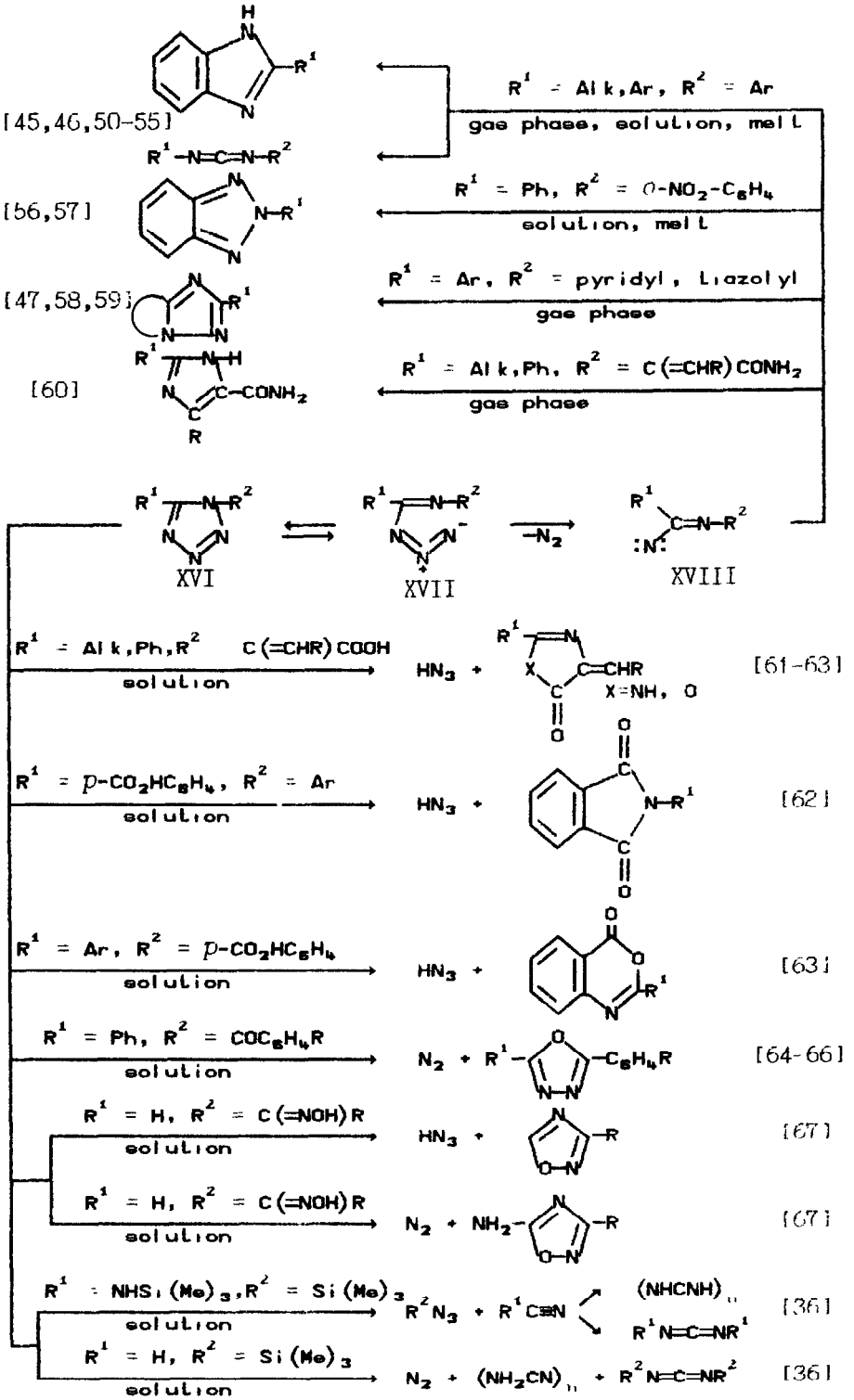
As a rule, 1,5-disubstituted tetrazoles decompose with nitrogen release. It is assumed [45,46] that elimination of a nitrogen molecule is preceded by isomerization of 1,5-disubstituted tetrazoles (**XVI**) to azide (**XVII**) (Scheme 3), although there is no direct evidence for the existence of the azide structure. The authors of refs. 47–49 showed that the intermediate product of thermal transformations of 1,5-disubstituted tetrazole is mainly singlet nitrene (**XVIII**) which, most probably, is formed from azide (**XVII**) and acts primarily as an electrophilic reagent rather than a biradical, which might be expected of a triplet particle. The reactions leading to the nitrene (**XVIII**) stabilization mainly determine the final composition of the thermolysis products.

