INVESTIGATION OF THE THERMOLYSIS OF 5-METHYL-1-PHENYLTETRAZOLE BY COMBINED DERIVATOGRAPHY AND MASS SPECTROMETRY

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The thermolysis of 5-methyl-1-phenyltetrazole was studied at 20-350°C by derivatography and mass spectrometry, and it was shown that thermal decomposition proceeds with the elimination of a molecule of nitrogen and is accompanied by skeletal rearrangement of the intermediately formed nitrene to 2-methylbenzimidazole or migration of the methyl group to the nitrogen atom with the formation of methylphenylcarbodiimide (MPCD). In addition, symmetrical dimethyl- and diphenylcarbodiimides, methylphenylguanidines, and aniline are formed. It is assumed that the formation of these compounds in the pyrolyzate is due to polymerization of MPCD and subsequent thermal destruction of the polymerization products. A scheme for the thermolysis of 5-methyl-1-phenyltetrazole is proposed.

During a study of the mass spectra of p-substituted 5-methyl-1-phenyltetrazoles it was observed that the first step in the fragmentation of the molecular ions (M^+) is a rearrangement process that involves ejection of a molecule of nitrogen and leads to the formation of pseudomolecular ions of 5-substituted 2-methylbenzimidazole and 1-substituted 3-methyldiazirine [1]. The observed analogy between the dissociative ionization and thermal decomposition processes [2] makes it possible to assume that the formation of these compounds or their derivatives is also possible under thermal conditions.

The thermolysis of 1,5-disubstituted tetrazoles was investigated in [3, 4]. 2-Arylbenzimidazoles and diarylcarbodiimides, the overall concentration of which did not exceed 30%, were detected in the pyrolyzate. It has been reported that trace amounts of 2-methylbenzimidazole were obtained when 5-methyl-1-phenyltetrazole was heated; however, the corresponding carbodiimides or their derivatives could not be isolated [5]. Data regarding the compositions and structures of the other thermolysis products are not available. The available data regarding the composition of the pyrolyzate of 1,5-disubstituted tetrazoles do not make it possible to explain the formation of the identified products only by means of thermal decomposition.

In the present research we made a detailed analysis of the products of thermolysis of 5-methyl-1-phenyltetrazole (MPT) and made an attempt to describe the mechanism of the thermal decomposition. To solve this problem we used derivatography and mass spectrometry.

The results of thermal analysis of the phase and chemical transformations of MPT at 20-350°C are presented in Fig. 1. Two heat effects are observed on the differential thermal analysis (DTA) curve. The endothermic minimum at 100°C coincided with the melting point of the starting tetrazole, and the mass spectrum of a sample taken at this temperature was found to be identical to the mass spectrum of MPT. Consequently, the structure of MPT does not undergo any changes during the phase transformation. The loss in weight of a weighed sample of MPT observed on the differential thermogravimetric (DTG) curve reaches a maximum rate at 290°C and coincides with the peak of the exothermic process on the DTA curve at 200-310°C. Samples for mass-spectral analysis were selected with allowance for the results of derivatography (Table 1) by method A (see the experimental section).

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TABLE 1. Mass Spectra of the Pyrolyzate of 5-Methyl-1-Phenyltetrazole

Low resolution			High resolution		
thermolysis temp., °C			measured	calc.	empirical composition
200	250	290			
132 (100)	132 (100)	132 (100)	132,0688	132,0675	$C_8H_8N_2$
		146 (12,6)	146,0798	146,0843	$C_9H_{10}N_2$
160 (0,4)	160 (0,32)	160 (0,26)			
		163 (11,3)	163,1136	136,1109	$C_9H_{13}N_3$
	194 (0,75)	194 (47,4)	194,0811	194,0843	$C_{13}H_{10}N_2$
	202 (0,1)	202 (6,3)			
	225 (0,04)	225 (40,0)	225,1301	225,1265	$C_{14}H_{15}N_3$
		250 (9,5)			
	264 (0,9)	264 (91,6)	264,1342	264,1374	$C_{16}H_{16}N_4$
		287 (60,0)	287,1468	287,1422	$C_{19}H_{17}N_3$
		312 (0,16)			
	319 (0,01)	319 (0,18)			
	326 (0,03)	326 (9,5)	326,1505	326,1531	$C_{21}H_{18}N_4$
	334 (0,04)	334 (13,7)	334,1879	334,1905	$C_{19}H_{22}N_6$
	396 (0,02)	396 (34,6)	396,2045	396,2062	$C_{24}H_{24}N_6$
		458 (4,1)			
		528 (0,6)			

