Mechanism of the monomolecular thermal decomposition of 1,5- and 2,5-disubstituted tetrazoles

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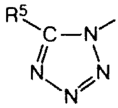
The kinetic parameters of the thermal decomposition of several pairs of 1(2)-R-5-R′-disubstituted tetrazoles have been determined using the manometric method. The isomers differ only by the position of the substituents linked with the heterocyclic nitrogen atom. The activation entropies are equal to *ca.* +8 cal mol^{-1} K^{-1}, the activation energies range from 39 to 48 kcal mol^{-1}. A linear correlation between the logarithms of the rate constants of decomposition of the isomers has been established. The limiting stages of the stepwise mechanism of the monomolecular decomposition, which determines the experimental rates of nitrogen evolution, include the reversible formation followed by decomposition of intermediate azidoazomethines in the case of 1,5-disubstituted tetrazoles and azodiazo compounds for isomeric 2,5-disubstituted tetrazoles. The enthalpies of formation of $R(N_3)C{=}NR$ (R = Me, Ph), $C_2H_3(N_3)C{=}NMe$ and increments $\Delta_fH°[C_d{-}(C)(N_3)]$, $\Delta_fH°[C_d{-}(C_b)(N_3)]$, and $\Delta_fH°[C_d{-}(C_d)(N_3)]$ have been estimated.

Key words: disubstituted tetrazoles, thermal decomposition; monomolecular reactions.

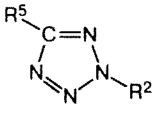
The thermal stability of 1,5- and 2,5-disubstituted tetrazoles[1,2] has been characterized only qualitatively, because data on the kinetics of their thermal decomposition are scarce and not systematized.[1–6] Meanwhile, tetrazoles are convenient objects for the study of general regularities of monomolecular reactions in different phases.

The purpose of this work is to obtain kinetic parameters of the monomolecular decomposition of several isomeric tetrazoles in order to give a more detailed basis for the mechanism of the reactions determining the observed decomposition rate and its relation with the structure of a molecule in the absence of an effect of the aggregate state of a substance.

The objects of the study are 1,5- and 2,5-disubstituted tetrazoles **1** and **2**.



1a—e



2a—e

a: $R^1 = R^2 = R^5 = Me$
b: $R^1 = R^2 = Me$, $R^5 = CH_2{=}CH$
c: $R^1 = R^2 = Me$, $R^5 = Ph$
d: $R^1 = R^2 = CH_2COMe$, $R^5 = Me$
e: $R^1 = R^2 = NH_2$, $R^5 = Ph$

Experimental

Compounds **1a—e** and **2a—e** were prepared and purified by the known methods,[1,2,7] and their properties corresponded to the published data.

Thermolysis was carried out at low initial pressures in the gas phase (GP) and at low concentrations in a solution of nitrobenzene, to ensure the monomolecular character of the decomposition. Nitrobenzene was purified by fractional crystallization and triple distillation over P_2O_5 and was used as a thermally stable solvent with a rather low pressure of saturated vapor.

The kinetics of the thermal decomposition was studied under isothermal (±0.05 °C) conditions by a manometric method using 500-mL Bourdon flasks (in the gas phase) or in $PhNO_2$ (5—8 mL). The pressure in the reaction vessel was detected continuously during fast (not less than 50 °C min^{-1}) heating of an air thermostat up to the temperature of the experiment and then during the thermal decomposition of the substance.

In the experiments on the gas-phase decomposition, the moment of the transition of a sample into the vapor state was controlled. The initial pressure in a glass reactor at $T < 300$ °C did not exceed 5—7 Torr. The kinetic curves obeyed first-order kinetics up to achieved degrees of conversion of the initial tetrazole not less than 80—95%.

