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TETRAZOLES: SYNTHESIS, STRUCTURES, PHYSICO-CHEMICAL PROPERTIES AND APPLICATION

INTRODUCTION

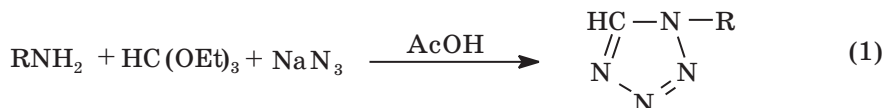
The paper represents a brief review of works published by the authors over a period of 1980-2003 years in the field of synthesis and investigations of properties of tetrazole derivatives. The main attention is given to problems of regioselective functionalization of the tetrazole ring and the development of simple and convenient methods for the synthesis of N- and C-substituted tetrazoles, to peculiarities of structure of crystalline tetrazoles including quaternary salts and complexes with transition metal salts as well as to the data on electronic, spatial structure and energetic characteristics of tetrazoles obtained using both quantum-chemical methods and IR-, ^1H , ^{13}C and ^{15}N NMR spectroscopy. The features of thermal decomposition and combustion of various tetrazoles and polyvinyltetrazoles determining the prospects of their use as effective components of different kind combustible and thermally decomposing systems, including those capable of liquid-flame combustion, which has been revealed for the first time, are considered.

1. SYNTHESIS OF TETRAZOLES

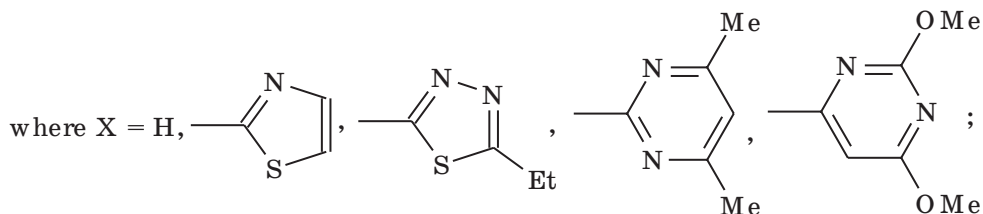
The development of novel procedures for the synthesis of tetrazoles as well as for the improvement of known methods of their preparation have been carried out in our laboratory mainly within the framework of two following approaches: the heterocyclization of readily available nitrogen-containing substrates and the functionalization of heterocycles and substituents of the simplest tetrazoles.

1.1. Synthesis of 1-mono- and 1,5-disubstituted tetrazoles based on reactions of heterocyclization

The interaction of a wide variety of primary amines of different natures with ethylorthoformate and sodium azide resulting in formation of 1-monosubstituted tetrazoles has been studied [1–9]:

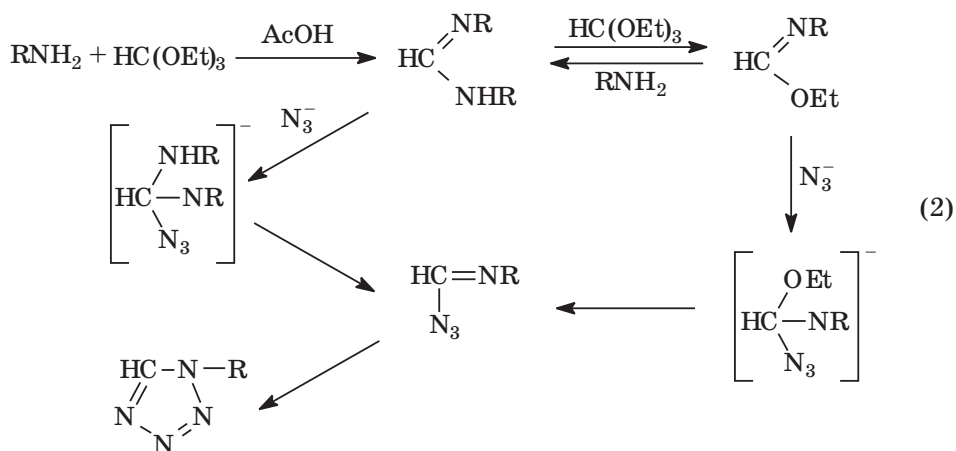


R = Me; Et; Bu; *t*-Bu; Allyl; CH₂CF₃; (CH₂)₂X, where X = Ph, OH, COOH, NMe₂, N₃; CH₂COOH; C(CH₂Cl)₃; CH(COOH)CH₂Ph; *cyclo*-Pr; *cyclo*-C₆H₁₁; CH₂Ph; Ph; *p*-XC₆H₄, where X = Me, MeO, MeCO, *p*-NO₂C₆H₄, Cl, Br, OH, COOH, NO₂; *m*-XC₆H₄, where X = MeO, MeCO, CH=CH(COOH), Cl, Br, OH, NO₂; *o*-XC₆H₄, where X = OH, COOH, NO₂; 2-OH-5-NO₂C₆H₃; 2-OH-4-NO₂C₆H₃; 2-Me-4-JC₆H₃; 3-Cl-4-FC₆H₃; 2,4,6-Me₃C₆H₂; 2-OH-3,5-(NO₂)₂C₆H₂; *p*-C₆H₄SO₂NHX,

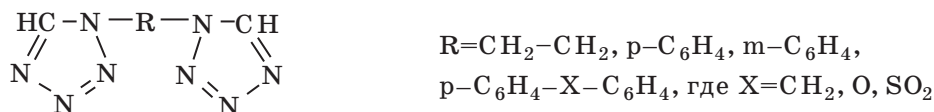


naphthyl; NH₂ (from Ph-CH=N-NH₂); 2-thiazolyl; 1-adamantyl (Ad); AdCHMe.

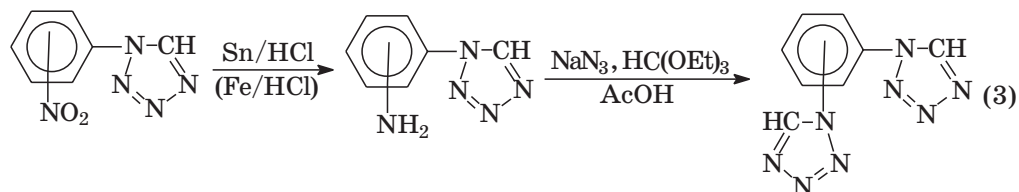
The brief patent data on synthesis of several tetrazole derivatives which have been known by the onset of our investigations (USA Patent 3767667, 1980) did not allow to form a notion about peculiarities and preparative potentialities of this reaction. The detailed study of influence of ratio of reagents, procedure of their introducing into the reaction mixture as well as of reaction time and the conditions on the yield of desired product along with the simultaneous precise control over the amount of eliminated hydrogen azide allowed us to determine the optimum and safe conditions of reaction [6, 7]. Based on the data of identification of intermediate products (amidines, iminoethers), two the most probable mechanisms of reaction depending on the nature of amine have been proposed:



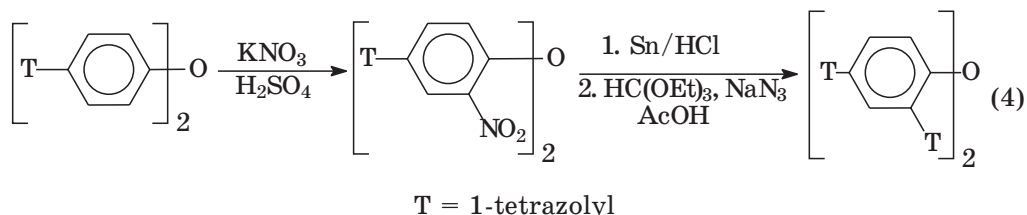
Bifunctional amines react easily involving both amino groups resulting in formation of the corresponding bistetrazolyl derivatives [5-7, 10]:



o-Ditetrazolylbenzene as well as tetrazole-containing o-, p- and m-aminobenzenes can be obtained starting with the corresponding nitrotetrazoles according to scheme 3:

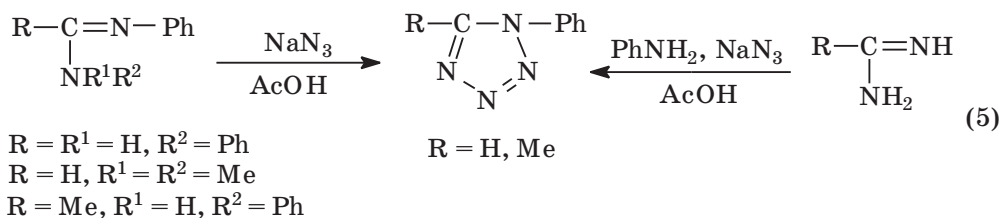


This method which includes the previous nitration of aryltetrazoles is also appropriate for the synthesis of polynuclear tetrazoles [11], for example:

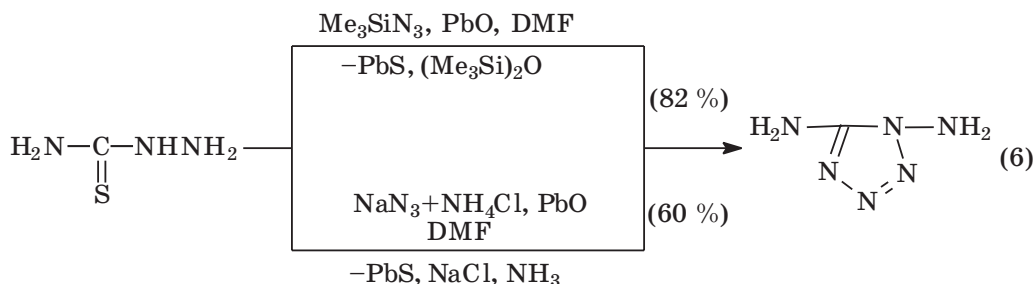


The data obtained in studies of reactions 1-4 allowed us to elaborate the simple and convenient procedures for the synthesis of a wide variety of 1-substituted tetrazoles, which are generally characterized by high yield (80%). It seems likely that the considered reaction provides a basis for the multi-purpose method, which is also convenient for the synthesis of unsubstituted tetrazole starting with ammonium chloride [12, 13]. However, it has some restrictions conditioned by the nature and the basicity of used amines. We have studied in this reaction more than 70 aliphatic, aromatic and heterocyclic amines including those containing various functional groups (halogens, N₃, NO₂, OH, COOH, SO₂NH and others). The corresponding tetrazoles have not been obtained in the cases of phenylhydrazine, melamine, guanidine, thiosemicarbazide, o-phenylenediamine, some arylamines with low basicity (2,4-dinitroaniline, 3-nitro-4-fluoroaniline, 2,6-dibromo-4-nitroaniline) and polynitrogen azoles (1-methyl-5-aminotetrazole, 5-aminotetrazole, 4-amino-1,2,4-triazole). The data on heterocyclization of the two last aminoazoles are probably incorrect [5] and not confirmed in the subsequent studies [9]. It is apparent that when using amines which are unexplored in the considered reaction, especially functionally substituted ones, the possibility of proceeding of competitive reactions which is characteristic of orthoethers has to be taken into account.

The fact of the formation of intermediate disubstituted amidines under the heterocyclization (scheme 2) allowed us to propose these compounds as the initial substances for the synthesis of 1-mono- and 1,5-disubstituted tetrazoles and to develop a new method of their synthesis which is of interest in the cases, when amidines are more readily available, than the corresponding amines and orthoethers [14]:

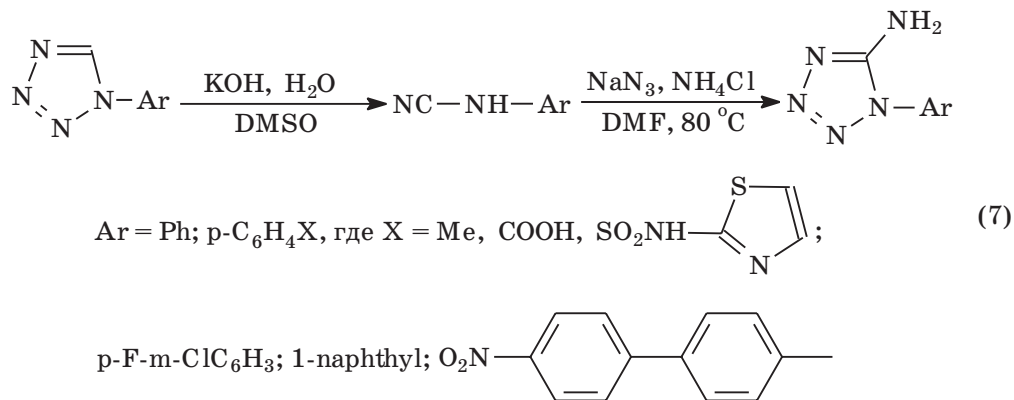


The study of reactions of thiosemicarbazide heterocyclization in the presence of PbO resulted in the developing of two procedures for the synthesis of 1,5-diaminotetrazole [7, 15, 16]:



The used trimethylsilylazide can be easily obtained by interaction of sodium azide with trimethylsilylchloride [17].