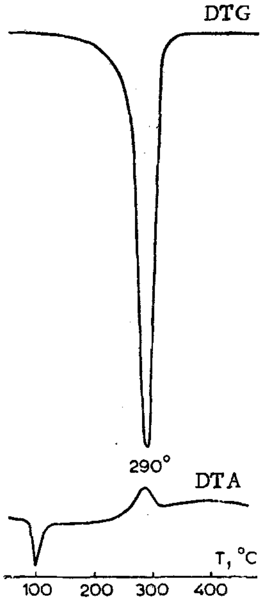


Fig. 1. Derivatogram of the thermolysis of 5-methyl-1-phenyltetrazole.

The loss in weight of a weighed sample of MPT during the exothermic reaction was 96%. This value appreciably exceeds the weight loss that one should have expected in the case of splitting out of a molecule of N_2 during thermolysis (17.5%) previously observed [3, 4] for 1,5-disubstituted tetrazoles. Consequently, other volatile products are formed, and (or) intensive evaporation of MPT itself occurs. An analysis of the pyrolysis products (including the gas phase) carried out in a closed system under the same temperature conditions (method B) with subsequent analysis of the composition did not demonstrate differences in the composition of the products obtained under different experimental conditions. At the same time, the relative percentages of the individual components are determined by the thermolysis conditions, and the pyrolytic mixture is enriched in compounds with higher molecular weights in the case of method A (Table 2).

The mass spectra were recorded by means of direct introduction of the samples into the ion source and by introduction through a chromatographic column (chromatographic mass spectoscopy). The difficulties that arise in the identification of the molecular and fragment ions in the first case (Table 1) were eliminated by means of the technique of chromatographic mass spectroscopy [6], which, although it makes it possible to obtain the mass spectra of the individual components of the pyrolyzate, nevertheless does not exclude errors, since thermocatalytic transformations of the sample under analysis and possibly complete retention of some of the nonvolatile compounds in the column may occur under the conditions of gas-liquid

TABLE 2. Mass Spectra of the products of Thermolysis of 5-Methyl-1-phenyltetrazole

I: Ph—NH_2; 39 (17,3), 40 (5,8), 51 (4,3), 52 (5,2), 65 (22,3), 66 (37,4), 67 (9,0), 92 (10,0), 93 (100,0), 94 (6,5); 2,4%; 0.8 **min.**

II: $CH_3N{=}C{=}NPh$; 51 (15,3), 64 (10,0), 65 (12,7), 77 (33,3), 91 (14,7), 103 (5,3), 104 (5,3), 117 (4,7), 131 (40,0), 132 (100,0); 4,6%; 2,8 **min.**

II′: $CH_3NHC(OCH_3){=}NPh$; 58 (40,1), 64 (21,0), 65 (26,3), 72 (36,8), 77 (57,9), 91 (73,7), 92 (26,3), 106 (84,2), 107 (57,9), 118 (21,0), 119 (57,9), 120 (21,0), 132 (5,8), 133 (31,6), 134 (10,5), 159 (5,0), 163 (21,5), 164 (100,0); 4,6%; 3,6 **min.**

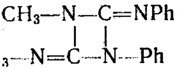
III: **1,2–dimethylbenzimidazole** 51 (15,8), 58,5 (3,6), 77 (29,0), 104 (15,8), 118 (4,2), 119 (4,4), 131 (47,5), 132 (18,4), 145 (47,4), 146 (100,0); 1,8%; 5,9 **min.**

IV: **2-methylbenzimidazole** 63 (14,5), 64 (12,0), 65 (10,0), 66 (8,3), 77 (6,0), 90 (6,8), 91 (4,9), 92 (7,8), 104 (9,3), 131 (65,4), 132 (100,0), 133 (7,7); 9,2%; 8,0 **min.**

V: $CH_3NHC(NHPh){=}NCH_3$; 63 (12,0), 64 (11,0), 65 (8,0), 77 (5,2), 90 (5,8), 91 (4,6), 92 (68,0), 104 (6,4), 118 (3.0), 131 (60,0), 132 (100,0), 133 (9,6), 163 (2,0); 4,6%; 8,6 **min**.