The kinetics of the thermal decomposition of nonvolatile tetrazoles **1e** and **2e** were studied only in nitrobenzene solutions. The procedure of the study of the decomposition in $PhNO_2$ was developed using samples of compounds **2a—c**. The initial concentrations of tetrazoles did not exceed 1 wt.%. During one experiment, at the temperatures T_{min},

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Table 1. Observed rate constants (k_{obs}) of thermal decomposition of tetrazoles **1** and **2** in the gas phase and in nitrobenzene

GP										PhNO$_2$					
T/°C	$10^5 \cdot k_{obs}$/s^{-1}				T/°C	$10^5 \cdot k_{obs}$/s^{-1}				T/°C	$10^5 \cdot k_{obs}$/s^{-1}				
	1a	**1b**	**1c**	**1d**		**2a**	**2b**	**2c**	**2d**		**2a**	**2c**	**2d**	**1e**	**2e**
230	—	—	—	5.5	190	1.2	—	2.0	13	150	—	—	—	—	2.0
240	—	—	1.8	13	200	3.5	—	4.9	36	160	—	—	0.31	0.18	6.0
250	—	—	4.0	31	210	8.1	8.8	14	82	170	0.071	—	0.94	0.54	17
260	—	—	10	71	220	20	22	30	190	180	0.21	0.40	2.8	1.4	42
270	10	8.6	24	150	230	50	60	74	420	190	0.69	1.0	7.6	3.8	110
280	24	20	51	310	240	100	120	180	—	200	1.7	2.6	21	9.0	—
290	48	42	110	—	250	250	270	—	—	210	4.1	7.1	48	22	—
300	95	84	—	—	260	510	—	—	—	220	9.2	16	—	—	—
310	210	170	—	—						230	—	41	—	—	—
320	410	360	—	—											
330	—	710	—	—											

Table 2. Activation parameters of thermal decomposition of tetrazoles **1** and **2** in the gas phase and in nitrobenzene

Parameter	GP								PhNO$_2$				
	1a	**1b**	**1c**	**1d**	**2a**	**2b**	**2c**	**2d**	**2a**	**2c**	**2d**	**1e**	**2e**
E/kcal mol^{-1}	47.13 ±1.8	47.49 ±1.1	47.72 ±1.4	44.79 ±0.9	42.21 ±1.0	42.95 ±3.0	42.38 ±1.7	39.92 ±1.7	42.39 ±2.3	42.03 ±1.5	42.25 ±1.1	39.80 ±0.8	38.81 ±1.0
log(A/s^{-1})	14.97 ±0.7	15.05 ±0.4	15.56 ±0.6	15.20 ±0.4	15.01 ±0.4	15.38 ±1.3	15.29 ±0.8	14.97 ±0.8	14.78 ±1.1	14.85 ±0.7	15.82 ±0.5	14.34 ±0.4	15.35 ±0.5
$\Delta S^{\neq}$/cal mol^{-1} deg^{-1}	6.7 ±3.2	7.1 ±1.9	9.5 ±2.6	7.9 ±1.7	7.2 ±1.9	8.8 ±5.9	8.5 ±3.4	7.0 ±3.5	6.2 ±4.9	6.5 ±3.1	11.0 ±2.4	4.3 ±1.8	9.9 ±2.2

T_{min} + 10 °C, ..., T_{max} − 10 °C, the linear regions of the kinetic curve corresponding to not more than the 5% decomposition at a given temperature (T_i) were registered. At $T_i = T_{max}$, the kinetic curves obeyed the first-order equation up to ~90% decomposition. The rate constants for $T_i < T_{max}$ were calculated with corrections for the heat expansion of the gaseous products and for the degree of decomposition.

Results and Discussion

Complete decomposition of 1 mole of the initial tetrazole gives 1 mole of N$_2$. This indicates that the experimental values of the rate constants presented in Table 1 and the activation parameters calculated from these rate constants (Table 2) are related to the decomposition of the tetrazole heterocycle accompanied by the separation of nitrogen.

The kinetic parameters obtained for the decomposition of 2,5-disubstituted tetrazoles in a nitrobenzene solution according to the procedure described above corresponded within the experimental accuracy to the values determined for the gas phase from the overall kinetic curves.

