Mechanism of the monomolecular thermal decomposition of tetrazole and 5-substituted tetrazoles

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The kinetic parameters of the thermal decomposition of tetrazole and 5-alkyl- and 5-aryl-substituted tetrazoles in melts of neat substances and in nitrobenzene solutions have been determined using the manometric method. The limiting stages of the monomolecular decomposition, which determine the observed rate of nitrogen formation, include the fast reversible transformation of the 1*H*- and 2*H*-forms and the reversible opening of the 2*H*-form followed by the formation and subsequent cleavage of the corresponding intermediate diazo compound.

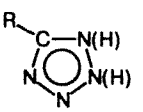
Key words: 5-substituted tetrazoles, thermal decomposition; monomolecular reactions.

In a continuation of the study[1] of the kinetics and mechanism of the monomolecular decomposition of disubstituted tetrazoles, we studied the thermal decomposition of tetrazole and a series of its 5-substituted derivatives. Comparatively high melting points (>200 °C) are typical of the latter, which make it possible to study the mechanism of their monomolecular decomposition in the crystalline state. This requires detailed information on the mechanism and parameters of the decomposition under conditions that are not complicated by collective effects. Another peculiarity of these compounds is the known ease of the prototropic tautomerism[2] of azoles, which hampers the determination of the parameters of the initial state of tetrazole[3] and some its 5-substituted derivatives. The presence of a hydrogen atom at positions 1 and 2 of the heterocycle should result in distinctly different stability levels (rate constants of monomolecular decomposition) and a fairly weak influence of the substituents at position 5.[1] Therefore, it is of interest to estimate the direct effect of prototropic tautomerism on the parameters of decomposition.

As in the previous work,[1] our main attention here is paid to the correlation between the observed rate of the decomposition of tetrazoles and the reactions determining its value.

Experimental

Tetrazole (**1**) and its 5-substituted derivatives **2**—**8** were synthesized and purified by the known methods. The properties of the compounds obtained corresponded to the published data.[4,5]



1—**8**

R = H (**1**), 5-tetrazolyl (**2**), Me (**3**), C_2H_3 (**4**), Ph (**5**), *p*-$MeOC_6H_4$ (**6**), *m*-$NO_2C_6H_4$ (**7**), *p*-ClC_6H_4 (**8**)

The kinetic studies of the thermal decomposition of tetrazoles were carried out using the manometric procedure described in the previous work.[1] The decomposition of compounds **1** and **3** was studied in the gas phase (GP), and the completeness of the transition of a sample (~2 mg) into the vapor state was monitored. Since the increase in pressure when tetrazole **3** decomposes is very low, the attempts to determine the parameters of its GP-decomposition failed. The decomposition of compounds **1**, **3**, and **5** were also studied in the liquid phase (LP), *i.e.*, in a melt of the initial substance, while that of compounds **1**—**8** was studied in nitrobenzene solutions at initial concentrations of 0.05—0.10 mol L^{-1}.

Results and Discussion

The complete decomposition of tetrazoles **1** and **3**—**8** results in the formation of not less than 1 mole of N_2, while the decomposition of compound **2** gives 2 moles of N_2. The kinetic curves are first-order up to degrees of transformation not less than 80—95%.

The first-order rate constants obtained and the activation parameters calculated from them, which characterize the elimination of nitrogen from the tetrazole cycle, are presented in Tables 1 and 2, respectively.

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Table 1. Observed rate constants (k_{obs}) of the thermal decomposition of tetrazoles in the gas phase, liquid phase, and in a nitrobenzene solution

T/°C	$10^5 \cdot k_{obs}/s^{-1}$											
	1			**2**,	**3**		**4**,	**5**		**6**,	**7**,	**8**,
	GP	LP	$PhNO_2$	$PhNO_2$	$PhNO_2$	LP	$PhNO_2$	$PhNO_2$	LP	$PhNO_2$	$PhNO_2$	$PhNO_2$
150	—	—	0.92	—	—	—	0.34	—	—	—	—	—
160	—	—	2.4	—	0.26	—	1.1	0.61	—	0.81	0.63	0.57
170	—	—	6.3	—	0.66	—	3.6	1.9	—	2.3	1.8	1.7
180	7.5	11	13	3.3	1.9	1.9	10	4.4	—	6.5	5.4	5.1
190	18	28	28	8.9	5.4	5.6	24	13	—	16	13	13
200	34	66	—	26	15	16	61	33	—	44	36	36
210	70	150	—	55	35	41	—	79	—	—	—	—
220	150	320	—	130	80	100	—	180	190	—	—	—
230	265	—	—	—	—	—	—	—	410	—	—	—

Table 2. Activation parameters of the thermal decomposition of tetrazoles **1**—**8** in the gas phase, liquid phase, and in a nitrobenzene solution