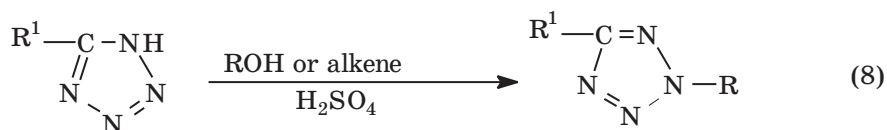
Finally, heterocyclization of arylcyanamides produced from 1-aryltetrazoles was found to be a convenient method for the synthesis of 1-aryl-5-aminotetrazoles [9, 18]:



1.2. Alkylation of tetrazoles

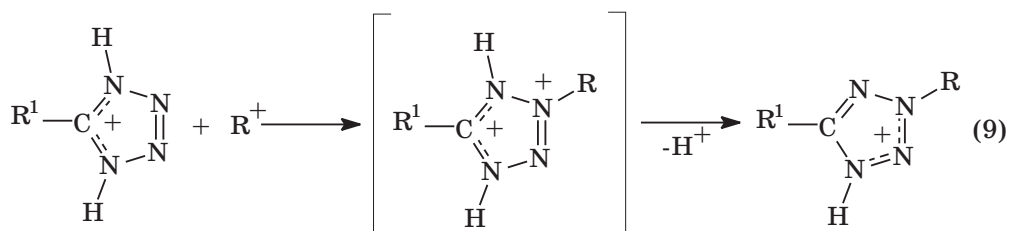
1.2.1. 2-Mono- and 2,5-disubstituted tetrazoles starting with N-unsubstituted tetrazoles and alcohols (olefines) in acidic media

The reactions of tetrazoles alkylation in strong acidic media have been studied for the first time. It has been shown that the interaction of tetrazoles with alcohols and olefines having the structures which are favourable for the stabilization of the formed carbocations including tert-butyl-, iso-propyl- and cyclohexyl alcohols, propylene, iso-butylene and cyclohexene proceeds readily without heating in sulphuric acid media. In all cases, independently on the nature and the size of the substituents at position «5» of the tetrazole cycle, the formation of solely 2-substituted tetrazoles with high yields (up to 100%) is observed [7, 19-21]:

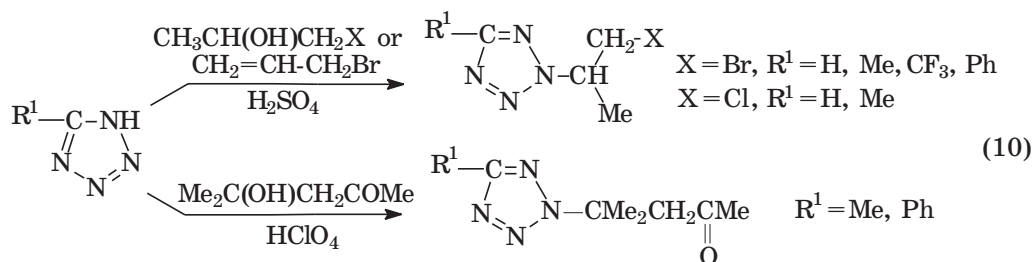


R = *i*-Pr, R¹ = H, (CH₂)₂NMe₂, Ph, *p*-MeC₆H₄, *p*-ClC₆H₄, *m*-BrC₆H₄, *m*-NO₂C₆H₄, *p*-NO₂C₆H₄; R = *t*-Bu, R¹ = H, Me, *t*-Bu, (CH₂)₂NMe₂, CF₃, Ph, NH₂; R = *cyclo*-C₆H₁₁, R¹ = H, Ph

The study of kinetics and mechanism of the alkylation process by the example of isopropyl alcohol and substituted 5-phenyltetrazoles with invoking of quantum-chemical calculations has demonstrated that the fully protonated symmetrical 1-H,4-H,5-R¹-tetrazolium cation act as a substrate of protonation, only one of the two equal atoms at the positions «2» and «3» of the ring characterized by the negative *p*-charges being accessible for the attack of electrophile [22, 23]:

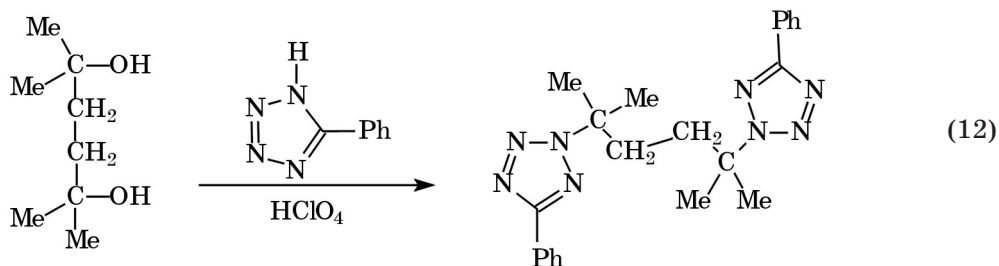
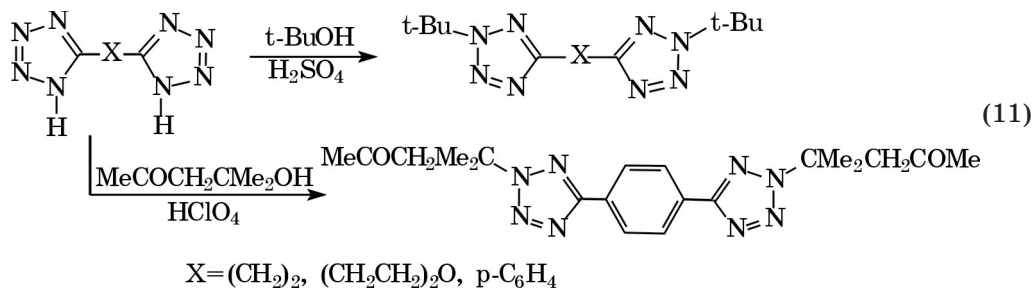


The main factor determining the possibility of reaction proceeding and its rate is the valid concentration of the carbocation, which depends on its stability, all other factors being equal. Therefore, the alkylation of tetrazoles with tert-butyl alcohol proceeds with higher rate than with isopropyl and cyclohexyl alcohols in media of the same acidity. When using alcohols which are unexplored in the considered reaction, it is necessary to take into account the conditions of generation of the corresponding carbocations. For example, in the case of halogen-containing alcohols, high yields of resulting products were obtained only under their long-term interaction with tetrazoles [24] (scheme 10). Diacetone alcohol which form easily the corresponding carbocation, reacts with tetrazoles as rapidly as tert-butyl alcohol [25]:

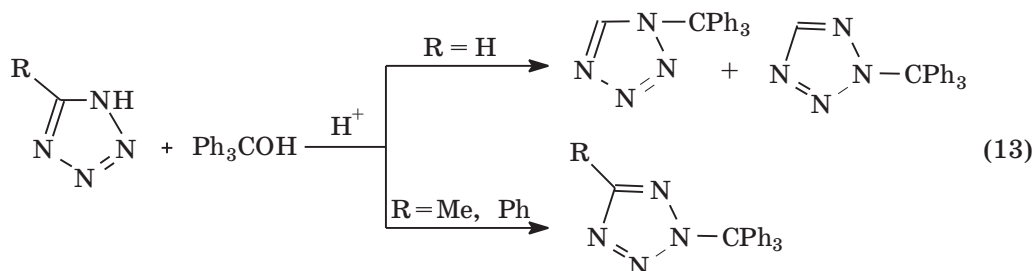


It is notable that the yield of 2-tert-butyl-5-R-tetrazoles in the 1-H-5-R-tetrazole-*t*-BuOH- H_2SO_4 reaction system decreases with time because of splitting out of heterocycle – substituents bond followed by transformation into the corresponding 1-isomer. The experiments performed using individual isomers have confirmed this phenomenon and have shown that the reversible process is also possible, when 1-isomer converts into 2-isomer [26]. Because of the larger stability in acidic media, 1-isomer predominates in the equilibrium mixture. The introduction of substituents into position «5» of the ring hinders ($\text{R}^1=\text{Me}$) or exclude ($\text{R}^1=\text{Ph}$) the possibility of isomerization of 2-tert-butyltetrazoles. Isomerization transformations may be responsible for the deterioration of selectivity of the process and the formation of 1-tert-butyltetrazoles along with the corresponding 2-isomers under the alkylation of tetrazole and 5-methyltetrazole by iso-butylalcohol in acidic medium [27].

In the case of synthesis of bi- and polynuclear tetrazoles, when the usual methods lead to formation of multicomponent mixtures of various isomers, separation of which is not always possible or is labour consuming and is accompanied by a significance losses of resulting products, the developed methods of regioselective alkylation of the tetrazole cycle are of special importance. The selectivity of the considered reactions is shown to retain when N-unsubstituted ditetrazole – alcohol and mononuclear tetrazole – tert-diol systems used [25, 28–30]:

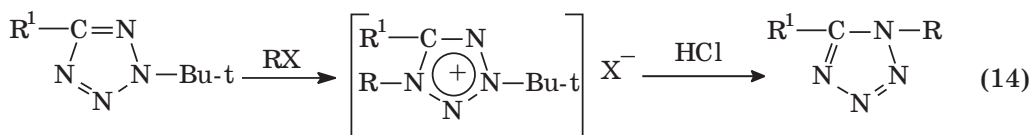


Thus, the alkylation of 5R-tetrazoles with alcohols and olefines in acidic media under definite conditions is a simple, convenient and exceptionally regioselective method for the synthesis of 2-mono- and 2,5-disubstituted tetrazoles with secondary and tertiary substituents. It should be noted, that alkylation process occurs also, when the catalytic quantities of sulphuric acid is used in the media of organic solvents under azeotropic removal of water [31]. In so doing, in the case of 5-methyltetrazole a mixture of 1- and 2-isomers is formed, whereas for 5-phenyl- and 5-trifluoromethyltetrazoles, the formation of solely 2-isomers is observed. Triphenylcarbinol reacts in similar cases according to the scheme [32]:

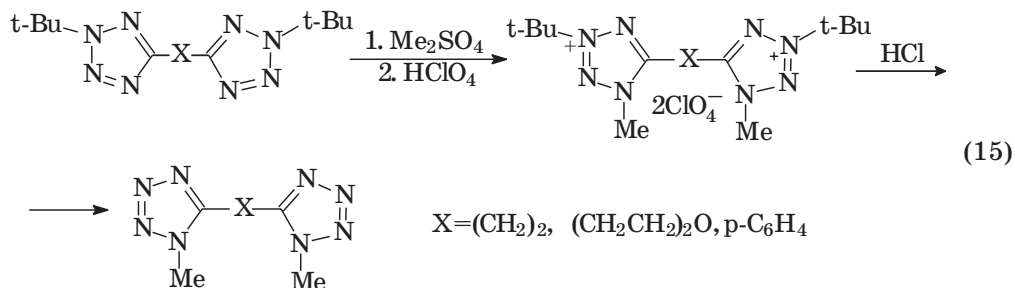


1.2.2. 1-Substituted tetrazoles starting with 2-tert-butyltetrazoles

A convenient selective method for the preparation of 1-alkyltetrazoles starting with 2-tert-butyltetrazoles which came readily available (see sect. 1.2.1) has been elaborated [33]:

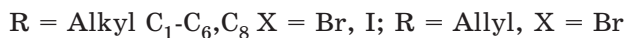
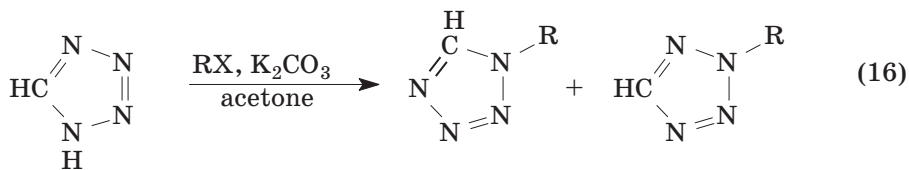


2-Tert-butyltetrazoles are subjected to exhaustive alkylation which proceeds exclusively on the position «4» of the cycle. Then the tert-butyl group can be removed from the ring in a relatively mild conditions. Even in the case of electron-accepting (CF_3), phenyl and vinyl substituents at the position «5» of the ring, the reaction provides the selectivity and high yields of resulting products (78–96 %). The applicability of the considered approach has been also demonstrated for bistetrazoles [28–30]:



1.2.3. 1- and 2-Alkyltetrazoles starting with tetrazole and 1- halogenoalkanes in the presence of bases

The described above procedures are not suitable for synthesis of 2-alkyltetrazoles with substituents of normal structure. In spite of voluminous literature on alkylation of tetrazoles, there were no methods providing a synthesis of a wide variety of N-alkyltetrazoles including those with higher n-alkyl substituents. The influence of the nature of solvents (alcohols, ketones, dimethyl formamide) and condensed agents (MOH, M_2CO_3 ; $\text{M}=\text{Na}, \text{K}$) as well as of reaction conditions on the yield of products has been studied by the example of tetrazole and allylbromide. The reaction was found to proceed easily giving a quantitative yield of a mixture of N-alkyltetrazoles [3, 34]:

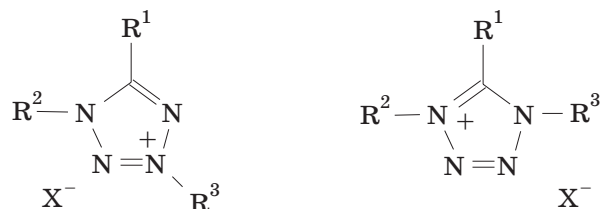


In the case of other n-alkyliodides and n-alkylbromides, the reaction also proceeds readily, however the ratio of formed isomers is substantially changed (from ~2:1 for CH_3I to ~1:2 in the case of $\text{C}_8\text{H}_{17}\text{I}$) [7]. Simultaneously, the yield of products is lowered.