If the substituent R^2 (Scheme 3) has no potential reaction centres for interaction with nitrene, then the main product of thermolysis in a gas phase [50], solution [45,51,52] and melt [46,53] is disubstituted carbodiimide which results from 1,2 migration of the substituent R^1.

The nitrene may join in the ortho position of the aryl substituent R^2 [45,46,50–55] and form benzimidazoles. This is a competing reaction of the reaction discussed above. If there is a nitro group in the ortho position, then on thermolysis of 1-(2-nitrophenyl)-5-phenyltetrazole 2-phenylbenzotriazole forms with a large yield [56,57]. The nitrene is also cyclized by means of selective addition to the nitrogen atom which is in the ortho position of the thiazole [47] or pyridine [58,59] cycles. Nitrene (**XVIII**) readily joins to a double bond. For instance, amides of the α-(1-tetrazolyl)acrylic acid derivatives [60] decompose in the gas phase at a low pressure in the temperature range 180–230°C, yielding 2,4-disubstituted imidazole-5-carboxamide.

It is known [61], however, that in solution amides of the α-(1-tetrazolyl)acrylic acid derivatives decompose mainly with elimination of HN_3 and formation of amidazolones (see Scheme 3). The explanation of this effect is, perhaps, analogous to that proposed for 1-(*o*-carboxy)phenyl-5-phenyltetrazole [62] and 5-(*o*-carboxy)phenyl-1-phenyltetrazole [63] that form internal salts of the tetrazolyl ion




[45,46,50–55]
[56,57]
[47,58,59]
[60]
R¹ = Alk,Ar, R² = Ar
gas phase, solution, melt
R¹ = Ph, R² = o-NO₂-C₆H₄
solution, melt
R¹ = Ar, R² = pyridyl, triazolyl
gas phase
R¹ = Alk,Ph, R² = C(=CHR)CONH₂
gas phase
XVI
XVII
XVIII
–N₂
R¹ = Alk,Ph,R² C(=CHR)COOH
solution
HN₃ +
X=NH, O
[61–63]
R¹ = p-CO₂HC₆H₄, R² = Ar
solution
HN₃ +
[62]
R¹ = Ar, R² = p-CO₂HC₆H₄
solution
HN₃ +
[63]
R¹ = Ph, R² = COC₆H₄R
solution
N₂ +
[64–66]
R¹ = H, R² = C(=NOH)R
solution
HN₃ +
[67]
R¹ = H, R² = C(=NOH)R
solution
N₂ +
[67]
R¹ = NHSi(Me)₃, R² = Si(Me)₃
solution
R²N₃ + R¹C≡N
(NHCNH)n
R¹N=C=NR¹
[36]
R¹ = H, R² = Si(Me)₃
solution
N₂ + (NH₂CN)n + R²N=C=NR²
[36]