VI: $PhN{=}C{=}NPh$; 51 (21,4), 63 (4,8), 65 (5,2), 77 (31,4), 91 (18,6), 97 (3,0), 103 (4,8), 104 (4,3), 118 (3,8), 194 (100,0), 195 (23,8); 18,4%; 10,4 **min.**

VI′: $PhNHC(OCH_3){=}NPh$; 51 (33,8), 63 (9,1), 64 (14,0), 65 (19,0), 77 (66,7), 91 (66,7), 92 (10,0), 93 (11,3), 97 (3,3), 103 (5,2), 104 (6,2), 106 (19,0), 107 (13,3), 119 (100,0), 134 (66,7), 167 (3,8), 169 (5,2), 194 (96,0), 195 (25,0), 210 (4,8), 225 (14,3), 226 (61,9), 227 (7,6); 18,4%; 11 **min.**

VII: 
$$\begin{array}{l} CH_3{-}N{-}C{=}NPh \\ \quad\;\; | \quad\, | \\ CH_3{-}N{=}C{-}N{-}Ph \end{array}$$
; 77 (25,0), 91 (9,4), 131 (21,5), 132 (100,0), 133 (9,4), 194 (25,0), 195 (4,1), 207 (7,5), 208 (0,2), 264 (3,3); 3,0%; 11,7 **min.**

VIII: $CH_3NHC(NHPh){=}NPh$; 77 (46,2), 91 (16,2), 92 (8,5), 93 (100,0), 104 (6,5), 105 (3,8), 116 (6,8), 118 (17,3), 131 (19,2), 132 (65,4), 159 (4,6), 166 (5,0), 169 (3,0), 188 (5,8), 194 (17,3), 208 (3,0), 210 (4,3), 224 (7,0), 225 (38,5); 4,0%; 13 **min**

IX: **triphenylguanidine** 65 (13,3), 66 (10,0), 77 (31,3), 91 (15,3), 92 (11,3), 93 (40,0), 194 (100,0), 195 (20,0), 220 (3,3), 249 (3,0), 250 (4,7), 264 (2,4), 287 (11,0); 11,3%; 16,8 **min.**

X: **trimer of carbodiimides** II **and** VI: 77 (21,6), 91 (17,4), 131 (13,0), 132 (100.0), 133 (13,0), 194 (6,5), 326 (17,4), 327 (4,0); 3,0%; 17,6 **min.**

XI: **dimer of dimethylcarbodiimide and two molecules of carbodiimide** II; 77 (14,2), 91 (6,7), 103 (2,0), 104 (3,0), 131 (14,2), 132 (100,0), 194 (4,2), 243 (3,5), 284 (3,0), 334 (19,2); 6,0%; 18,3 **min**

VII: **trimer of carbodiimide** II; 77 (41,7), 91 (16,7), 93 (16,7), 131 (20,8), 132 (100,0), 133 (12,5), 194 (62,5), 234 (2,5), 305 (3,1), 325 (3,3), 326 (7,3), 396 (33,3); 3.0%; 20,4 min.

XIII: **trimer of carbodiimide** II: 77 (23,0), 91 (9.2), 131 (21,5), 132 (100,0), 133 (15,4), 194 (12,4), 264 (3,0), 305 (3,0), 396 (35,4); 29,0%; 22 **min.**

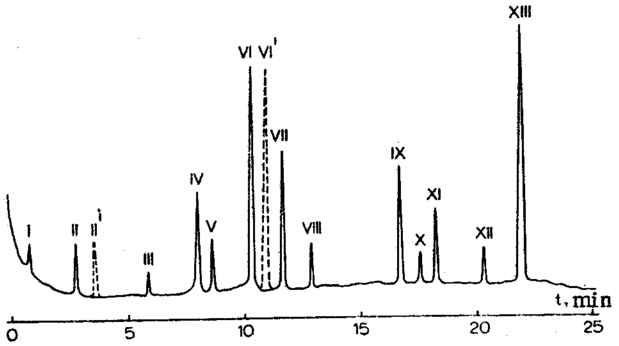


Fig. 2. Chromatogram of a sample of the pyrolyzate at 290°C in solution in acetone (———) and methanol (– – –).

chromatography (GLC). The method of direct introduction of the samples does not have this disadvantage and also makes it possible to obtain high-resolution mass spectra.