For both series of isomers, decomposition is characterized by increased activation entropy, with an average increase of +8 cal mol^{-1} deg^{-1}. The thermal stability is mainly determined by the activation energy (E_{exp}) and depends substantially on the nature of substituent R^1 or R^2 at the N atom. Its dependence on the nature of substituent R^5 at the C atom of the tetrazole heterocycle is considerably weaker. This conclusion agrees with the published data for 2,5-disubstituted tetrazoles. The rate constants of the decomposition of 1,5-disubstituted tetrazoles **1a—e** are lower by 1.5—2 orders of magnitude than those for isomers **2a—e**.

It can be seen from Fig. 1 that the changes in the rate constants of decomposition in the series of 1,5- and

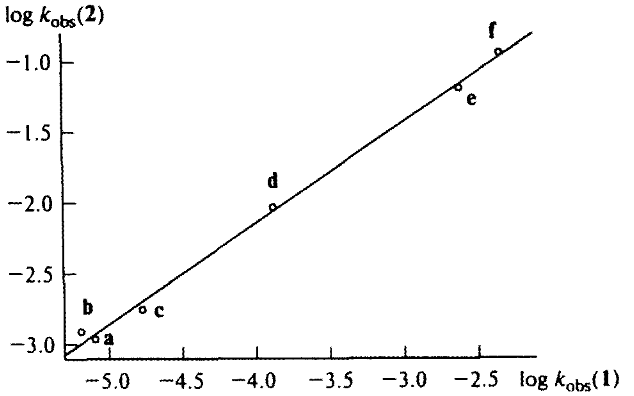
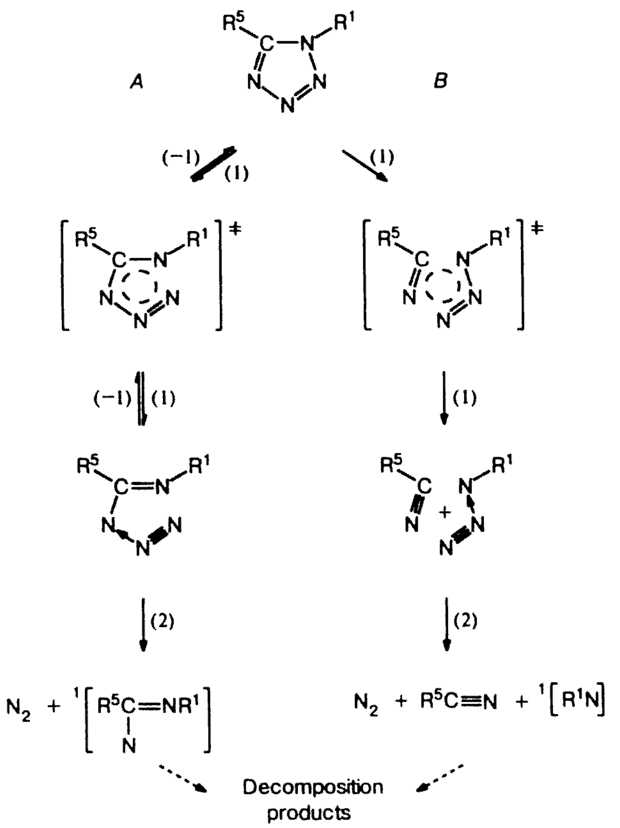


Fig. 1. Ratio between observed rate constants (k_{obs}) of decomposition of isomeric tetrazoles **1** and **2** (r = 0.998) at 240 °C. Point **f** was calculated for diphenyltetrazoles **1f** and **2f** by the published data and $\Delta S^{\neq}$ = +8 cal mol^{-1} deg^{-1}.

2,5-disubstituted tetrazoles with various substituents in the heterocycles are similar. The high correlation coefficient ($r = 0.998$) for the linear dependence between the logarithms of the rate constants makes it possible to assume that the established interrelation is not accidental.