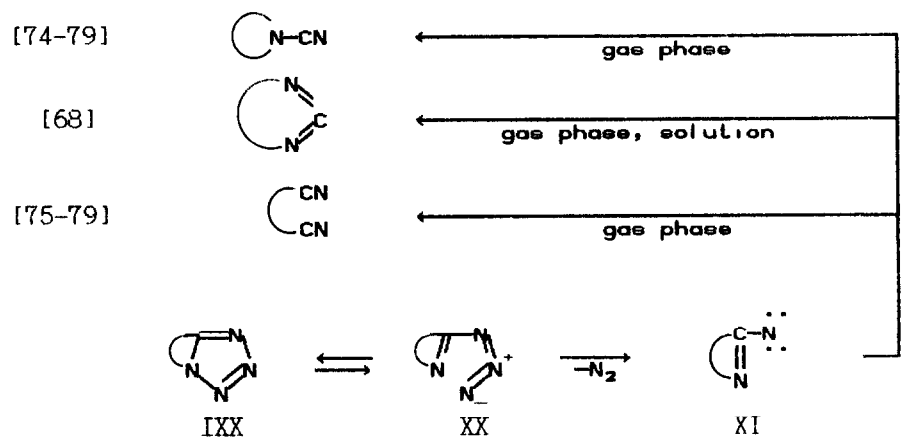
Scheme 3

which is capable of elimination of HN_3. On thermolysis of benzoyltetrazole solutions at 80–135°C, corresponding 1,3,4-oxydiazoles are formed. It has been established [66] that electron-donor substituents R (Scheme 3) decrease the thermal stability of 1-benzoyltetrazoles while electron-acceptor ones increase it.

In the literature, there is only one example of thermal decomposition of 1,5-disubstituted tetrazoles with formation of organic azide and monosubstituted cyanamide. For instance, 1-trimethylsilyl-5-trimethylsilylaminotetrazole [36] in hexamethylsilane solution decomposes at 160°C with formation of cyanamide, which then disproportionates into disubstituted carbodiimide and polymeric cyanamide and trimethylsilylazide.

The thermal decomposition of 1-substituted tetrazoles has been studied very little and, because of this, generalizations cannot be made. However, the studies reported [36,37] show that thermolysis pathways of 1-substituted tetrazoles are similar in many respects to the decomposition of 1,5-disubstituted tetrazoles. Therefore, on thermolysis of 1-hydroxomoyltetrazoles [67], two competing thermolysis pathways with N_2 and HN_3 evolution (Scheme 3) are observed. On elimination from the cycle of a nitrogen atom, 3-substituted 5-aminooxadiazole forms and elimination of the hydrogen azide molecule leads to the formation of 3-substituted oxadiazole. It is assumed [36] that on thermal decomposition of 1-trimethylsilyltetrazole, a nitrogen molecule is eliminated and monosubstituted carbodiimide which disproportionates into carbodiimide and polymeric cyanamide, is formed.

Condensed tetrazoles can be considered as a particular case of 1,5-disubstituted tetrazoles, but, unlike the latter, there are a sufficient number of experimental results for them, confirming the existence at room and higher temperatures of the cyclic tetrazole and azide tautomeric forms [68–70]. The equilibrium depends on the chemical properties of the nitrogen-con-



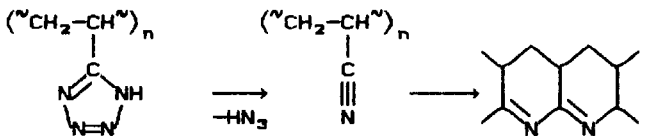
Scheme 4.

taining heterocycle, the electron-donor properties of the substituents in it and the temperature [71–73]. The general pathways of the thermolysis of condensed tetrazoles (Scheme 4) are analogous to those for 1,5-disubstituted tetrazoles. The primary process is the equilibrium shift at elevated temperature towards the azide form (**XX**). Then the obtained azide loses nitrogen and gives the nitrene (**XXI**) which, depending on the chemical surroundings can stabilize by different mechanisms analogous to 1,5-disubstituted tetrazoles. In addition to those described above, in condensed tetrazoles there are pathways of nitrene (**XXI**) stabilization due to the narrowing [74–79], widening [75–79] or splitting [68] of the heterocycle (Scheme 4). The reactions involving nitrene which affect the heterocycle proceed, as a rule, in a gas phase at high temperature, although they are also possible in a solution [75].