1.2.4. Synthesis of 1,3(1,4)-disubstituted and 1,3,5(1,4,5)-trisubstituted tetrazolium salts

One can suppose that the regioselective character of monoalkylation of 5- R^1 -tetrazoles in acidic media (sect. 1.2.1) can be extended into the reactions of quaternization of N-substituted tetrazoles. This approach could provide the development of effective methods for the synthesis of tetrazolium salts and for preparation of a wide variety of novel substances at the sacrifice of using of new

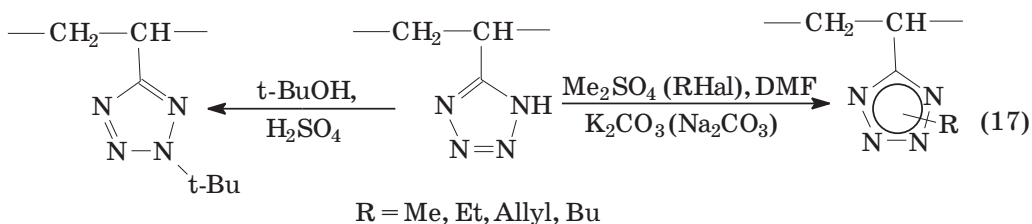
alkylating agents leading to the formation of salts with ramified substituents at the «pyridine-like» nitrogen atom of the cycle. For this purpose, a behavior of a number of alcohols has been studied in reactions with tetrazoles in different mineral acids including sulphuric, perchloric and tetrafluoroboric ones. The conditions for the selective synthesis of the following 1,3- and 1,4-di- as well as 1,3,5-tri-substituted tetrazolium salts have been determined:



The results of these investigations are presented in papers [8, 28, 35-40], generalized in thesis [41] and in review [42]. It is remarkable that synthesis of these salts can be carried out using not only N-substituted tetrazoles, but also tetrazole and its 5-substituted derivatives resulting in a considerable extension of preparative potentialities of the considered method and allowing the use of more readily available tetrazoles. This approach has been extended to include reactions in neutral media. 5-R-Tetrazoles were found to react readily under heating with dimethyl sulphate resulting in the formation of a mixture of 1,3,5- and 1,4,5-trisubstituted tetrazolium salts, the ratio of which determined by the steric factors changed significantly from 4:1 to 1:9 when going from R=CH₃ to R=t-Bu. The individual isomers can be isolated easily in the form of salts with perchloric and picric anions [43].

1.2.5. Synthesis of polyvinyl- and vinyltetrazoles by alkylation reactions

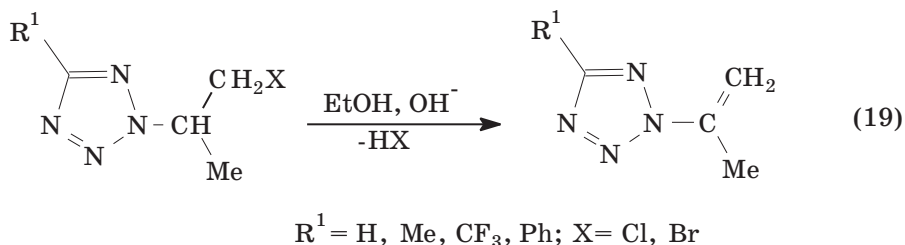
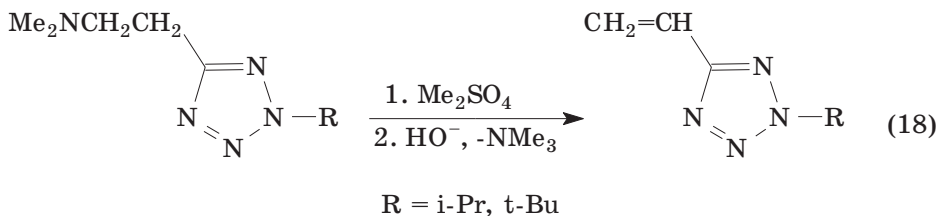
Polymers based on vinyltetrazoles characterized by unique combination of physico-chemical and operating properties are considered as prospective materials for many purposes. However, until recently, the initial monomers for synthesis of polyvinyltetrazoles have not been easily accessible. Taking this into account, we have studied in detail some polymeranalogous transformations leading to formation of polyvinyltetrazoles, namely, polyacrylonitrile (PAN) tetrazolation and alkylation of the formed poly-5-vinyltetrazole (PVT) [44, 45]:



A simple and convenient method of PVT synthesis using inexpensive and available PAN was developed. The method allows to obtain polymeric products with a wide range of PVT fragments content including PVT with structure and properties which are practically identical to that of 5-vinyltetrazole homopolymer. The use of the method permits to obtain PVT with a required molecular weight distribution by means of selection of the initial PAN with appropriate molecular weight characteristics [44].

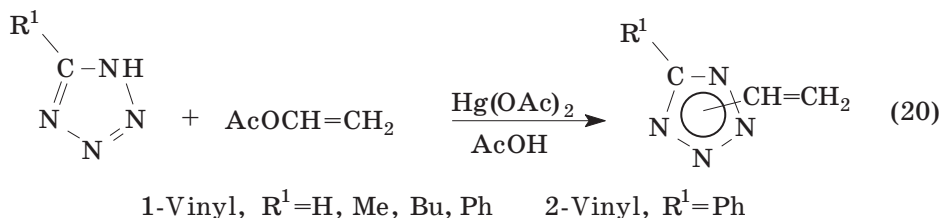
Alkylation of PVT in the presence of bases proceeds at two N-positions of the tetrazole ring and results in formation of copolymers of 1-alkyl-5-vinyl- and 2-alkyl-5-vinyltetrazoles [45]. The specific character of solutions of polymeric substrates caused by their high aggregating state leads to an increasing of a content of 1-isomer in the product with growing of a proton component of H₂O-DMF solvent. In general, the variation of the reaction conditions as well as the nature of the alkylating agent and counter-ion allows to obtain copolymers with a sufficiently wide range of the isomeric compositions variations and, correspondingly, with different physical and chemical properties. On the contrary, upon alkylation of PVT by tert-butyl alcohol, the reaction proceeds solely at position «2» of the heterocycle and leads to the formation of poly-2-tert-butyl-5-vinyltetrazole which is characterized by sufficiently high thermal stability and solubility in different organic solvents [46].

The developed method of selective alkylation (sect. 1.2.1) provides the possibility of synthesis of a variety of previously not available tetrazole-containing monomers containing not only primary, but also secondary and tertiary alkyl groups at the tetrazole cycle [47] as well as of α -substituted 2-vinyltetrazoles [24]:



The use of this method allow one to avoid the formation of a considerable amounts of by-product isomers which is characteristic of other methods of synthesis of N-vinyltetrazoles and, consequently, to increase essentially the yield of the resulting substances.

A direct N-vinylation of 5-R-tetrazoles based on the reaction of catalytic exchange with vinyl acetate is also of preparative interest [7, 48, 49]:



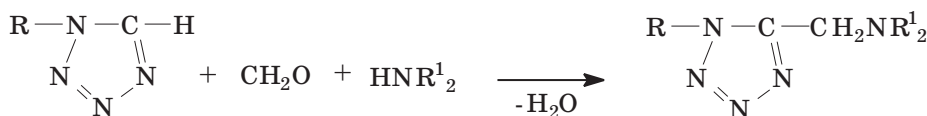
The direction of the reaction proceeding and the yield of products depend substantially on various factors including the natures of substituents R^1 and catalyst as well as on its amount and the procedure of its introduction into the reaction mixture. In the case of $\text{R}^1=\text{H}, \text{Me}$, the reaction occurs with formation of mainly 1-isomers, and yield of products amounts up to 90%. When $\text{R}^1=\text{Ph}$, on the contrary, 2-isomer predominates among products of the reaction.

It should be noted, that a wide variety of novel tetrazole-containing monomers can be prepared by exhaustive alkylation of C- and N-vinyltetrazoles in neutral and acidic media [42, 50]. In this case, the account must be taken of the necessity of use of the polymerization inhibitors [50].

1.3. Synthesis of 1,5-disubstituted tetrazoles by substitution at the cycle carbon atom

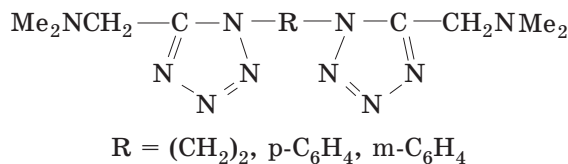
Because of the ease of synthesis of 1R-tetrazoles (sect. 1.1), they attract an attention as initial substances for the synthesis of different functionally substituted tetrazoles by reactions at the carbon atom of the tetrazole cycle. Earlier, such reactions have been poorly known because the electrophilic substitution of hydrogen atom at the carbon atom was considered to be hinder as a consequence of deactivation of this position by annular nitrogen atoms. At the same time, the data on rates of H/D exchange [51] as well as evaluation of C-H-acidity using spectroscopic and quantum-chemical methods [7] gave grounds to expect that such reactions are practicable for 1-substituted tetrazoles.

1-R-tetrazoles are found to enter readily into aminomethylation reaction as C-H-acidic component [52–54]:

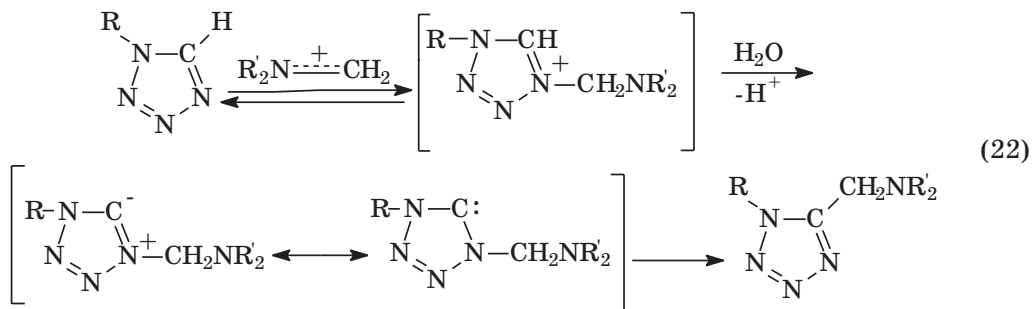


$\text{R}^1 = \text{Me}, \text{R}=\text{Me}, \text{Et}, \text{Allyl}, \text{CH}_2\text{CF}_3, (\text{CH}_2)_2\text{OH}, (\text{CH}_2)_2\text{N}_3, \text{Vinyl}, \text{Ph}, \text{p-MeOC}_6\text{H}_4, \text{p-BrC}_6\text{H}_4, \text{p-NO}_2\text{C}_6\text{H}_4, \text{m-ClC}_6\text{H}_4$; $\text{R} = \text{R}^1 = \text{Et}$; $\text{R} = \text{Me}, \text{R}_2^1 = (-\text{CH}_2-)_5$; $\text{R}^1 = \text{Me}, \text{R}=\text{H}$

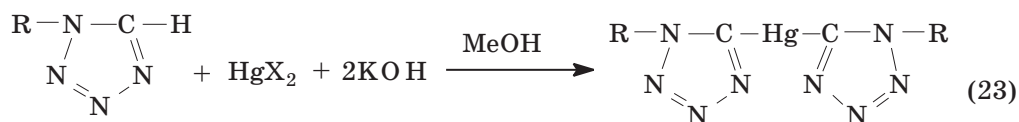
The yield of aminomethylation products (60–95%) depends substantially on the nature of R and the reaction conditions (acidity of reaction medium, azeotropic removal of water, etc.). Three variations of this method have been elaborated. The interaction of binuclear tetrazoles proceeds with involving of both tetrazole cycles resulting in formation of bis-Mannich-bases [10, 54]:



Judging from some experimental data, the aminomethylation process proceeds by an ilide mechanism, the proton splitting out from the tetrazolium cation being the rate-determining factor:

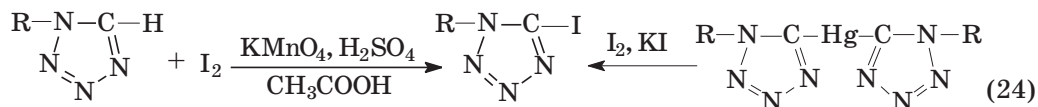


Similar to other C-H-acids with $\text{pK}_a=23\div 25$, 1-R-tetrazoles are mercuroated at the carbon atom of the cycle easily by mercury(II) salts in the presence of bases leading to formation of symmetric C-mercuroated tetrazoles with 80–95% yield. Several variations of this method have been developed. One of them corresponds to the following scheme [55–57]:



The reaction proceeds without heating, its rate being determining by the base force. The formation of symmetrical mercuroated tetrazoles can be explained by both high reactivity of carbanions and initial coordination of Hg(II) with two molecules of 1-substituted tetrazoles. In neutral and acidic media, mercuration leads to formation of R_2Hg and RHgX compounds depending on the ratio of reagents.