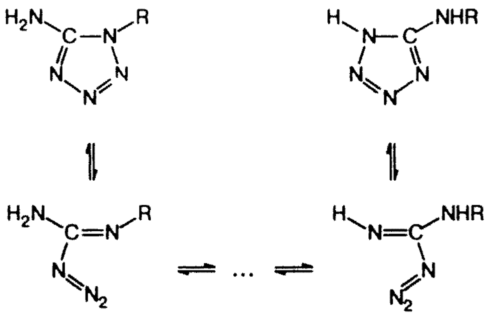
The results obtained taking into account the published data substantiate the relation between the kinetic parameters and the mechanism of the decomposition of compounds **1** and **2**. The possible channels of the decomposition of 1,5-disubstituted tetrazoles are presented in Scheme 1.

Scheme 1



For example, the formation of carbodiimides and their derivatives during the decomposition of 1,5-disubstituted tetrazoles and benzimidazoles from aryltetrazoles[1,2] and the known examples of azidomethine-tetrazole tautomerism[1,8,9] can be considered quite reasonably as arguments in favor of a mechanism of the thermal decomposition of type **1** compounds *via* the stage involving the reversible opening of the cycle followed by the decomposition of the corresponding azidomethine (channel *A*). The detection of nitriles and the products of their cyclization after the decomposition of some tetrazoles has been related previously[5] to the possibility of the parallel decomposition of type **1** compounds *via* another channel (*B*) that includes a retro-1,3-cycloaddition type reaction as the primary reaction. No discussion about the kinetic parameters of the channels considered above has been published.

In our opinion, a rather exact estimation of the parameters of reaction (1), channel *A*, can be obtained by detailed analysis of the experimental data[8] (and by the correction of assumed inaccuracies) on the isomerization of 1-R-5-aminotetrazoles:



In this multistage sequence of transformations, the observed isomerization rate should be determined by the slowest stage, the primary opening of the heterocycle, because, according to the recent published data, the inversion energy barriers at the amine N atom for the prototropic shift and internal rotations are considerably lower than the values of the isomerization activation energy obtained experimentally. The values of the energy (E_1), which range from 33 to 36 kcal mol^{-1} for the series R = Alk, Ar, correspond to the activation entropy of reaction (1) $\Delta S^{\ne}_1$ = +4 cal mol^{-1} deg^{-1} (which is close to the average experimental value[8] and corresponds reasonably to the structure of the activated complex of the opening of the cycle), which we chose as a reference value. Similar values of the activation energy E_1 of reaction (1), channel *A*, should also be expected for compounds **1a—e**.

From the experimental data on the cyclization of azidomethines followed by the formation of tetrazoles we have the values of the parameters of reaction (−1), channel *A*:[8,9] E_{-1} = 17—18 kcal mol^{-1}, $\Delta S^{\ne}_{-1}$ = −7 cal mol^{-1} deg^{-1}. The values obtained are almost independent of the structure of the molecule.

There are no direct data on the decomposition of (intermediate) azidoazomethines, however, according to current views,[10] it is highly improbable that there would be noticeable deviations of the parameters of reaction (2), channel *A*, from those values typical of the monomolecular decomposition of vinyl- and benzoylazides (which coincide if the accuracy of the kinetic experiment is taken into account). Therefore, it can be accepted that $E_2 \approx$ 27—29 kcal mol^{-1}, $\Delta S^{\ne}_2 \approx$ 0 cal mol^{-1} deg^{-1}.

The estimations presented result in the following correlations between the rate constants of reactions (1), (−1), and (2), which occur *via* channel *A* (see Scheme 1):

$$k_1 \ll k_{-1},\ k_1 \ll k_2,\ k_{-1} \gg k_2.$$

Table 3. Estimation of enthalpies of formation ($\Delta_f H°$) of intermediate compounds and group contributions to $\Delta_f H°$ values

Compound	$\Delta_f H°$/kcal mol^{-1} (average)	Group	$\Delta_f H°$ /kcal mol^{-1}
$MeN_3C{=}NMe$	84.2, 84.8 (84.5)	$C_d{-}(C)(N_3)$	83.4
$C_2H_3N_3C{=}NMe$	109.6, 110.6 (110.1)	$C_d{-}(C_d)(N_3)$	85.8
$PhN_3C{=}NPh$	144.9, 141.5 (143.7)	$C_d{-}(C_b)(N_3)$	88.4