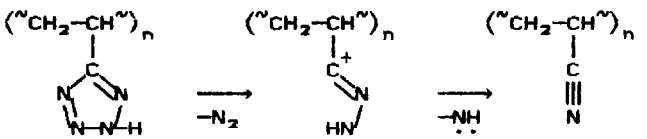
THERMAL DECOMPOSITION OF POLYVINYLTETRAZOLES

In the literature, there is no information on the thermal decomposition of poly-1-vinyltetrazoles. The thermolyses of 1- or 2-alkylsubstituted poly-5-vinyltetrazoles have mainly been studied. The mechanism of thermal splitting of the tetrazole cycle fixed on a carbon-chain matrix is similar, to a great extent, to the thermolysis of low molecular weight compounds, but there are also differences. The thermolysis of the investigated polyvinyltetrazoles occur in the solid phase without polymer melting.

By analogy with 5-substituted tetrazoles, poly-5-vinyltetrazole can decompose in two alternative pathways [80,81] with elimination of HN_3 or N_2, depending on the temperature. The nitrile groups formed following loss of HN_3 interact to yield polycyclic structures [80]



It is assumed [81] that the nitrile groups may also arise by the elimination of nitrene from intermediate nitrilimine

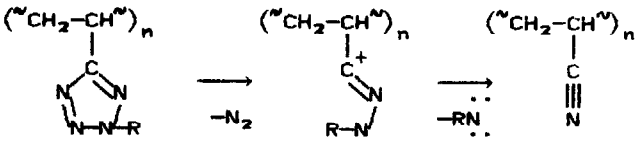


The crosslinking of the polymer chains observed during the thermolysis of poly-5-vinyltetrazole is attributed to either the joining of active nitrene to the neighbouring polymer chain [80] or the interaction of nitriles with

intermediate nitrilimines by the mechanism of 1,3-dipolar addition. Poly-1-methyl-5-vinyltetrazole decomposes by analogy with 1,5-disubstituted tetrazoles (Scheme 2), but the nitrene formed is stabilized owing to the interaction with the neighbouring carbon chains, which leads to their crosslinking [82].

Poly-2-alkyl-5-vinyltetrazoles are less thermostable than poly-1-alkyl-5-vinyltetrazoles. At an initial stage of their decomposition, N_2 splits off and nitrilimine is formed [81,83,84].

Further stabilization of nitrilimine by the mechanism of cyclo-addition is impeded by the low elasticity of the polymer chains in the solid state; therefore part of the nitrilimine eliminates from nitrene and passes into nitrile



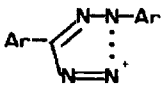
If a *tert*-butyl group is the alkyl substituent, then simultaneously with nitrogen elimination, detachment of the substituent from a part of the tetrazole cycle occurs, after which the polymer with non-substituted heterocycles undergoes thermolysis.

KINETICS OF THE THERMOLYSIS OF TETRAZOLES

Kinetic studies of the thermal decomposition of tetrazole have been carried out in the molten phase by various experimental methods [16,19]. The activation parameters (activation energy and pre-exponential factor) were shown [16] to depend considerably on the experimental conditions, because tetrazole evaporation is superimposed on the main process of thermal decomposition. The dependence of the activation energy on the degree of tetrazole decomposition in the melt under a self-generated atmosphere, has a complex form [19]: it decreases at the initial stages and then a plateau appears. Such a dependence is interpreted by means of the kinetic scheme $A \rightleftarrows B \rightarrow C + D$, where tetrazole reversibly transforms into the azide form B and then decomposes with the elimination of nitrogen C and corresponding nitrene D.