The course of the thermolysis of MPT as the temperature is raised can be observed from the data in Table 1. An analysis of the mass spectra of samples of the pyrolyzate taken successively at 200, 250, and 290°C shows an appreciable decrease in the relative intensity of the M^+ peak of the starting tetrazole (m/e 160). At 250°C peaks of ions with higher mass numbers appeared in the mass spectrum of the pyrolyzate. The relative intensities of these peaks increased as the temperature and heating time were increased. The appearance of additional peaks of ions with mass numbers 146, 163, 458, and 528 indicates the formation of new thermolysis products.

The chromatogram of a sample of the pyrolyzate taken at 290°C is shown in Fig. 2. The mass spectra of each component in the order of its energence, the retention times, the relative percentages, and the structures of the thermolysis products are presented in Table 2. A number of compounds in the pyrolytic mixture were identified by comparison of the emergence times and the mass spectra. Thus it was established that 2-methylbenzimidazole (IV), diphenylcarbodiimide (VI), and aniline (I) are present in the pyrolyzate. The problem of the structure of component III was solved by comparison of its mass spectrum with the mass spectrum of 1,2-dimethylbenzimidazole [7].

The methylphenylcarbodiimide structure for fraction II follows from the analogy in the M^+ fragmentation pathways of II and VI. The addition of alcohol, which can be expected for carbodiimides as structural analogs of ketenes (II' and VI', Table 2 and Fig. 2), serves as an additional confirmation of this assignment. Chromatographic mass-spectral analysis of a solution of a portion of the pyrolyzate in methanol showed the appearance of an additional chromatographic peak of II' with a molecular weight of 164. The observed character of the fragmentation of M^+ under electron impact is in complete agreement with the addition product (Table 2). A similar reaction is also observed for diphenylcarbodiimide (see the mass spectrum of VI').

According to the data from high-resolution mass spectrometry (Table 1) V, VIII, and IX, which have odd-numbered molecular weights of 163, 225, and 287, respectively, contain three nitrogen atoms and differ in composition by a C_5H_2 fragment; considering the structure of the starting tetrazole, this can be explained by replacement of a methyl group by a phenyl group. Elimination of aniline in the first step of the M^+ fragmentation of VIII and IX gives fragment ions with m/e 132 and 194, the subsequent fragmentation of which recalls the spectra of carbodiimides II and VI (Table 2). These data, as well as the presence of aniline in the pyrolyzate, make it possible to regard V, VIII, and IX as products of the addition of aniline to carbodiimides II and VI and $CH_3-N=C=N-CH_3$, i.e., as the corresponding guanidines. This conclusion is confirmed by treatment of a portion of the pyrolyzate with aniline and subsequent analysis by chromatographic mass spectroscopy. The triphenylguanidine structure for fraction IX was proved by alternative synthesis of this substance from aniline and model compound VI and by comparison of their chromatographic labilities and mass spectra.

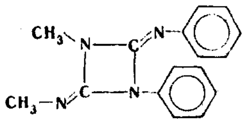
The structure of component V may serve as an indirect confirmation of the formation of dimethylcarbodiimide under thermolysis conditions, although this compound itself was not detected by chromatographic mass-spectral analysis. From the noted difference in the chromatographic mobilities of fractions II and VI (9 min, Table 2), it may be assumed that dimethylcarbodiimide emerged from the column together with the solvent. To verify this assumption, we analyzed the gas phase of the pyrolyzate (method B) and by means of mass fragmentation detected the presence of a compound with M^+ 70, which corresponds to the molecular mass of dimethylcarbodiimide.