The third reaction proceeding at the carbon atom of the tetrazole cycle which has been revealed in our investigations, is the direct oxidizing iodation of 1-R-tetrazoles [58] (scheme 24). The reaction occurs only in the case of 1-n-alkyl-tetrazoles including 1,2-bis-(1-tetrazolyl)ethane leading to the corresponding diiodo-containing derivative and, probably, proceeds by the ilide mechanism. One of the methods for introducing of halogens into the organic molecules is mercuration followed by the mercury replacement for halogen. We proposed this way to prepare 5-iodo-(bromo-)tetrazoles [57] including those which can not be obtained by the direct iodation:

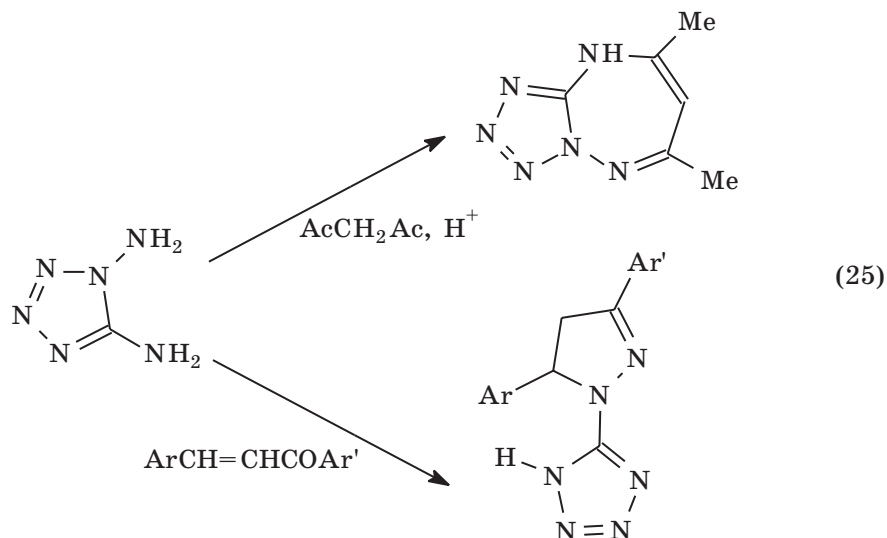


R=H, Me, Et, t-Bu, Allyl, Vinyl, Ph

It should be noted that aminomethylation and mercuration reactions do not proceed in the case of 2-monosubstituted tetrazoles which represent more weak bases [59] and C-H acids [51] compared to the corresponding 1-isomers.

1.4. Other reactions of tetrazoles with retention of the tetrazole ring

In this section, the data on some transformations of available N-substituted tetrazoles demonstrating their potentialities for the synthesis of other tetrazole derivatives are presented [7, 16], for example:

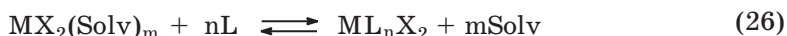


1-(2-Hydroxyethyl)tetrazole is oxidized readily by KMnO_4 forming a tetrazolylacetic acid, however, this reaction is accompanied by the competitive processes [7]. It has been shown, that the electrochemical oxidation using Ni/NiO/OH-electrode which acts as a redox-catalyzer, is a promising way for synthesis of tetrazolylacetic acid. In an optimal conditions, the oxidation process proceeds selectively with the rate of 1,5–1,7 % in hour, the yield of the resulting product by the current being amount up to 98 %. The obtained tetrazolylacetic acid is characterized by the high degree of purity and appropriate for preparation of antibiotics of broad range of application of «Cephazolin» type.

To obtain the data necessary for the single-minded synthesis of polymeric products with the determined composition and structure, the reactivity of a variety of C- and N-vinyltetrazoles in radical (co)polymerization has been studied [47, 60–66].

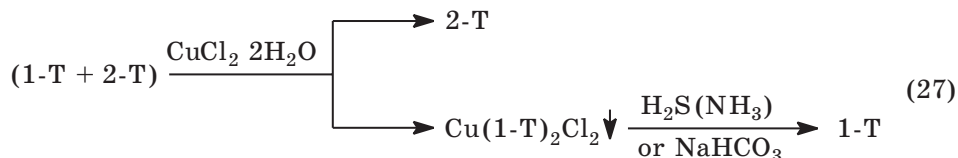
It has been confirmed experimentally that the obtained by quantum-chemical and spectroscopic investigations quantitative data on electronic and spatial structures of vinyltetrazoles allow one to predict correctly their reactivity in polymerization processes. The radical polymerization of 1-vinyltetrazole, 1-methyl-5-vinyltetrazole, 2-R-5-vinyltetrazoles (R=Me, Et, i-Pr, t-Bu) and 2-isopropenyl-5-methyltetrazole with standard monomers including styrene, methyl methacrylate and acrylonitrile as well as copolymerization of 1- and 5-vinyltetrazoles, 1- and 2-methyl-5-vinyltetrazoles have been studied. The fundamental characteristics of their reactivity, namely, copolymerization reactivity ratios and Alfrey-Price Q, e values have been determined. An analysis of the obtained data shown that the type of alkyl substituents in the position «2» of the ring does not essentially influence the electronic structure of the vinyl group of 2-alkyl-5-vinyltetrazoles and, consequently, their reactivity id radical copolymerization with vinyl monomers. Moreover, it seems that the size of the alkyl group is not important in copolymerization of 2-alkyl-5-vinyltetrazoles, too. These data permit to evaluate the composition of copolymers based on novel 2-alkyl-5-vinyltetrazoles using the copolymerization reactivity ratios for the investigated monomers of this series. The peculiarities of polymerization of 1-vinyl-5R-tetrazoles (R = CH, CH₃) determined by their ability to association and specific solvation have been revealed. The polymerization of vinyltetrazoles in water and aqueous solutions of NaSCN is found to proceed more quickly than in organic solvents leading to formation of high-molecular products with high yield [67].

The reactions of complex formation of a wide variety of N-substituted tetrazoles with salts of transition metals have been studied [10, 11, 29, 30, 49, 68–90].



The procedures for the synthesis of more than 80 complexes of tetrazoles with transition metal salts have been elaborated, the composition and the structure of which depend on the nature and the position of the substituents in the cycle.

The isomeric 1- and 2-substituted tetrazoles is shown to vary in their ability to complexes formation. This provides the basis for developing an original method for the separation of mixtures of isomeric N-substituted tetrazoles [91, 92]:

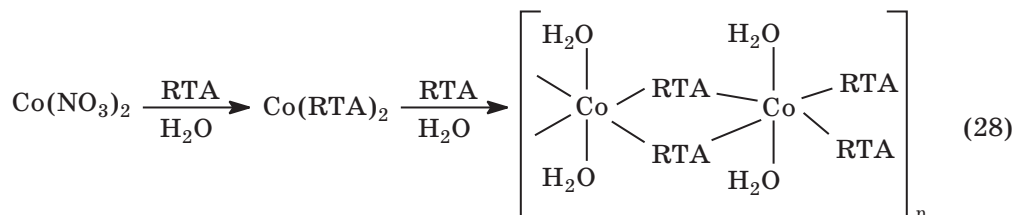


T = N-Substituted tetrazole

This approach based on precipitation of tetrazoles in the form of complexes followed by their hydrolysis and elimination of the ligand, is especially effective in the case of hardly volatile, easily polymerized and sensitive to heating 1- and 1,5-substituted tetrazoles [7, 49, 93]. It should be noted that vinyltetrazoles in

the form of complexes loss the ability to polymerization. Therefore, their complexation can be used as a method for the storage of monomers.

5-R-Tetrazolate anions (RTA) are known to react readily with transition metals salts (Ni^{2+} , Co^{2+} , Fe^{2+}) with formation of salt-similar complexes of $\text{M}(\text{RTA})_2$ composition. We have found that the formed complexes then gradually dissolved in water under the action of an excess of RTA. The dissolution is accompanied by a sharp increasing of the solution viscosity and formation of water-soluble polymers in which metal ion is six-coordinated and RTA serves as a bridging ligand, the coordination being occur via nitrogen atoms at «2» and «3» positions of the tetrazole cycle [13]:



The time of dissolution depends on the nature of ligands and the temperature and increases in the following order:



The formation of polymeric products are not observed in the case of anions of strong acids ($\text{R}=\text{NO}_2$, CF_3). It is interesting that for $\text{RTA}=\text{vinyltetrazolate}$, the frontal polymerization may proceed in the formed viscous solutions or gels under the action of initiators. Taking into account that such polymeric complexes are characterized by a rigid «rod-like» type structure, one can assume that the polymerization of vinyl groups should result in formation of polymeric products with a rigorously ordered structure.

It should be noted that the formation of similar complexes is also characteristic of 1,2,4-triazolate anions whereas anions of pyrazoles and imidazoles do not interact with salt-similar complexes formed at the first stage. In general, it is felt that water-soluble polymeric complexes can be obtained in the cases only when pK_a and pK_{BH}^+ values of azoles lie inside the range of 3,5÷12 and -4÷+5 correspondingly.

2. PHYSICO-CHEMICAL PROPERTIES AND STRUCTURES OF TETRAZOLES

By the time of statement of our investigations, the available literature data on the physico-chemical properties of tetrazoles were of fragmentary character since they were obtained mainly for the individual representatives of various tetrazoles using non-comparative conditions and procedures. Besides, the systematical investigations were hindered by the restricted accessibility of tetrazoles as well as by a specificity of their properties including high energetics, sensitivity and poor solubility in common solvents, requiring the overcoming of a considerable experimental difficulties.

In the present section, the obtained in our laboratory data of the experimental (IR, ^1H , ^{13}C , ^{15}N NMR, X-ray, methods of thermal analysis and investigation of burning processes) and the theoretical (quantum-chemical calculations using modern semiempirical and *ab initio* methods with different basis sets and DFT model) investigations of electron and geometrical structure, dipole moments, energetic characteristics, molecular and crystal structure of a wide variety of tetrazoles, the data on evaluation of some characteristics of tetrazolyl groups including their Hammett and Taft constants and the data of systematical study of the regularities of thermal decomposition and combustion of tetrazoles are presented.

2.1. Quantum-chemical calculations

The main part of the published previously papers concerning the theoretical study of tetrazoles deal with either the parent compounds of tetrazoles, namely, 1-H- and 2-H-tetrazoles or wide series of azoles or azines in which tetrazole compounds are considered only as particular objects. In this connection, it seemed expedient to carry out a systematic quantum-chemical investigation of a wide range of tetrazole derivatives with substituents of different natures by a set of semiempirical and *ab initio* methods and to reveal the applicability of the used methods for the correct prediction of various characteristics and properties of tetrazoles.

Using the set of various methods, we have carried out quantum-chemical calculations of enthalpies of formation, energies of protonation and deprotonation, charge distributions, dipole moments, spatial structures and a number of other characteristics of more than 50 tetrazoles including 1-, 2-, 5-, 1,5- and 2,5- substituted derivatives with alkyl-, alkenyl-, amino-, phenyl-, substituted phenyl-, halogen-, trifluoromethyl- and nitro-groups in the cycle [7, 94]. A semiempirical calculations by the CNDO/2, MINDO/3, MNDO, AM1 and PM3 approaches have shown that the two last methods are the most suitable for evaluating the energetic characteristics of tetrazoles. We have established a reliable correlations between the computed and the available experimental data on $\Delta H_{f(\text{gas})}^0$ of tetrazole derivatives including those obtained in Laboratory of Thermodynamics of Organic Substances [95, 96]. The fairly high correlation coefficients ($r=0,994$ for MNDO calculations and $r=0,983$ for PM3 method) and the fact, that the tetrazole derivatives with substituents of different natures obey these dependencies, allow us to assume that they can be used for estimating the heats of formation of tetrazoles using quantum-chemical calculations.

Based on the MNDO, AM1 and a wide set of *ab initio* methods, we have studied a relative stability of isomeric 1- and 2-substituted tetrazoles in gaseous state and in solutions in comparison with the appropriate experimental data [97]. The obtained results have shown that non-empirical calculations only provide the correct evaluation of the relative stability of N-substituted tetrazoles, the MP2/6-31G*, MP2/6-31G**//HF/6-31G* and MP2/6-31G*** theory levels predicting some larger stability of the corresponding 2-isomers (by 19,5–22,5 kJ/mol) in the gas phase and in non-polar media, being the most suitable for this purpose. The neglect of the electron correlation leads to significant deterioration of the correspondence between the calculated and the experimental data. The solvent nature influences essentially on the equilibrium content of N-substituted tetrazoles. The calculated

by the Polarizable Continuum Model isomerization energies of 1,5-dimethyltetrazole into the 2,5-isomer vary within the range from $-19,5 \text{ kJ/mol}^{-1}$ in the absence of solvent to $-1,6 \text{ kJ/mol}^{-1}$ in water showing a considerable stabilization of 1-isomer in the polar media [97].