To study in detail the mechanism of the thermal decomposition of 5-aryltetrazoles [24] and 2,5-diaryltetrazoles [85–87], the influence of substituents [87] and solvents [24,85,86] on the kinetics of their thermolysis was investigated. The decomposition rate of 2,5-diaryltetrazoles is practically independent of the nature of the solvents, whereas increasing polarity of the solvent decreases the decomposition rate of 5-aryltetrazoles. However, there is a contradiction [24,85,86] in the interpretation of these data

because both conclusions are considered to favour the existence of a highly polar intermediate product — nitrilimine. The Gammet constants of the substituents correlate with the rate constants of 2-aryl-5-phenyltetrazoles ($\rho = 1.16$) and 2-phenyl-5-aryltetrazoles ($\rho = 0.23$) [87], and it is therefore assumed that nitrogen elimination (1,3-cis elimination) is either an unsimultaneous or a simultaneous process, with a polar transient state. An activated process in which the N_2–N_3 bond is weakened to a greater extent than the N_4–C_5 bond permits the interpretation of the data obtained in ref. 87.



The thermal decomposition rate of 1-aryl-5-chlorotetrazoles [88] also decreases on passing from non-polar to polar solvents. The electron-acceptor substituents in the aromatic ring increase the thermolysis rate, although this effect is less pronounced. It has been shown experimentally that thermolysis of both 2,5-disubstituted [26,89] and 1,5-disubstituted tetrazoles [88] follows a first-order reaction.

Compared with that of low molecular tetrazoles, the thermal decomposition of tetrazole-containing polymers proceeds, generally, at a lower rate and with a greater activation energy [81–83]. The introduction of an alkyl substituent into the tetrazole cycle of the polymer increases the activation energy of the thermolysis process. Such an increase in the thermal stability is explained by the "heat shielding effect" of alkyl groups providing fast relaxation of the energy of thermal excitation of heterocycles [81].

The dependence of the activation energy on the degree of poly-5-vinyltetrazole decomposition has a complex character [80] with an extremum: first, it increases up to the degree of decomposition 0.2, and then decreases. To explain such a dependence, the kinetic scheme $C_{gas} + D_s \leftarrow A_s \rightleftharpoons B_s \rightarrow E_s + F_{gas}$ is proposed. This scheme presupposes two pathways of the thermal decomposition: elimination from the tetrazole ring (A) of HN_3 (C) with nitrile (D) formation, an equilibrium transition to the azide form (B) and elimination of nitrogen (F) with the formation of corresponding nitrene (E). In the thermal decomposition of poly-2-*tert*-butyl-5-vinyltetrazole, in addition to the opening of the tetrazole cycle, the detachment of the substituent from the heterocycle was observed, which was also confirmed by kinetic studies [84].

CONCLUSION

This brief analysis of the literature data on the thermal decomposition of tetrazoles shows that the compounds of this class are uniquely suitable for investigating the role of structural factors in thermal transformations. The

thermal stability and the mechanism of tetrazole thermolysis is dependent, first of all, on their isomeric form, i.e. on the position of the substituent in the heterocycle. There are two radically different pathways for the splitting of the tetrazole cycle: nitrogen elimination or azide elimination. Depending on the isomeric form of the tetrazoles, electron density redistribution in the heterocycle occurs, and various bonds are broken. The chemical nature of the substituents affects significantly the thermal stability of the tetrazoles, the greatest effect being produced by the substituents bonded to nitrogen atoms. The influence of solvents manifests itself in either reducing or increasing the possibilities of stabilization of the intermediate products.

On elimination of the nitrogen molecule from the tetrazole cycle, highly reactive intermediate products (nitrilimine, nitrenes, carbenes) form. The wide variety of final products of thermolysis depends, generally, on the reactions of active intermediate particles: however, as kinetic studies show, the limiting stage of the thermolysis is the destruction of the tetrazole cycle. The peculiarities of the thermolysis of tetrazole derivatives can be used in syntheses, in particular for obtaining almost unavailable substituted carbodiimides [29,30,36] and dihydrotetrazines [24].

It should be noted that the majority of the investigations made are concerned, to a certain extent, with the thermal decomposition of 1,5- or 2,5-substituted aryltetrazoles, because the stabilization of their intermediate products is possible. A considerable number of papers is devoted to the study of their further transformations and to the identification of the final and intermediate products of thermolysis. At the same time, there are very few papers on the thermal decomposition of 1-substituted tetrazoles, and the thermolysis of 2-substituted tetrazoles has not been studied at all.

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