The formation of compounds with molecular weights that exceed the molecular weight of MPT (Table 1) is naturally associated with polymerization of the carbodiimides. A theoretical

TABLE 3. Composition of the Products of Copolymerization of $CH_3N=C=NCH_3$ (a), $CH_3N=C=NPh$ (b), and $PhN=C=NPh$ (c)

Polymer	M of the polymerization products	Polymer	M of the polymerization products
2a	140	2a+b	272
2b or a+b	264	2a+c or a+2b	334
2c	388	2b+c or a+2c	458
a+b	202	2c+b	520
b+c	326	4a	280
3a	210	4b	528
3b	396	4c	776
3c	582		

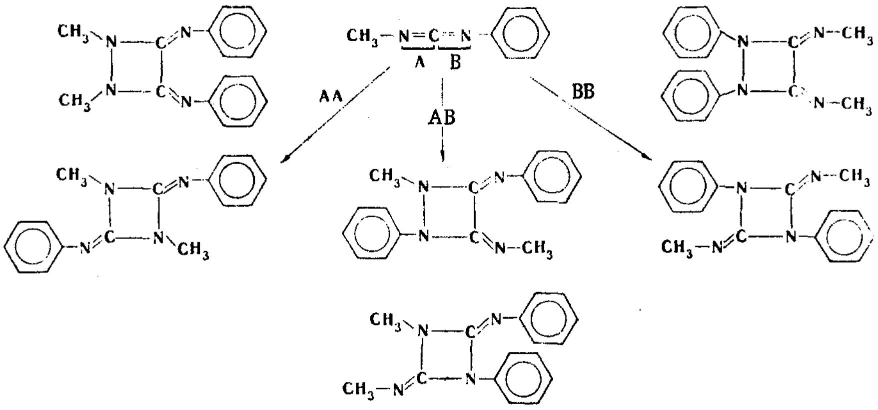
analysis of the possible composition of the polymeric products of the investigated reaction is presented in Table 3. The dimers with molecular weights of 264, 326, and 334 correspond to fractions VII, X, and XI, respectively (Fig. 2). A trimer with a molecular weight of 396 is represented by two fractions, viz., XII and XIII, and this indicates the formation of isomers. The empirical compositions of the corresponding ions were confirmed by the high-resolution spectra. Identification of the polymerization products on the basis of the available data is not possible because of the multivariant character of the system. Thus the dimerization of methylphenylcarbodiimide through opening of two nonequivalent C—N bonds and addition of the "head-to-tail" and "head-to-head" type (Scheme 1) theoretically gives six possible structures. The data from chromatography and the mass spectra indicate the formation of only one product with the structure from which the observed elimination of a fragment with 70 amu ($CH_3{-}N{=}C{=}N{-}CH_3$) from M^+ may be assumed.



The number of possible structures to which the theoretical analysis of the polymerization process leads increases sharply when one examines the copolymerization products or trimers. In this case the mass-spectrometric data are not adequate for an unambiguous interpretation.

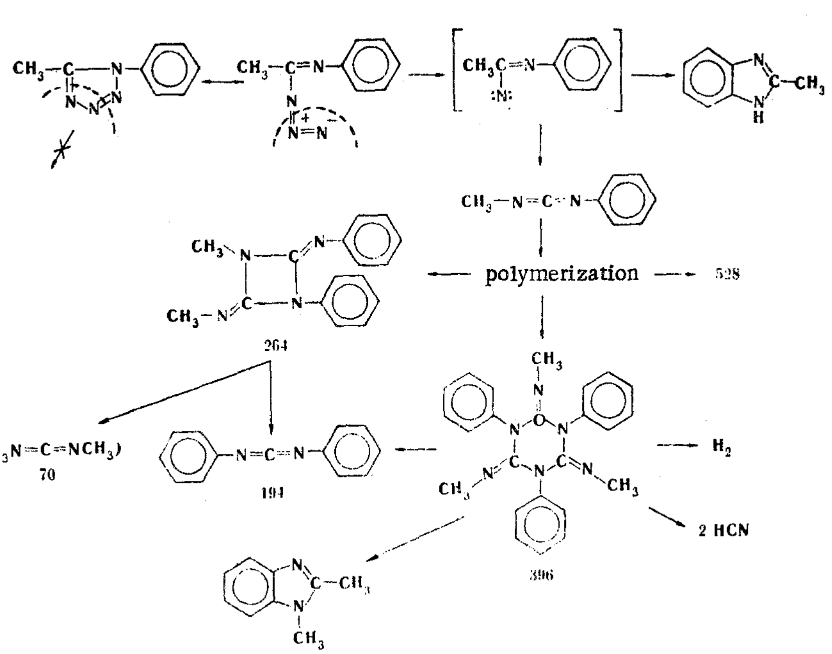
Fractions with molecular weights of 158 and 528 were not detected during an analysis of the pyrolyzate by chromatographic mass spectroscopy. This is the only difference from the mass-spectral data obtained by the direct introduction method and consequently may affirm that the components of the pyrolyzate do not undergo thermal destruction under the chromatographic conditions.