The values of protonation energies of different electron-donor centers of molecules of tetrazole derivatives can be used as a criterion in solving question about protonation site and are of great importance for elucidating the mechanism of some reactions involving tetrazole cycle, in particular, reactions of 5-R-tetrazoles alkylation in acidic media (sect. 1.2.1) as well as exhaustive alkylation and complex formation. We have carried out calculations of proton affinity (PA) of each nitrogen atom of the tetrazole cycle of a wide range of tetrazoles [7, 94]. The obtained data indicate that irrespective of the calculation methods including the MNDO, AM1, PM3, 6-31G and 6-31G*, the N(4) atom is characterized by the greatest values of PA. Our recent X-ray study of crystal and molecular structure of 1,5-diamino-1H-1,2,3,4-tetrazolium picrate (DATP) show [98] that even in the case of tetrazole derivative with the two amino groups, protonation under formation of salt proceeds on N(4) nitrogen atom. The results of *ab initio* calculations of electronic structure and relative stability of various tautomeric forms of protonated 1,5-diaminotetrazole using MP2/6-31G* and B3LYP/6-31G* levels of theory are in a good agreement with the X-ray data and show that there are substantial differences in s-electron overlap populations for the C-N bonds in the cation in DATP, while p-electrons are delocalized [98]. At the same time, the performed calculations show that 1-substituted tetrazoles are characterized by a relatively small difference between the values of protonation energies for the N(4) and the N(3) atoms. For the MNDO calculations, ΔPA is 8,3 and 9,5 kcal/mol, respectively, for 1-methyltetrazole and 1,5-dimethyltetrazole, whereas for 2- and 2,5-isomers this difference is more significant (ΔPA amounts to 22,8 and 20,9 kcal/mol, respectively, for 2-methyltetrazole and 2,5-dimethyltetrazole) [94]. These data are in a good agreement with results of investigation of tetrazole derivatives quaternization processes and can explain the formation of a mixture of 1,3,5- and 1,4,5-tetrazolium salts with predomination of 1,4,5-isomer upon exhaustive alkylation of 1- and 1,5-substituted tetrazoles and the high selectivity of the quaternization processes of 2- and 2,5-substituted tetrazoles when alkylation occurs exclusively at the N(4) atom of the ring [42, 50]. It should be noted, that our last data on calculations of PA of tetrazoles by the *ab initio* methods show that the expansion of the basis set along with electron correlation leads to a decreasing of ΔPA , whereas the use of B3LYP/6-31G* level of theory provide practically the same PA values for the N(4) and the N(3) atoms of the cycle of 1- and 1,5-substituted tetrazoles.

All the considered semiempirical methods except for the PM3 one, show the non-uniform distribution of electron density in the cycle of tetrazole derivatives, the maximum values being characteristic of the «pyrrol-like» nitrogen atoms [7]. It should be mentioned that a considerable difference in density distribution in the cycle of 1- and 2- substituted tetrazoles is observed. All the studied 1-mono- and 1,5-disubstituted tetrazoles are characterized by the essential localization of charges on the N(1) and the N(4) atoms of the ring, whereas the electron density in the cycle of 2- (2,5-)substituted tetrazoles is more delocalized and distributed between the N(1), N(2) and N(4) atoms. This agrees with the experimental data

and testify to a larger polarity of 1-substituted tetrazoles and more uniform distribution of bond lengths in the cycle of 2-substituted tetrazoles. Moreover, a significant localization of charges on the N(1) and the N(4) atoms of the ring of 1- and 1,5-substituted tetrazoles accounts, to a certain degree, for their high reactivity in exhaustive alkylation [7, 42] and complex formation [10, 11, 29, 30] reactions. We have established a reliable correlation between the MNDO-calculated π -charges of nitrogen atoms and the chemical shifts of these atoms in ^{15}N NMR spectra. For the series of 1-alkyl(alkenyl)-tetrazoles, this dependence is described by the equation:

$$\delta(^{15}\text{N}) = (-317,3 \pm 14,1)p_z + (349,3 \pm 17,9) \\ r = 0,979, S = 12,7, n = 24$$

An inclusion of 2-isomers and disubstituted derivatives of tetrazole in this series leads to a considerable decrease of the correlation coefficient:

$$\delta(^{15}\text{N}) = (-230,9 \pm 17,4)p_z + (237,2 \pm 22,4) \\ r = 0,861, S = 27,1, n = 64$$

The deterioration of correlation is probably because, in this case, the charge characteristics of isolated molecules are compared with chemical shifts of nitrogen atoms in solutions where the phenomena of association and specific solvation of molecules that show up differently for tetrazoles with substituents in different positions of the cycle takes place [7, 99, 100].

We have established also a good correspondence between changes of the net effective charges on vinyl carbon atoms of vinyltetrazoles and their chemical shifts in ^{13}C NMR spectra [47, 50, 64, 99]. In general, the presence of the above correlations show that among the semiempirical methods, the MNDO one makes it possible to describe the electronic structure of tetrazole derivatives with sufficient accuracy. At the same time, a systematical study of electronic and spatial structure of a series of 1-, 2-, 5-vinyltetrazoles and 2-(1-methylvinyl)tetrazoles using a set of semiempirical and *ab initio* methods [101–105] show that non of the semiempirical approaches are suitable for the correct description of the dependencies of energetic and geometric characteristics of the considered alkenyltetrazoles on the dihedral angle between the vinyl group and the plane of the tetrazole cycle. The MP2/6-31G** and MP2/6-31G**//HF/6-31G* levels of theory provide the correct prediction of alkenyltetrazoles spatial structure, the equilibrium content of S-cis- and S-trans-conformers for 2-alkyl-5-vinyltetrazoles [101] and 2-vinyl-5-R-tetrazoles [102] being not essentially depend on the nature and the size of the substituent in the cycle, whereas in the case of 1-vinyl-5-R-tetrazoles, the equilibrium content of S-trans(R)-conformer increase with the size of the substituent and the relative conjugation energies in molecules decrease as the electron-accepting properties of the substituent increase [103].

A variety of properties of tetrazole derivatives are conditioned by their high polarity determined by dipole moments which differ significantly for 1- and 2-substituted tetrazoles. One can expect that the semiempirical methods predicting adequately the electron density distribution should provide the correct evalu-

ation of dipole moments of tetrazole derivatives. The obtained using the MNDO and MNDO/M methods data show [7, 94] the tendency for a decreasing of dipole moments values when introducing the electron-accepting substituents into 1- and 5-positions of 1-substituted tetrazoles. This is agree with the direction of the dipole moment vector from the N(1) to the N(3) atom, whereas this one for the corresponding 2-isomers is directed from the N(2) to N(4) atom. Hence it follows that the introduction of electron-accepting substituents into the «5» position of the ring of 2-substituted tetrazoles should increase their dipole moments and the cases possible where, contrary to popular opinion, the dipole moments of 2-substituted tetrazoles can exceed those of the corresponding 1-isomers. We have carried out calculations of dipole moments of a wide variety of tetrazoles and have revealed that 2,5-disubstituted tetrazoles containing the CF_3 group at the position «5» of the ring are characterized by the larger values of dipole moments than the corresponding 1-isomers [7].

We have calculated the energies of heterolytic breakdown of C-H bond (deprotonation energies) for a series of N-substituted tetrazoles as well as the geometrical and electronic parameters of structural realignment of molecules caused by the deprotonation [7]. The obtained data suggest a larger stability of carbanions of 1-substituted tetrazoles comparative to those of 2-isomers by 61–77 kJ/mol which is in agreement with larger deprotonation energies of 2-substituted tetrazoles (by 52–65 kJ/mol). The values of the net effective charges on C(5) atoms of the ring of N-substituted tetrazoles and their changing upon the deprotonation depending on the nature of the substituent correlate with changing in their kinetic C-H acidity. Moreover, for a series of 1-monosubstituted tetrazoles, a reliable linear correlation have been established between the calculated using some semiempirical methods values of deprotonation energies and the exponent of the rate of H/D exchange.

In recent years, *ab initio* methods were used for the calculation of electronic and magnetic characteristics of complexes of of copper(II) chloride with some 1-substituted tetrazoles including the evaluation of energies of ferro- and anti-ferromagnetic ordering [106] and for the estimation of electronic structure of a series of 5-R-tetrazolate anions as well as of spatial structure of polymeric chain formed by Co^{2+} ions and 5-methyltetrazolate anions [13].

The obtained data show that some of the semiempirical methods provide a correct evaluation of various characteristics of tetrazole derivatives including enthalpies of formation, dipole moments, geometrical parameters of the tetrazole cycle and spatial structure of molecules. However, non of them provide a good agreement between the calculated and the experimental data for all the considered characteristics simultaneously. MNDO is the most all-purpose method, whereas AM1 is the best suited for calculations of geometrical parameters and spatial structure of molecules. PM3 method gives the best agreement for heats of formation but nusjuges the charge distribution in molecules of tetrazoles as well as their dipole moments. An analysis of applicability of *ab initio* calculations for studying the energetic characteristics of tetrazoles show that the correct data can be obtained when using 6-31G* or 6-31G** theory levels with MP2 electron correlation.

2.2. X-ray analysis of tetrazoles

The single crystal X-ray analysis of more than 30 tetrazole derivatives including 1-, 2- and 5-substituted tetrazoles, tetrazolium salts and complexes has been carried out [28–30, 36, 38, 39, 81–89, 98, 107–113]. A number of peculiarities of crystal and molecular structure of complexes of these types has been revealed. In contrast to 2-monosubstituted tetrazoles, the corresponding 1-isomers are characterized by the presence of well defined intermolecular $C_{(5)}-H...N_{(4)}$ hydrogen bonding which determine the peculiarities of structure of formed polymeric chains. The exhaustive alkylation of tetrazoles is accompanied by the redistribution of bond lengths in the ring and by equalizing of $N_{(1)}-C_{(5)}=N_{(4)}$ and $N_{(1)}-N_{(2)}=N_{(3)}$ bond orders in 1,4- and 1,3-substituted salts accordingly. These results along with the NMR and quantum-chemical calculations data indicate the presence of appreciable conjugation within the mentioned fragments. 2-Substituted tetrazoles and 1,3-disubstituted tetrazolium salts are characterized by a larger range of angles variation in the cycle amounting to $102\div 115^\circ$ ($100\text{--}116^\circ$ for compounds with electron-accepting substituents in the ring), whereas the corresponding values for 1-substituted tetrazoles and 1,4-disubstituted salts account for $105\text{--}111^\circ$.

In all the considered substances the tetrazole ring is essentially of planar with mean deviation from the least-square plane of atoms is not exceed 0,004 Å. Substituents also lie in the ring plane and the corresponding atoms are characterized by the planar triangle bonds configuration, where the sum of angles at these atoms amounts to 360° .

The importance of investigations of structure of complexes of N-substituted tetrazoles with salts of transition metals is conditioned primarily by the searching of correlations between peculiarities of structure and magnetic properties in the novel group of low-temperature ferromagnets of general formula $Cu(1-R\text{-tetrazole})_2Cl_2$ [74, 75, 77, 78]. It has been shown that the copper(II) ion in such complexes possesses an octahedral coordination environment and the ligands molecules are linked via $N_{(4)}$ atom of the tetrazole cycle. The ligands with voluminous substituents ($R=t\text{-Bu}$, mesityl) are characterized by cis-coordination [85, 86] whereas those with $R = Et$, allyl, azidoethyl possess trans-coordination [77, 78, 82]. Complexes with ligands coordinated in cis-position form chain polymeric structures in which chains are linked together by Van der Waals interactions only. Both chain-polymeric and polymeric layered structures are formed by $-Cl-Cu-Cl-$ bonding.

The study of structure of complexes of copper(II) chloride with 2-ethyltetrazole has demonstrated for the first time that this compound acts as bidentate bridging ligands coordinating by the $N_{(4)}$ and $N_{(1)}$ atoms which leads to formation of layered polymeric structures at the expense of bridging tetrazole heterocycles [89].

A number of complex of non-usual composition has been synthesized and studied including $Cu_3(2\text{-allyltetrazole})_4Cl_6$ [88], $[Cu(1\text{-phenyltetrazole})_3BF_4]BF_4$ [81], and $CuLCl_2$, where $L = 2\text{-tert-butyltetrazole}$ [87], 1-methyl-5-dimethylaminomethyltetrazole [84].

Binuclear tetrazoles act primarily as chelating and bridging ligands. The structure of a variety of such type substances has been studied [29, 30, 83].

2.3. Spectroscopic study of tetrazoles

The obtained data on the electron density distribution in the ring of 1- (1,5)- and 2- (2,5)- substituted tetrazoles suggest a sufficient difference in some spectral parameters of the mentioned tetrazole derivatives. This can be used for both the evaluation of their reactivity and identification. Therefore, it seemed expedient to carry out a systematical study of vibrational and NMR spectra of a wide range of tetrazoles.

For the correct assignment of the absorption bands of the ring in IR spectra of tetrazole derivatives, we carried out a comparative study of the theoretical and the experimental spectra of tetrazole and deuteriotetrazole [114], tetrazolate-anion (the experimental spectra of tetrazolates of ammonium, alkali and earth-alkali metals have been analyzed) [115], as well as of a series of N-substituted [116] and 5-substituted [117] tetrazoles. The theoretical study included calculations of distribution of potential energy of vibrations which is necessary for the quantitative evaluation of the contribution of one or another type of vibrations into the spectroscopic pattern. Besides, a systematical analyses of the experimental IR spectra of 1- and 2-alkyltetrazoles with $R=CH_3 \div n-C_8H_{17}$ and their complexes with some Cu(II) salts [72], vinyltetrazoles [47] and some other tetrazole derivatives [11, 29, 76, 79, 80, 90] have been studied.

The obtained data allowed us to reveal several features, peculiar to the IR spectra of tetrazoles. Firstly, a mixing of different types of vibrations is observed for all the absorption bands attributed to the tetrazole cycle. Only in specific cases, one can identify the frequencies characterized by the predomination of contribution of definite type of vibrations into the distribution of their potential energy. Within the tetrazole-N-substituted tetrazoles series, among them are the stretching vibrations of C-H bonds which appear at $3100-3145\text{ cm}^{-1}$ and $1225-1289\text{ cm}^{-1}$, respectively. Within tetrazole-5substituted tetrazoles series, deformation vibrations ρ_{N-H} are the most characteristic by the frequency. Secondly, in spite of sufficient differences in the force field of molecules of 1- (1,5)- and 2- (2,5)- substituted tetrazoles determined by features of electron density distribution in the cycle, the IR spectra of both 1- and 2-substituted tetrazoles contain, as a rule, a closely related set of absorption bands attributed to the tetrazole cycle which differ mainly by the intensity distribution. Nevertheless, the detailed analysis of IR spectra of individual and coordinated N-monosubstituted tetrazoles allow us to establish that absorption bands at $1204-1309\text{ cm}^{-1}$ and $1273-1289\text{ cm}^{-1}$ in spectra of 1- and 2-monosubstituted tetrazoles, respectively, determined mainly by the stretching vibrations of the cycle N-N bonds. In spectra of individual 1-monosubstituted tetrazoles, ν_{N-N} appear as a set (2÷4) of bands of low intensity, whereas in spectra of individual and coordinated 2-isomers, ν_{N-N} is recorded as a singlet. These features permit one to identify the position of the substituent in the tetrazole cycle of isomers.