Parameter	**1**			**2**,	**3**		**4**,	**5**,	**6**,	**7**,	**8**,
	GP	LP	$PhNO_2$	$PhNO_2$	$PhNO_2$	LP	$PhNO_2$	$PhNO_2$	$PhNO_2$	$PhNO_2$	$PhNO_2$
E/kcal mol^{-1}	32.3 ±1.4	37.4 ±0.9	33.2 ±2.1	40.8 ±2.8	41.3 ±1.2	43.8 ±0.8	41.2 ±1.7	40.3 ±1.1	40.4 ±1.3	41 ±1.6	42.1 ±1.0
$\log(A/s^{-1})$	11.5 ±0.7	14.1 ±0.4	12.1 ±1.0	15.2 ±1.3	15.2 ±0.6	16.4 ±0.4	15.8 ±0.8	15.1 ±0.5	15.3 ±0.6	15.5 ±0.8	16 ±0.5
$\Delta S^{\neq}$/cal mol^{-1} deg^{-1}	— —	3.0 ±1.9	−5.7 ±4.7	8.1 ±5.9	8.2 ±0.7	13.6 ±1.8	11.2 ±3.8	7.7 ±2.4	8.7 ±2.9	9.5 ±3.4	11.8 ±2.2

The determined rate constant of the decomposition of 5-phenyltetrazole **5** in nitrobenzene at T = 180.6 °C is only 9% higher than the value measured previously.[6] The rate constants of the decomposition of compounds **1**, **3**, and **5** in solutions of $PhNO_2$ and in melts differ insignificantly, *i.e.*, the rate constant is independent of the concentration. In the case of tetrazole **1**, a change in the concentration affects the activation parameters, which for its decomposition in a melt are close to the values obtained for the other compounds. The rate constants of the decomposition of tetrazole **1** in the GP are on the average twofold lower than those in a melt or in a nitrobenzene solution, and both the activation energy and entropy are decreased.

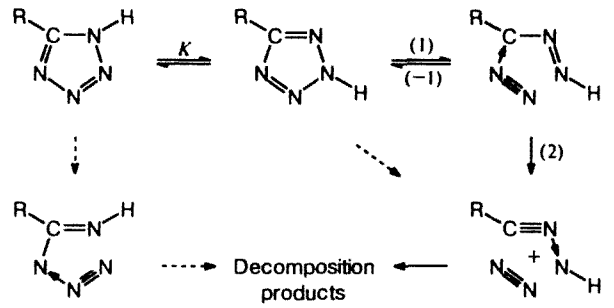
As in the case of disubstituted tetrazoles,[1] high values of the activation entropies are typical of the decomposition of compounds **2**—**8**. The maximum change in the rate constants of the decomposition of tetrazoles **1**—**8** corresponds to the previously mentioned[1] weak sensitivity of the decomposition rate on the nature of the substituent at the C atom of the heterocycle. On the average, the rate constants of the decomposition of compound **3** are 5—10 and 10^3 times greater than those determined for 2,5- and 1,5-dimethyltetrazoles, respectively.

It follows from these data that the decomposition of compounds **1**—**8** results in the elimination of an N_2 molecule mainly from the 2*H*-form of the tetrazole cycle, while the 1*H*-form is almost stable under the experimental conditions. This is also consistent with many known data[7] on the possibility of the almost quantitative "capture" of intermediate nitrile imines in the decomposition of 5-substituted tetrazoles in the presence of dipolarophiles.

Some authors[3] point out the experimental evidence that the 1*H*-form of tetrazole and 5-substituted tetrazoles predominates in solutions at room temperatures. The parameters of the prototropic tautomerism of tetrazoles are still unknown, but they should not differ substantially from those measured for other azoles. It has been shown[2] that even monomolecular prototropic shifts of triazoles and pyrazoles occur very easily, because the energy barrier does not exceed 7 kcal mol^{-1}. Therefore, the main channel of the thermal decomposition of tetrazoles **1**—**8** should include, along with the reversible formation and subsequent cleavage of intermediate azodiazo compounds substantiated in our previous work,[1] very fast tautomerism according to Scheme 1.

Here K is the equilibrium constant, and the rates of the direct and reverse reactions of this equilibrium are considerably higher than the rates of reactions (1), (−1), and (2). The parallel decomposition channels, which, according to our data,[1] do not make a noticeable contribution to the observed rate constants, are shown in

Scheme 1



Scheme 1 by dashed arrows. For example, the predominance of concerted, one-stage retro-1,3-cyclization to form a nitrogen molecule and the corresponding nitrile imine at the kinetic decomposition parameters determined is as improbable here as for 2,5-disubstituted tetrazoles.[1] In the opposite case, this would imply that direct 1,3-cycloaddition between these molecules would be easy, which contradicts the known inertness of nitrogen even in reactions with carbenes.