Scheme 1



The compositions and structures of the identified products (Table 2), the derivatographic data, and the dynamics of the thermolysis process (Table 1) show that the thermal decomposition of MPT involves the ejection of a molecule of nitrogen. The theoretical structure of the starting tetrazole permits two pathways for elimination of a molecule of nitrogen, viz., ejection of N_2—N_3 or N_3—N_4 atoms. In the latter case, in analogy with the thermolysis of 5-substituted tetrazoles [8], one might expect the formation of derivatives of triazoles and tetrazines. The absence of these compounds in the composition of the pyrolyzate constitutes evidence in favor of elimination of the N_2—N_3 atoms. This selectivity in the direction of the thermolysis of MPT is understandable, if one assumes that the starting structure under the influence of the temperature undergoes a tautomeric transformation to the azide form (Scheme 2); splitting out of a molecule of nitrogen proceeds with the formation of a nitrene, the stabilization of which is possible either through intramolecular cyclization to benzimidazole or through migration of a methyl group to the nitrogen atom with the formation of a carbodiimide. This thermolysis scheme, which was previously proposed to explain the formation of only benzimidazoles [5], is also valid for the explanation of the formation of all the compounds that are detected in the pyrolyzate.

Scheme 2



The origin of the remaining products is evidently associated with polymerization of methylphenylcarbodiimide and subsequent thermal destruction of the polymers. Symmetrical carbodiimides, the copolymerization of which with carbodiimide II leads to the formation of compounds with molecular weights of 326 and 334, are formed in this way. The subsequent thermolysis of the trimer (one of the possible structures is presented in the scheme) proceeds in accordance with the stoichiometry to give diphenylcarbodiimide, 1,2-dimethylbenzimidazole, hydrogen, and hydrogen cyanide. The evolved hydrogen probably participates in the formation of aniline. Of course, the proposed scheme for the formation of the compounds under consideration is hypothetical in many respects, but it nevertheless explains the appearance of the products that are detected in the pyrolyzate.

EXPERIMENTAL

The thermal analysis was made with a MOM derivatograph (Hungary) under the following conditions: the temperature ranged from 20 to 350°C, the heating rate was 5 deg/min, the crucible charge was 150 mg, and the reference sample was calcined Al_2O_3. Samples were selected directly from the crucible of the derivatograph at the temperatures of the maxima of the heat effects observed on the DTA curve (method A). In view of the possibility of the formation of volatile products, the conditions of thermal analysis (the heating rate, the temperature at which samples were selected, etc.) were reproduced in the thermolysis of the tetrazole in a sealed glass ampul. The ampuls were frozen in liquid nitrogen prior to opening (method B).

The mass-spectrometric studies were made with a Varian MAT 311-A mass spectrometer by means of direct introduction of the samples into the ion source and by chromatographic mass spectrometry. The recording conditions were as follows: the accelerating voltage was 3 kV, the electron energies were 70 and 20 eV, the cathode emission current was 300 μA, and the temperature of the ionization chamber was 200°C. The high-resolution ($M/\Delta M = 15000$) spectra were obtained under the same conditions with perfluorinated kerosene as the standard.

The chromatographic studies were made with a 180 by 0.2 cm glass column filled with 1.5% Merck OV-101 on Merck Chromosorb WHP (100-120 mesh). The carrier-gas (He) flow rate was 2 ml/min, the column temperature was 80-300°C, and the heating rate was 10 deg/min.

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