The application of the quasi-stationary concentration method therefore becomes justified with respect to intermediate azidoazomethines, and hence, the following correlations are fulfilled for the rate constants observed experimentally:

$$k_{obs} = k_1k_2/(k_{-1} + k_2);$$

at $k_{-1} \gg k_2$: $k_{obs} = k_1k_2/k_{-1}$,

$$E_{exp} = E_1 - E_{-1} + E_2,$$
$$\Delta S^{\ne}_{exp} = \Delta S^{\ne}_1 - \Delta S^{\ne}_{-1} + \Delta S^{\ne}_2.$$

It can be seen from these correlations that the experimental parameters for the decomposition of tetrazoles **1a—d** agree satisfactorily with the estimations presented above, although the possibility of a small contribution of the parallel channel (*C*) to the observed rate of decomposition cannot be excluded.

One of the consequences of the discussion presented is that it is now possible to estimate the enthalpies of formation of intermediate azide structures by the equations

$$\Delta_f H°(R^5N_3C{=}NR^1) \cong \Delta_f H°(\mathbf{1}) + E_1 - E_{-1},$$

and

$$\Delta_f H°(R^5N_3C{=}NR^1) \cong \Delta_f H°(\mathbf{1}) + E_{exp} - E_2.$$

Using for compounds **1a**, **1b**, and 1,5-diphenyltetrazole (**1f**) the known and estimated values of $\Delta_f H°$, the values E_1 = 36 and 34 kcal mol^{-1} corresponding to the corrected experimental data[8] for the isomerization of 5-amino-1-ethyl- and 5-amino-1-phenyltetrazoles, respectively, and the average values of E_{-1} = 17.5 kcal mol^{-1} and E_2 = 28 kcal mol^{-1} (see above), we obtain the estimations of the enthalpies of formation of the intermediate compounds and the group contributions[11] to the enthalpies of formation (Table 3). For each compound, the difference in the values obtained is noticeably less than the formal errors (on an order of ±5 kcal mol^{-1}) corresponding to the two schemes of estimations.

Based on the discussion presented, we can also estimate the limiting values of the activation energies of the 1,3-cycloaddition of azides to nitriles. A significant contribution of channel *B* to the observed rate constant should correspond to similar (with a correction for the possible and most likely small difference in entropy factors) values of the experimental activation energy E_{exp} and the barrier E_1 to direct 1,3-cycloreversion (channel *B*). Hence, the correlation follows

$$E_{exp} \cong E_1 = E_{-1} + \Delta H,$$

where $\Delta H = \Delta_f H°(R^5CN) + \Delta_f H°(R^1N_3) - \Delta_f H°(\mathbf{1}\text{ or }\mathbf{2})$ and E_{-1} is the activation energy of bimolecular (and, therefore, insignificant for the gas-phase decomposition) reverse 1,3-cycloaddition, which is not shown in Scheme 1 (channel *B*).

The aforemade conclusion about the small contribution of channel *B* means that

$$E_{-1} > E_{-1,min} = E_{exp} - \Delta H.$$

The data in Table 4, which reflect the known difficulty[1,13] of the noncatalyzed 1,3-cycloaddition of azides to nitriles, attest to the low probability of the occurrence of channel *B*. The values of E_{-1} obtained using the value $\Delta_f H°(MeN_3)$ = 58.0 kcal mol^{-1} (see Ref. 12) cast some doubt on this conclusion, while the values of E_{-1} obtained using the current estimation of $\Delta_f H°(MeN_3)$ = 71.9 kcal mol^{-1} (see Ref. 18) favor this conclusion.