The IR spectra of 1-methyl-5-vinyltetrazole (1-MVT) and 2-methyl-5-vinyltetrazole (2-MVT) were found to contain absorption bands at 1098 cm^{-1} and 735 cm^{-1} , correspondingly, which are characteristic of only each isomer. This allowed us to elaborate the method for the determination of the content of 1-MVT and 2-MVT chains in their copolymers which are of great practical importance, because the commonly used elemental analysis is unsuitable in this case [118].

The performed analysis allowed to refine and to identify a number of absorption bands in the IR spectra of tetrazole and some its derivatives. In particular, it has been shown that the band at 1570 cm^{-1} in the IR spectra of tetrazole is caused solely by the $\nu_{\text{C}=\text{N}}$ and $\nu_{\text{N}=\text{N}}$ vibrations rather than by $\delta_{\text{N-H}}$ ones as expected previously. The assignment has been carried out also for absorption bands at $1688\text{--}1690\text{ cm}^{-1}$ and $1792\text{--}1794\text{ cm}^{-1}$ in IR spectra of tetrazolates of ammonium and alkali metals [115], which are considered earlier for sodium tetrazolate as combined bands. A special experiments on the temperature dependence of the maxima and the shape of absorption bands in IR spectra of ammonium tetrazolate in the crystal state and in the melt when using different samples (pellets with KBr, emulsions with Vaseline oil) allow one to conclude that the considered bands are determined by the influence of salts crystal lattice [115].

The data of ^1H and ^{13}C NMR spectra allow one to clearly recognize the isomeric N-monosubstituted tetrazoles. The chemical shifts (CSs) of the cycle carbon atoms in the ^{13}C NMR spectra were found to be acutely sensitive to the isomer type. The CSs of 2-monosubstituted tetrazoles are displaced to a weak field by $10,4\pm 1,8$ ppm comparative to those of the corresponding 1-isomers, the nature of the N-substituent being exert insignificant influence on CS values. For a rich series of 1-monosubstituted tetrazoles, CS values of the cycle carbon atom appear within $140\text{--}145$ ppm, whereas in the case of 2-monosubstituted tetrazoles these values amount to $152\text{--}154$ ppm [99, 119]. In the case of 1,5- and 2,5-substituted tetrazoles, CS of the cycle carbon atom depends substantially on the nature of the substituent at the C(5) atom [7, 99, 101–104].

The CSs of hydrogen atom at the carbon atom of the tetrazole cycle in ^1H NMR spectra are displaced to a weak field comparative to those of the corresponding 2-isomers [99]. However, CSs of these atoms in the case of 1-isomers, in contrary to 2-isomers, depend significantly on the nature of solvent and, in some cases, on the solution concentration. This is conditioned by the ability of molecules of 1-substituted tetrazoles to association and specific solvation [99, 100].

The obtained data on ^{13}C NMR spectra of tetrazolium salts [42, 50] show the significant difference between CSs of the cycle carbon atom of 1,4- (1,4,5)- and 1,3- (1,3,5)-substituted tetrazolium salts identical to that for N-substituted tetrazoles.

An analysis of ^1H and ^{13}C NMR spectra of a wide series of p- and m-substituted 1-phenyltetrazoles and the establishment of linear correlations ($r\geq 0,992$) between the CSs of C(5)-H proton and CSs of protons of phenyl groups allowed us to evaluate precisely the Hammett constants $\sigma_{\text{m}}=0,53\pm 0,04$; $\sigma_{\text{p}}=0,50\pm 0,04$; $\sigma_{\text{I}}=0,56\pm 0,03$ and the Taft constants $\sigma_{\text{R}}=-0,04\pm 0,04$; $\sigma_{\text{R}}^0=-0,04\pm 0,01$ of 1-tetrazolyl group [119].

The data of ^{13}C NMR spectra of a series of 1- and 2-alkyl(allyl)-tetrazoles and the comparison of CSs of carbon atoms of alkyl substituents with CSs of the corresponding atoms of unsubstituted alkanes allowed one to estimate the values of increments of N-tetrazolyl groups which amount to $\alpha=+36,3\pm 2,0$; $\beta=+9,1\pm 1,5$; $\gamma=-3,3\pm 1,1$ for the 1-tetrazolyl group and $\alpha=+40,8\pm 1,3$; $\beta=+8,1\pm 1,2$; $\gamma=-3,4\pm 1,1$ for the 2-tetrazolyl group. The obtained values are close to those of NHR and NR₂ groups, respectively [99].

The results of quantum chemical calculations of electronic and spatial structure of 1-, 2- and 5-vinyltetrazoles are in a good agreement with the data on CSs and coupling constants in ^1H and ^{13}C NMR spectra [101–103]. The possibility of

predicting of reactivity of vinyltetrazoles in radical polymerization based on the data of their ^1H and ^{13}C NMR spectra have been shown [47, 60, 64].

^{15}N NMR spectroscopy was used in our investigations to obtain the direct evidences of the position of reaction proceeding upon protonation, quaternization and formation of complexes [7, 120]. The most displacement of CS of N(4) of the tetrazole cycle comparative to those of other nitrogen atoms under the addition of phenole, acetic and sulphuric acids as well as AlEt_3 show that the protonation and the formation of donor-acceptor bond occur on the position «4» of the ring. The displacement of N(4) CS to a strong field is in agreement with the data of quantum-chemical calculations predicting an increasing of p-electron density on the N(4) atom under protonation. Acetic acid and phenole displace the N(4) CS of 1-butyltetrazole by 5–10 ppm. This indicates that acidic-basic interaction comes to rest at the stage of formation of complex at the expense of hydrogen bond. In the case of sulphuric acid, the displacement by 96 ppm corresponds to full protonation of the N(4) atom. The same displacement is observed for quaternized nitrogen atom [42]. The formation of complex with AlEt_3 leads to displacement of CS by 18–22 ppm which corresponds to the formation of sufficiently strong donor-acceptor bond.

Based on the analysis of ^{15}N NMR spectra of a wide range of N-substituted tetrazoles we got the conclusion about the misinterpretation of the data of ^{15}N NMR spectra of 2,5-disubstituted tetrazoles and carried out the correct assignment of CSs of these substances [120].

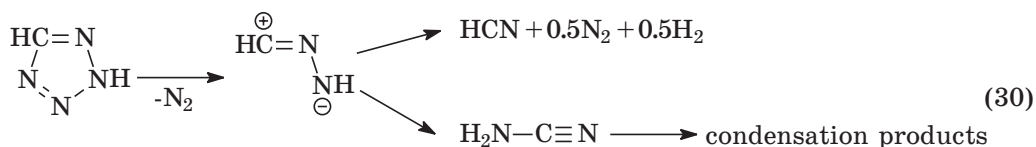
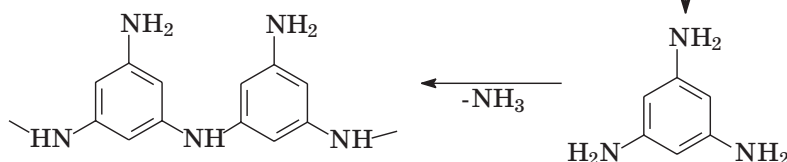
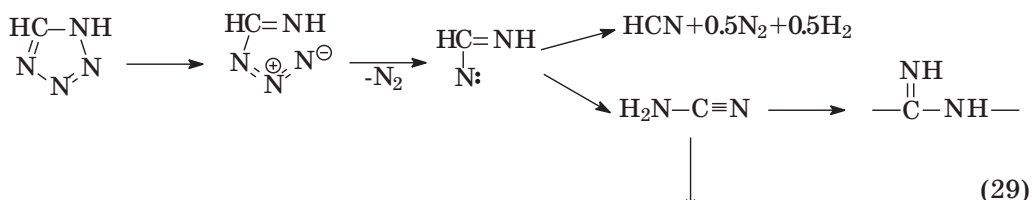
2.4. Thermal decomposition of tetrazoles

Tetrazole and its derivatives possess a unique combination of properties. In spite of large positive enthalpies of formation [95, 96], they exhibit surprisingly high thermal stability and have the highest content of nitrogen among all organic substances (for example, 82,3 wt.% for 5-aminotetrazole and 84,0 wt.% for 1,5-diaminotetrazole). Therefore, tetrazoles are prospective materials for generation of nitrogen, as blowing agents, solid propellants and other combustible and thermally decomposing systems. However, until to the beginning of our investigations in this field, the information concerning the thermal changes of tetrazoles was restricted mainly by the data on decomposition of separate representatives of 5-, 1,5- and 2,5-substituted tetrazoles [121]. Besides, a comprehensive study of the thermal decomposition of tetrazole derivatives was also of great interest in connection with their ability to formation of different isomeric forms determined by the prototropic, ring-chain and amino-imino isomerism and the possibility of the elucidating the role of structural specificities on thermal changes.

The ability of tetrazoles to isomerism as well as their volatility and explosiveness make difficult the experimental study of thermal transformations of these compounds [121]. Because of this, a wide variety of methods was used allowing to study the thermal decomposition of tetrazoles both in condensed and in gaseous states and to determine the composition of solid and volatile products of thermal degradation. The peculiarities of the experimental procedures and calculations of kinetic parameters of thermolysis of tetrazole and its derivatives are presented in Refs. [122–125].

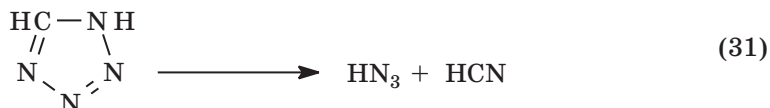
2.4.1. Thermolysis of tetrazole

It should be stated [122, 123, 126], that unsubstituted 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 predominately from the 1-H-form via the intermediate azide (scheme 29) whereas in the gaseous state it eliminates from the cyclic 2-H-form (scheme 30):



The stabilization of the intermediate products leads in both cases to formation of cyanamide followed by its thermal transformations resulting in linear polycyanamide, melamine and products of its condensation (melem, melam and melon). An insignificant part of the intermediates breaks down into hydrogen cyanide, hydrogen and nitrogen (schemes 29, 30).

Additionally, about 5 % of substrate decomposes in the melt by another mechanism with formation of hydrogen azide and hydrogen cyanide:



The evolved gaseous HN_3 and HCN interact with ammonia which is formed under condensation of melamine giving the corresponding salts revealed among the volatile products of thermolysis [126]. It should be noted that the composition of the tetrazole thermal decomposition products depends substantially on the experimental conditions, and can be adjusted by changing the proportion of substrate subjected to thermolysis either in the melt or in the gaseous state [126].

The obtained data are in a good agreement with results of quantum-chemical calculations of thermodynamical evaluation of the possibility of proceeding of different reactions under fragmentation of 1-H- and 2-H-tetrazoles and the most possible ways of stabilization of the formed intermediate products [127].