Under quasi-stationary conditions with respect to the concentrations of the intermediate diazo compounds, the observed rate constant of decomposition (k_{obs}) should include a coefficient taking into account the fast prototropy:

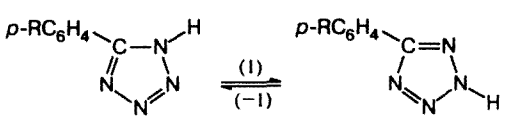
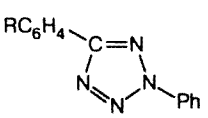
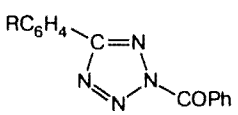
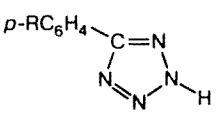
$$k_{obs} = [K/(K+1)] \cdot [k_1k_2/(k_{-1}+k_2)];$$
at $k_{-1} \gg k_2$: $k_{obs} = [K/(K+1)] \cdot k_1k_2/k_{-1}$.

The existence of the equilibrium between the decomposing 2*H*-forms and the 1*H*-forms, which are almost stable under the experimental conditions means the observed rate constant of the decomposition is lower than the value determined by the barriers of the "elementary" reactions (1), (−1), and (2), because the ratio $K/(K+1)$ is always <1.

There is a distinct linear dependence between the rate constants of the decomposition of 1-R-5-R′- and 2-R-5-R′-disubstituted tetrazoles, the main contribution to which is made by the change in the rate constants of the opening of the heterocycles.[1] It can be expected that the corresponding data for the compounds with R = H will not distort this regularity due to the common mechanism of decomposition. As can be seen from a comparison with the data obtained previously for disubstituted tetrazoles,[1] 2*H*-tetrazoles decompose more slowly than 2-Ph-substituted derivatives and more rapidly than 2-Me-substituted derivatives. This corresponds to the ratios between the isomerization[8] rates of 5-arylamino- and 1-R-5-aminotetrazoles, in which a change in the rate is also determined by the slowest stage, which is the opening of the cycles (in which the effect of the R^5 substituent is also rather weak). It is difficult to analyze these compounds in more detail, because the data on these complicated transformations are limited.

In compounds **1**—**8**, the maximum rate constants were determined for the decomposition of tetrazole **1**. This can be partially associated with a somewhat greater (compared to compounds **2**—**8**) shift of the prototropic equilibrium to the formation of the 2*H*-form, especially in the GP. Probably, one of the reasons for the decrease in the rate constants and activation parameters of the thermal decomposition of tetrazole **1** in the GP is the

Table 3. Effects of substituents on the prototropic equilibrium and reaction rates of the thermal decomposition of tetrazoles

Reaction	*T*/°C	Solvent	ρ*
	23	$(CD_3)_2SO$	0.536[9]
	166	1-Cl-naphthalene	−0.24[10]
	70	MeCN	−0.65[11]
	185.6 180.6	PhCN	0.0049[6] 0.019[6]

* Calculated from the published data.

small size of this heptaatomic molecule and, hence, the occurrence of the reaction in the nonequilibrium region. In fact, on the one hand, there are no grounds for assigning the specific character of the decomposition of tetrazole **1** to the C—H fragment; on the other hand, we obtained "normal" values for the kinetic parameters for the decomposition of compound **2**, which can be considered in the given case to be a dimer of nonsubstituted tetrazole **1**.

The fact that it is necessary to take into account the prototropic equilibrium in the estimation of the thermal stability of tetrazoles not substituted at the N atom corresponds to the data obtained previously.[6] It has been established[6] that for the thermal decomposition (180.6 °C) of compound **5** in 0.18 *M* solutions in benzonitrile, nitrobenzene, dimethylaniline, diphenyl ether, and diphenylmethane the values of $10^5 \cdot k_{obs}$ are equal to 2.4, 4.6, 5.6, 12.1, and 13.5 s^{-1}, respectively. The authors of Ref. 6 explained this considerable change in the rate constants of the decomposition of compound **5** in this series of aprotic solvents by the shift of the acid-base equilibrium

$$\mathbf{5} \rightleftharpoons H^+ + B^-,$$

where B is the conjugated base, and compared (without any verification of the correlation) the rate constants of the decomposition and the values of the electroconductivity (resistance) of the solvent. The data in Table 3 indicate that the acid-base equilibrium plays an insignificant role and the prototropic equilibrium has the determining role. For example, for the first three compounds, the effects of the substituents at position 5 of the tetrazole cycle on the prototropic equilibrium constant (of 5-aryl-substituted tetrazoles) is the opposite of their effects on the rate constants of decomposition (of 2,5-disubstituted tetrazoles). The fact that the rate constants of the decomposition of 5-aryl-substituted tetrazoles are almost independent ($\rho \approx 0$) of the nature of the substituent (see the latter compound in Table 3) shows that the opposite effects of the factors mentioned above nearly completely balance each other out in benzonitrile.

The parameters obtained for decomposition in a nitrobenzene solution also correspond to a very weak dependence of the rate constants of the decomposition on the structure of the molecule of 5-substituted tetrazoles.

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