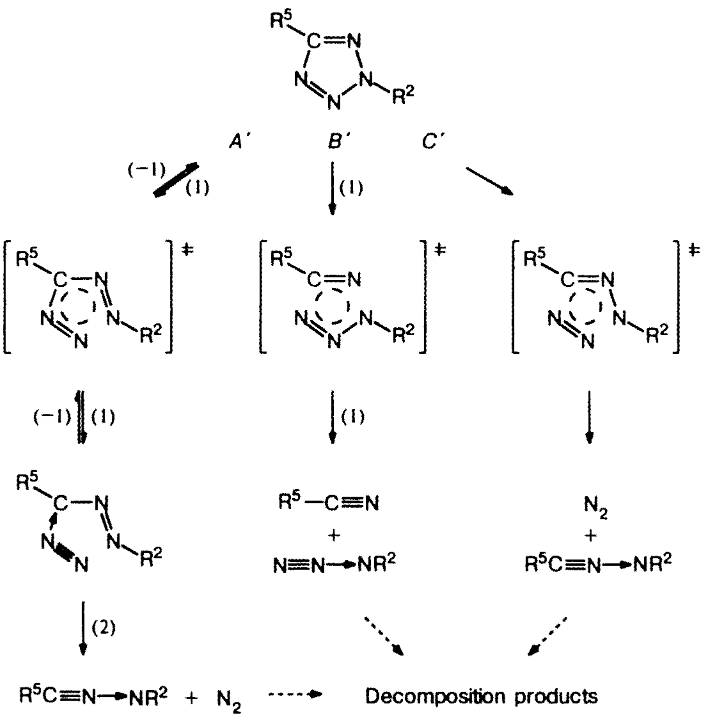
The parallel and correlated changes in the rate constants of decomposition in the series of tetrazoles **1** and **2** (see Fig. 1) coincide with the activation entropies, and the close activation energies point to the main role of a

Table 4. Data for the estimation of barriers to 1,3-cycloaddition of azides to nitriles

Tetrazole	R^1, R^2	R^5	$\Delta_f H°$/kcal mol^{-1}			ΔH[a]	E_{exp}[b]	E_{-1}[c]
			tetrazole	azide	nitrile	kcal mol^{-1}		
1a	Me	Me	65.7[16]	67.0[11]	21.0[15]	22.3	47.1	24.8
1b	Me	$CH_2{=}CH$	91.1[17]	67.0[11]	43.7[15]	19.6	47.5	27.9
1f	Ph	Ph	128.4[14]	92.3[12]	52.3[11]	16.2	41.1[d]	24.9
2a	Me	Me	60.1[16]	67.0[11]	21.0[15]	27.9	42.3	14.4
2b	Me	$CH_2{=}CH$	84.6[17]	67.0[11]	43.7[15]	26.1	43.0	16.9
2f	Ph	Ph	123.0[14]	92.3[12]	52.3[11]	21.6	37.8[d]	16.2

[a] Enthalpy of recyclization. [b] Experimental activation energy of decomposition. [c] Activation energy of cyclization. [d] Calculated from the published data[2] and $\Delta S^{\ne}$ = 8 cal mol^{-1} deg^{-1}.

Scheme 2

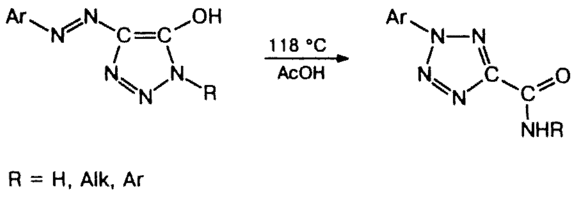


similar stepwise mechanism of the decomposition in the case of tetrazoles of series **2** as well (Scheme 2, channel *A′*) and indicate that equations similar to those presented above for compounds **1** are valid for the decomposition of compounds **2**. In addition, small contributions from the parallel channels *B′* and *C′* cannot be excluded, although they are highly improbable (especially for channel *B′*, see Table 4). Decomposition of the tetrazole cycle *via* these channels can be concerted. However, the character of the change in the rate constants of the reactions occurring *via* these channels should depend on the structure of the molecules and be determined by an energy barrier equal to the sum of the endothermal effect of primary 1,3-retrocyclization and the activation energy of 1,3-cycloaddition, which is the reverse of decomposition. Extreme influences of electronic factors of substituents on the reaction rates of 1,3-cycloaddition are known and are explained by the decisive role of orbital interactions.[13] For this reason it is highly improbable that the same type of effect of substituents in tetrazole cycles at different initial transformations limiting the observed decomposition rate would occur.