2.4.2. Thermal decomposition of aminotetrazoles

The thermal decomposition of 5-aminotetrazole (AT), 1-methyl-5-aminotetrazole (MAT), 1,5-diaminotetrazole (DAT) and sodium salt of 5-aminotetrazole (SAT) have been studied [124, 128–130]. As in the case of unsubstituted tetrazole, structural factors exert an essential influence on the mechanism of thermolysis of aminotetrazoles which can exist in various isomeric form according to scheme 32:

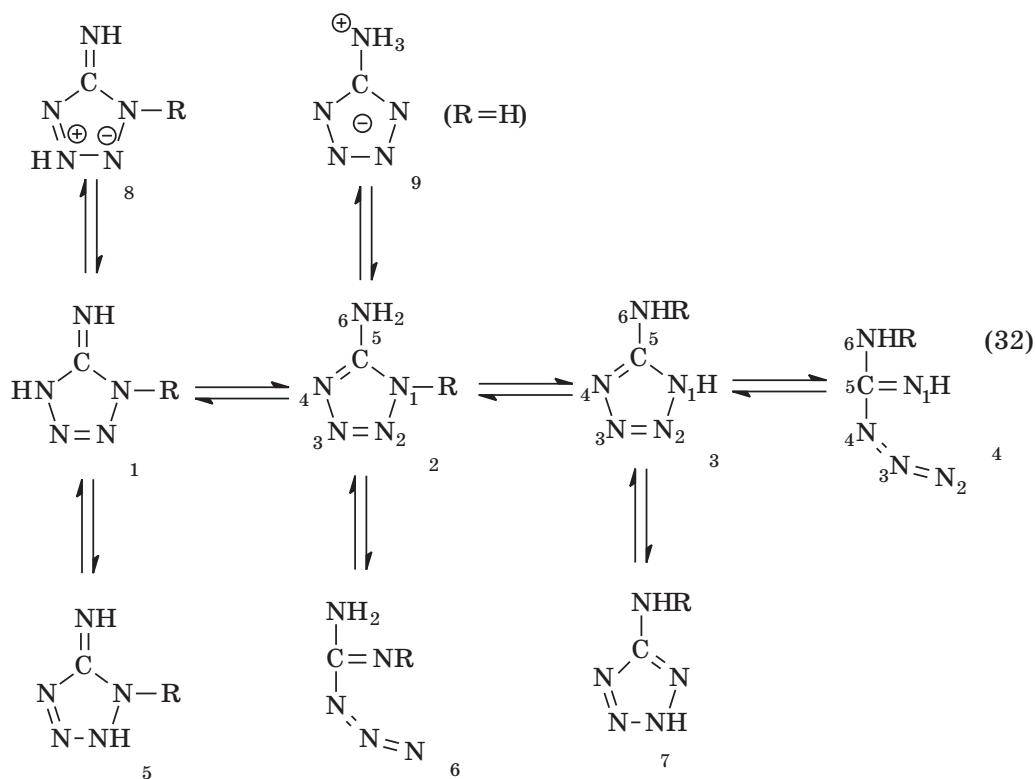


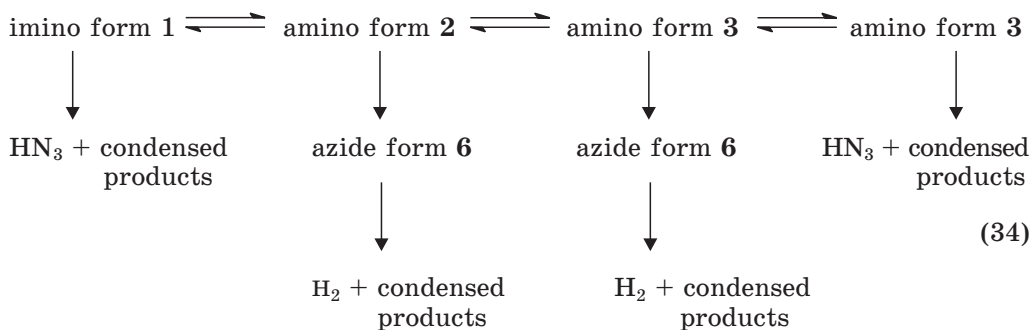
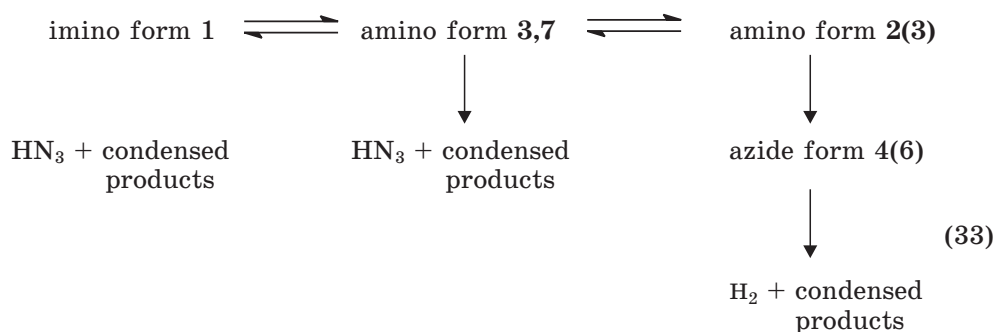
Table 1

Gaseous and volatile condensed products
of thermal decomposition of aminotetrazoles

Compound	Gaseous products	Volatile condensed products
5-AT	N ₂ , HN ₃ , NH ₃	NH ₄ N ₃ , melamine
MAT	N ₂ , HN ₃ , NH ₃ , HCN, CH ₃ NH ₂	NH ₄ N ₃ , CH ₃ NH ₂ , HN ₃ , trimethylmelamine
DAT	N ₂ , HN ₃ , NH ₃ , HCN	NH ₄ N ₃ , 1,2,4-triazole
SAT	N ₂ , HN ₃ , NH ₃	NH ₄ N ₃ , melamine

Based on the content of gaseous and volatile products as well as on the composition of condensed products of thermolysis of aminotetrazoles which are presented in Tab. 1, the kinetic consideration, the results of the study of amino-imino tautomerism and the data of MP2/6-31G* calculations of the relative stability of all possible isomeric forms and MNDO calculations of bond energies in aminotetrazoles, the mechanism of their thermal decomposition has been derived [130].

Two mechanisms of splitting of the tetrazole ring are effective in aminotetrazoles: evolution of hydrogen azide from the tautomeric forms with hydrogen atom by nitrogens in the ring and evolution of nitrogen molecule from the amino-tautomeric form. The general pattern of thermal decomposition of 1-R-5-aminotetrazoles is presented on schemes 33 (R=H) and 34 (R=CH₃, NH₂):



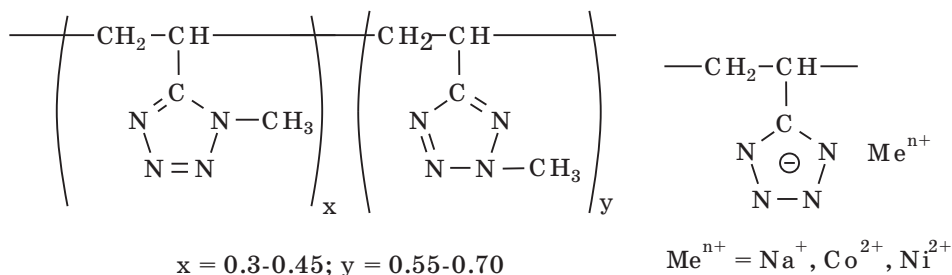
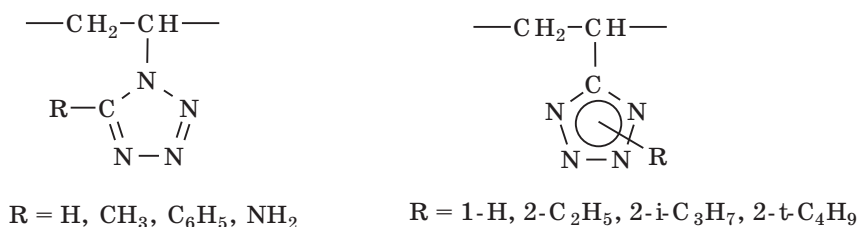
In the case of AT, MAT and DAT, the thermal decomposition of the imino form starts just after the melting and results in evolution of hydrogen azide. An increase of the temperature leads to another pathway of thermal decomposition involving corresponding amino forms, which decompose with elimination of nitrogen. Similar general pattern of thermolysis is observed for SAT, however, the last starts to decompose prior melting. All aminotetrazoles produce ammonium azide, *simm*-triazines and the products of their condensation. It is interesting to note, that sodium azide is an intermediate product of the SAT thermal decomposition [129].

The apparent activation energies of thermal decomposition of imino forms are in the range of 180–200 kJ mol⁻¹. Two mechanisms of splitting of the tetrazole ring are in agreement with the data of kinetics of thermal decomposition of 5-aminotetrazoles [130]. SAT has significantly higher activation energy (about 190 kJ mol⁻¹), and is more thermally stable than AT, MAT and DAT because the tetrazole ring in SAT is more aromatic than rings of other considered aminotetrazoles.

The general regularities revealed under investigation of thermal decomposition of tetrazole and aminotetrazoles have then been used when studying the thermolysis of tetrazole-containing polymers.

2.4.3. Thermal decomposition of polyvinyltetrazoles

We have studied for the first time the kinetics and the mechanism of thermal decomposition of a wide variety of tetrazole-containing polymers including poly-1-vinyl-5R-tetrazoles (I), poly-5-vinyltetrazole and poly-2-alkyl-5-vinyltetrazoles (II), copolymers of 1- and 2-methyl-5-vinyltetrazole (II) including those obtained by polymer-analogous conversions [44, 45] and some salts of poly-5-vinyltetrazole (IV):



The data on synthesis, characterization of polymers and the peculiarities of the experimental study of their thermal decomposition are given in Refs. [131–135].

Table 2 summarizes some thermoanalytical and kinetic parameters of thermal decomposition of polyvinyltetrazoles. The obtained data point clearly to the presence of dependence of their thermal stability on the position and the nature of the substituents in the heterocycle. The introduction of substituents at the position «5» of the

ring leads to a considerable increasing of the thermal stability of poly-1-vinyl-5R-tetrazoles comparative to unsubstituted poly-1-vinyltetrazole. In contrast to other poly-1-vinyl-5R-tetrazoles, the mechanism of thermal degradation of poly-1-vinyltetrazole is not depend on the thermolysis conditions and the single gaseous products of decomposition is nitrogen [131]. In the case of R=Me, Ph, NH₂, the composition of the thermolysis products is determined by the conditions of thermal decomposition. This is caused by two reasons. The first one is conditioned by the possibility of proceeding of two parallel processes: (1) fragmentation of the pendant tetrazole rings and (2) their splitting out from the macrochain resulting in formation of the corresponding 5-substituted tetrazoles followed by their thermal transformations. The last pathway is observed in the case of thermal decomposition of poly-1-vinyl-5-methyltetrazole and poly-1-vinyl-5-phenyltetrazole [134] and occurs mainly either in isothermal regimes within the temperature range corresponding to initial stage of thermolysis or under relatively low heating rates. The second process proceeds primarily at high heating rates and is accompanied by formation of unsaturated fragments in the macrochain and its partial destruction resulting in formation of aromatic structures [134].

Table 2

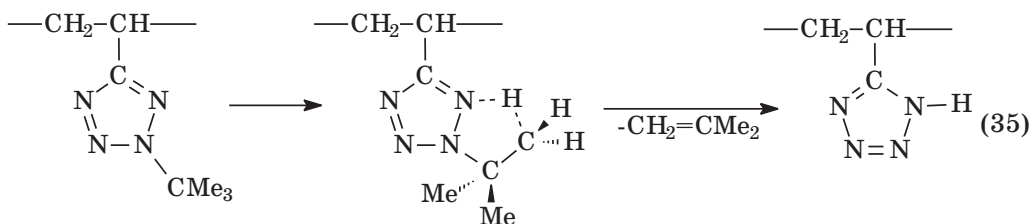
Temperature of decomposition (measured in TG experiments, heating rate 10 K min⁻¹) and kinetic parameters for the first stage of thermal decomposition of polyvinyltetrazoles and some tetrazole derivatives

Compound	Tdec. (K)	Kinetic parameters obtained from isothermal experiments		Ea obtained from nonisothermal experiments (kJ/mol)
		E _a (kJ/mol)	lg A (c ⁻¹)	
Poly-1-vinyltetrazole	453	148±9	13.7±1.0	140
Tetrazole	447	152.4±9.7	14.4±2.5	
Poly-1-vinyl-5-methyltetrazole	523			
5-Methyltetrazole	465			
Poly-1-vinyl-5-aminotetrazole	475			
5-Aminotetrazole	480			
Poly-1-vinyl-5-phenyltetrazole	470			
5-Phenyltetrazole	488			
Poly-5-vinyltetrazole (PVT)	460	164±7	13.8±0.8	140-165
Poly-1-methyl-5-vinyltetrazole	540	99.0		
Poly-2-methyl-5-vinyltetrazole	493	196±6	16.8±0.6	175
Poly-2-ethyl-5-vinyltetrazole	495			180
Poly-2-n-propyl-5-vinyltetrazole	495			
Poly-2-isopropyl-5-vinyltetrazole	485			175
Poly-2-n-butyl-5-vinyltetrazole	490	189±7	16.0±0.8	
Poly-2-t-butyl-5-vinyltetrazole	470	165±12	14.1±1.1	150-165
Sodium salt of PVT	613			
Nickel salt of PVT	473			
Cobalt salt of PVT	475			

The second reason of the substantial dependence of the mechanism of thermal decomposition on its condition is connected by the influence of isomerisation processes proceeding in pendant group under heating. This is observed in the case of poly-1-vinyl-5-aminotetrazole in which the pendant group may occur both in the amino- and imino-forms [135].

The mentioned factors as well as the specificity of the influence of polymeric matrix caused by the presence of intra- and intermolecular hydrogen bonding are responsible for the discrepancy between the thermal stability of poly-1-vinyl-5-1-R-tetrazoles which diminishes in the order $H < Ph \text{ NH}_2 < Me$ and thermal stability of the individual 5R-tetrazoles ($H < Me < NH_2 \text{ Ph}$) in comparative conditions (Tab. 2).

The thermal behaviour of poly-5-vinyltetrazoles also depends substantially on the presence and the position of alkyl substituents in the cycle. For poly-2-alkyl-5-vinyltetrazoles with ramified substituents, thermal stability and kinetic parameters of thermolysis are practically not depend on the substituents size (Tab. 2). These data are in agreement with results of quantum-chemical and spectroscopic investigations (see sect. 2.1, 2.3) showing a weak influence of alkyl substituents at the position «2» of the ring on the electronic and spatial structure of 2-alkyl-5-vinyltetrazoles. At the same time, poly-2-*t*-Bu-5-vinyltetrazole, in addition to usual for poly-2-*n*-alkyl-5-vinyltetrazoles mechanism of thermal degradation involving the splitting out of the ring with elimination of nitrogen, is capable of thermolysis at the expence of homolytical break-down of exocyclic N-C bond leading to formation of poly-5-vinyltetrazole followed by its thermal transformations:



The second process is realized mainly under high heating rates [132].