The similarity of the effects of electronic factors of substituents on processes *C* and *A* and *A′* is also reflected distinctly in the close values of the Hammett constants ρ, which are compared in Table 5 for reactions of these types. Table 5 also contains data on the isomerization of triazoles, which occurs through intermediate 1,3-dipolar structures of diazo compounds similar to those postulated for tetrazoles **2** (see Scheme 2, channel *A′*). The resemblance of reactions occurring at substantially different temperatures and, correspondingly, at different rates should be emphasized.

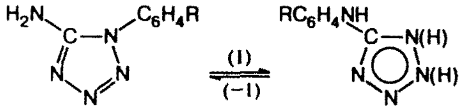
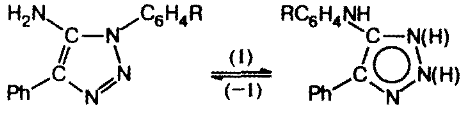
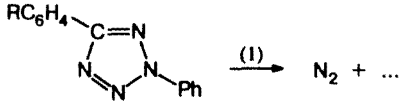
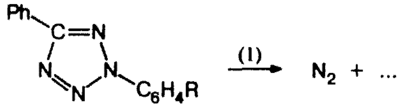
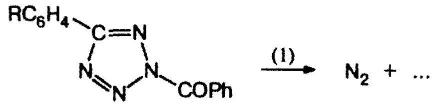
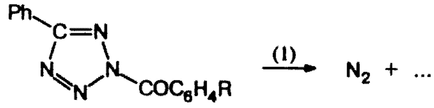
As in the case of channel *A* (see Scheme 1), in the case of channel *A′* (see Scheme 2), one can expect that the rate constants of cycle opening (k_1) would be more sensitive to the structure of a molecule than the ratio of the rate constants of the fast reactions of recyclization and decomposition of intermediate 1,3-dipolar structures (k_2/k_{-1}).

The example[19] of reaction (−1), channel *A′* only demonstrates that there is a considerably higher rate of intramolecular cyclization of the diazo group at the N=N bond than at the C=N bond under the conditions chosen.



When nitrogen is released in reaction (2), channel *A′*, no skeletal rearrangements are required for the formation of nitrile imine. In this it differs from reaction (2), channel *A*, and the similar Curtius and Wolf reactions as well as the decomposition of vinylazides. In these transformations, the elimination of N_2 should result in the formation of singlet intermediate valence-deficient species (nitrenes or carbenes) with a vacant orbital on the corresponding atom. In the course of reaction (2), channel *A′*, the interaction of a similar orbital with the orbitals occupied by four n-electrons of

Table 5. Effect of substituents at the N or C atoms of the cycle on the reaction rates of tetrazoles and triazoles

Reaction	T/°C	ρ (reaction)	
		N	C
	137	1.39[8] (1)	−0.45[8] (−1)
	150	1.12[20] (1)	−0.27[20] (−1)
	166		−0.24[3] (1)
	166	1.16[3] (1)	
	70		−0.65* (1)
	70	1.32* (1)	

* Calculated from the published data.[5]

the N=N bond can lead to the formation of a tricentered 1,3-dipolar π-system of nitrile imine followed by the detachment of nitrogen *via* an azocarbene type intermediate. The evident stabilization of the activated complex during this transformation should make a more significant contribution to the rate constants k_2 and k_{obs} of the decomposition of 2,5-disubstituted tetrazoles of series **2** than their 1,5-disubstituted isomers **1** when $k_{-1} \gg k_2$ or should cause k_{obs} to equal k_1 for the decomposition and recyclization of tetrazoles **2** when $k_{-1} \ll k_2$. The latter two correlations are less probable for the 1,5- and 2,5-disubstituted tetrazoles studied in this work, but they are likely for some of their N-acyl derivative type analogs (see Table 5).

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