The introduction of alkyl substituents into position «1» of the ring leads to a considerable increasing of thermal stability of polymers relative to both PVT and poly-2-alkyl-5-vinyltetrazoles (Tab. 2). Special attention should be given to enormous thermal stability of PVT sodium salt (PVTS) (Tab. 2). This may be caused by the fact that the tetrazole cycle in PVTS exists in anionic form. It should be noted that, similar to poly-1-vinyltetrazole, PVTS decompose both in isothermal and nonisothermal conditions with elimination of nitrogen and formation of polyacrylonitrile.

The specific peculiarity of thermal behaviour of all the considered polymers excluding poly-*n*-butyl-5-vinyltetrazole is the fact that the transition from usual thermal behaviour to explosion regime is observed under relatively high heating rates (10 K min^{-1}) within a sufficiently narrow temperature range (530–545 K). Previously, we have found [135] that some tetrazole derivatives including PVT, some salts of PVT and poly-2-methyl-5-vinyltetrazole are capable of self-propagating high-temperature decomposition. An analysis of the obtained data allow one to assume that the

main factor determining the possibility of self-propagating high-temperature thermolysis of tetrazole-containing polymers are the following: (1) considerable high positive enthalpies of formation; (2) high nitrogen content in the volatile products of decomposition; (3) formation of cross-linked condensed polymer residue which acts as a heat-insulated layer and (4) «micro-mesh» character of thermolysis of polyvinyltetrazoles, when the exothermal fragmentation of one tetrazole ring is capable of inducing the splitting out of a neighbour cycle.

2.5. Combustion of tetrazole and some mixtures of high nitrogen-containing energetic substances

The combustion of individual tetrazole has been studied in detail in paper [137]. The compressed pellets of tetrazole are ignited easily and burn both in air and in inert atmosphere with formation of slightly glowing flame of vapours destruction. The linear burning rate at atmospheric pressure is about 0,45 mm/s. The performed analysis of composition of formed products allow one to conclude that the main chemical process occurring under combustion of tetrazole can be presented by the following scheme:



When investigating the burning of pressed mixtures of tetrazole and sodium tetrazolate, we revealed a previously unknown type of self-organization in combustion accompanied by formation of a peculiar dynamic dissipative structure [138, 139]. The flame formed during combustion of the above structure has the appearance of a luminous mobile fluid sphere, which leads the process accompanied by considerable gas evolution and intensive dispersion of condensed products. The revealed phenomenon received the name liquid-flame combustion (LFC) while the flame formed during LFC was named liquid-flame structure (LFS) [140]. To gain insight into the nature of this phenomenon, we carried out a comprehensive study of liquid flame combustion including the following:

(1) investigation of the process by high-speed photography and macro-photography of high spatial resolution [140]

(2) measurements of the temperature distribution on the surface of LFS and the temperature profile in a combustion wave using optical pyrometry, as well as thermocouples and electrochemical methods [140, 141]

(3) measurements of the conductivity in a combustion wave [141]

(4) investigation of the morphology of condensed products formed under liquid-flame combustion

(5) investigation of peculiarities of thermal decomposition of mixtures capable of LFC and their individual components [122, 123, 142]

(6) determining of the composition of volatile and condensed products of LFC and chemical processes occurring under LFC [142, 143]

(7) revealing of the necessary conditions for the nucleation and the development of the LFS on combustion and choosing the systems capable of LFC [141, 144]

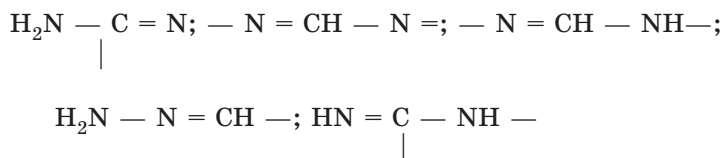
The visual examination and the detailed photographic recording of the process revealed allow us to conclude that the LFS arises only after formation of a crater on the pellet surface as a result of the development of a bubble structure from the decomposing melt foamed by gaseous products. The formed LFS represents a spheroidal envelope of melt with a multitude of gas bubbles sprinkled into the thickness of its walls. The envelope increases up to maximum size comprises 13–17 mm in diameter, until one of the bubbles forming it bursts. As a result, the pressure in the LFS falls, the envelope diminishes and regains the spheroidal form. Then the spot at which the break occurred heals under the action of the surface forces and the LFS begin increases again-repeating the evolution of the preceding one. The entry of the substance maintaining the combustion process into LFS takes place at the moment of its contact with crater surface [140].

The temperature profile measurements have shown that the temperatures inside the LFS and on its surface are approximately the same; these range, depending on the LFS's size, between 1050 an 1250 K, the temperature of small LFS's being higher than that of the large ones. The examination of the temperature distribution on the LFS surface leads to the following conclusions: (1) The LFS represents the formation of a spheroid, characterized by high uniformity of heat radiation; the difference between the maximum and the minimum temperatures on a visible surface of the LFS does not exceed 60 K (6 %); (2) One can distinguish between two types of temperature distribution on the LFS'S surface. In the first case, which is typical of small LFS's (5–6 mm in diameter), the temperature decreases smoothly with distance from its center. The second type is characterized by the presence of a distinctive plateau in the central area of the image and by the presence of a distinctive plateau in the central area of the image and by a sharp decrease in the temperature in a narrow peripheral zone. The latter is typical of LFS's of large diameter. These data suggest that small LFS's are capable of voluminous radiation whereas larger LFS's radiate as hollow envelopes with a wall thickness of ~1–2 mm; (3) occasionally observed on the LFS's surface are small regions with somewhat higher luminosity than neighbouring areas (the temperature difference may reach up to 30⁰). The appearance of such zones of local preheating is probably caused by burning down of the initial sodium tetrazolate, which gets on the interval surface of the LFS by dispersion from the melt under the LFS [141].

The dynamics of variation of signal from the electrochemical sensor under its passing through the LFS has supported the assumption that the formed LFS can be considered as an envelope containing foam-like structure [141]. The data on the morphology of internal surface of a quenched LFS obtained using optical and scanning microscopy allows that the LFS might containing gas bubbles. A characteristic size of a foam cell inside the LFS evaluated from the frequency spectrum of electrochemical sensor amounts to 2–2,5 mm while the average density of LFS estimated by a comparison of its size and the weight of product obtained by a quenching of LFS in liquid nitrogen accounts for ~0,1 g/cm³. Since the maximum size of the LFS itself does not exceed 16–17 mm, the data obtained lead to the conclusion that the average concentration of the foam inside the LFS is relatively small, and the LFS may be considered, to a considerable extent, as a hollow envelope.

To gain insight into the nature of processes occurring under LFC, we have studied the thermal decomposition of mixture and its individual components as well as the composition of the condensed and the volatile products of thermolysis and liquid-flame combustion. The main condensed product formed in the combustion wave is sodium acid cyanamide produced under thermal decomposition of sodium tetrazolate. The LFS envelope was found to consist mainly (up to 90%) of the melt of sodium acid cyanamide. Besides, the substance of the envelop contains about 5 % sodium cyanide formed under the partial decomposition of sodium acid cyanamide.

The obtained data indicate that this type of combustion is connected to the occurrence of specific chemical reactions, accompanied by the evolution of much heat and gas, with the basic gaseous product being nitrogen, and leading to the formation of of stable salts of alkali metals. The indications are that the necessary conditions for the nucleation and development of LFS on combustion are high nitrogen content in the initial substances, which have considerable thermal stability, along with large positive enthalpies of formation. Finally, the presence of definite chemical fragments and ions of alkali metals in molecules of at least one the components seems necessary. Taking into account that the cyanamide group displays a carbodiimide structure, we supposed that the following chemical fragments, which have a structure similar to that of carbodiimide group and are potentially capable of forming cyanamide ions during combustion, may be taken into consideration, namely,



and, probably, some others. Such group are contained in some types of organic compounds including 1,2,3- and 1,2,4-triazoles, guanidine and their amino-derivatives, as well as in cyanamide and products of its polymerization (dicyandiamide, melamine). We have studied the features of combustion of pressed solid mixtures of these compounds with tetrazole salts and azides of some alkali metals. As a result, more than 10 compositions have been revealed capable of LFC [141, 144]. It should be mentioned that, independently of the nature of the initial components, LFC occurs in cases when the average content of nitrogen in mixtures exceeds 63 wt.% and changes within a fairly narrow range of 63–71 wt.%. In all cases, development of the LFS is connected to the formation of acid cyanamides of an alkali metals in the combustion wave.

The results indicate that liquid-flame combustion is a relatively widespread phenomenon, which is typical of not only tetrazole derivatives, but a wide range of energetic systems of various chemical types containing large amounts of nitrogen. The stability of the LFS is probably provided by the relatively high chemical stability of the melt in combustion conditions and by a sufficiently high surface tension of the melt [141]. The LFS's envelope plays the part of heat-insulating cupola, under which and inside which the chemical processes considered above maintain the burning. The stationary nature of LFC is probably maintained by the dispersion of the condensed products from the melt under the LFS.

3. APPLICATION OF TETRAZOLES

At the present time, tetrazoles are profitably employed in medicine, biochemistry, agriculture, as prospective components of various combustible and thermally decomposing systems including solid propellants, blowing agents and initiating explosives. Some of tetrazole derivatives can be used for the selective recovering of palladium from the industrial wastes containing simultaneously Pd^{2+} , Cu^{2+} , Ni^{2+} , Fe^{2+} , Fe^{3+} , Cd^{2+} , Sn^{2+} and Al^{3+} . Among them, the effective precipitating agent, namely, 1,2-bis(1-tetrazolyl)ethane, providing the quantitative selective precipitation of palladium from solutions and the sorbent, poly-N,N'-dimethyl-5-vinyltetrazolium perchlorate, allowing the achievement of high recovering degree (up to 95-97%) of palladium in the form of PdCl_4^- have been revealed [7, 41].

The features of thermal decomposition and combustion of tetrazole derivatives, their capability of self-propagating high-temperature decomposition and liquid-flame combustion allow one to carry out a single-minded choosing of tetrazoles, which can be used as efficient components of different energetic compositions. In particular, poly-1-vinyltetrazole and sodium salt of poly-5-vinyltetrazole, which decompose at the temperatures about 155 °C and 335 °C, respectively, are suitable as highly efficient binders in formulations for the low- and high-temperature generation of pure nitrogen [132, 133]. We have elaborated several compositions for the generation of gases based on tetrazole derivatives including formulation for gas-generating devices of repeated energizing [145, 146]. Taking into account the fact that poly-N-methyl-5-vinyltetrazole (PMVT) obtained by polymer-analogous conversions of poly-5-vinyltetrazole has the composition and the properties similar to those of 2-methyl-5-vinyltetrazole homopolymer, one can conclude that the inexpensive and readily available PMVT can be used as the analogue of homopolymer in different compositions for special purposes. The introduction of about 5% of PMVT and some other polyvinyltetrazoles into the cellulose acetate based formulations for the preparation of ultra-filtration membranes followed by their decomposition provide the production of polymeric films characterized by the high uniformity of distribution of pores sizes and high retarding efficiency to the substances of molecular weight within 4000–6000 D [147].

The difficulties in the processing of polyvinyltetrazoles are connected mainly to their poor solubility in the common solvents. We developed methods for the synthesis of tetrazole-containing polymers which are readily dissolved in easily volatile organic solvents [46] and water [7] and proposed to use the aqueous solutions of some inorganic salts as solvents which are suitable both for synthesis of polymers by the polymerization and their subsequent processing [67, 148]. It has been shown also, that modified films of poly-2-tert-butyl-5-vinyltetrazole can be used as replicas for the creation of nanostructures [149].

The further investigations of tetrazole derivatives as ligands for the synthesis of complex compounds possessing the ferromagnetic properties are of great practical interest, because these complexes can be characterized by the unusual dynamic properties. Low specific weight, relatively high electric resistance and some other properties determine the significance of such materials for the creation of novel basis for the molecular electronics.

More than 60% of patents on the synthesis and application of tetrazole derivatives concern with their use in medicine. The tetrazole cycle is a constituent of a wide variety of both applied in practice and prospective drugs. Nowadays, the novel direction in the cardio-vascular therapy is the development of a new type of antihypertensives including «Lozartan» and «Valsartan» which provide the blockade of angiotensin II receptors. These medicines, containing (1-H-tetrazol-5-yl)diphenyl fragments are the most efficient among the pharmaceuticals used for the treatment of hypertension. N-Substituted tetrazoles, used in the technological schemes of synthesis of these medicinals including 2-tert-butyl-5-phenyltetrazole and 2-trityl-5-phenyltetrazole, are the most available by the developed in our works procedures.

It should be noted also a wide synthetical potentialities of simplest tetrazoles for the synthesis of different functionally substituted tetrazoles which are of great practical importance, as well as for preparation of a variety of other types of compounds including 2-aminobenzoxazoles, 2,4-quinazolinediones, arylcyanamides [8, 41, 150] and 3-methyl-5-R-pyrazoles [151].

In conclusion, it may be noted that some results of the performed investigations were published previously in reviews concerning the synthesis and properties of N-substituted tetrazoles [152], the thermal decomposition and combustion of tetrazoles [121, 153], quantum-chemical and spectroscopic study of tetrazoles [154] and synthesis, structure and properties of tetrazolium salts [42]. A significant part of our papers are embodied in reviews on the chemistry of tetrazoles [155, 156] and its separate problems (power-consuming tetrazoles [157], vinyltetrazoles [158], electrophilic reactions on the endocyclic nitrogen atoms [159]) published in the last decade.

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