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Substituent Effect on the Rate of Thermal Decomposition of 5-(R-Phenyl)-2-methyl-1,2,3,4-tetrazoles

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Abstract—Thermal decomposition of substituted 2-methyl-5-phenyltetrazoles in solution has been studied by manometric method with chromatographic determination of the evolved nitrogen. A relation has been found between the rate of thermal decomposition and nature of the substituent in the benzene ring. Effects of solvent and temperature on thermal decomposition of substituted tetrazoles have been revealed.

Keywords: substituted phenyltetrazole, thermal decomposition, mechanism, reactivity

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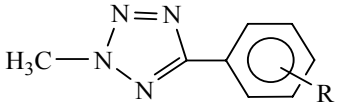
We have earlier shown that decomposition mechanism and thermal stability of energetic compounds based on 5-R-2-methyltetrazoles strongly depends on the nature of the R substituent [1–3]. Extending these studies, herein we report on thermal decomposition of compounds **I**–**VIII** aiming to reveal a quantitative relationship between the tetrazoles reactivity and nature of the substituent in the 5-phenyl ring.



R = *p*-OCH_3 (**I**), *p*-CH_3 (**II**), H (**III**), *p*-Cl (**IV**), *m*-Cl (**V**), *m*-Br (**VI**), *m*-NO_2 (**VII**), *p*-NO_2 (**VIII**).

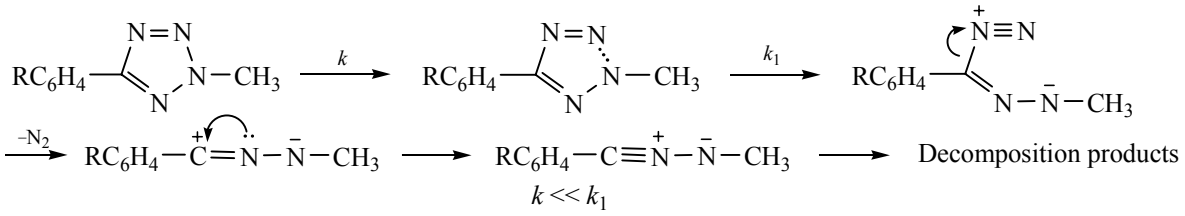
In order to eliminate the effects of crystal lattice and the decomposition products on reactivity of the substituted 5-phenyltetrazoles, their decomposition was studied in dilute solution in inert thermally stable solvents. In particular, solvents with different dielectric constants were used: 1,3-dinitrobenzene (ε = 20.6), 1,3,5-trinitrobenzene (ε = 7.1), and dibutyl phthalate (ε = 6.4). As shown in the representative cases of compounds **II**, **IV**, and **VIII**, the rate of their decomposition at 200°C was independent on the concentration when in the range of 1–8 wt %. The effect of solvent polarity (i.e., dielectric constant) on the rate of thermal decomposition was fairly weak. With 1,3-dinitrobenzene as solvent, the rate constants of compounds **I**, **III**, and **VII** decomposition increased by 10–14% as compared to the solutions in dibutyl phthalate. That could be rationalized by slightly better solvation of the transition state than that of the initial state in 1,3-dinitrobenzene. Weak solvation of transition state is typical of homolytic reactions [4].

Taking into account the above results, the temperature effect on the rate of decomposition of 5-phenyltetrazoles was studied in 2 wt % solution in dibutyl phthalate. Under those conditions, the thermal decomposition followed the first-order kinetics up to conversion of 45–48%. According to the GC data, the major gaseous product of thermal decomposition of all compounds **I**–**VIII** was molecular nitrogen (0.97–0.99 mol per mol of the substrate). The activation parameters are given in the Table along with the entropies of activation and the Hammett substituent constants σ.

As seen from the tabulated data, increase of the electron-withdrawing power of the substituent at C^5 atom in the tetrazole ring was accompanied by increase of the decomposition rate constant, due to reduction of electron density on the reaction center.

The kinetic studies [5] have shown that the primary act of thermal decomposition of 2,5-substituted tetrazoles is homolytic break of the N^2–N^3 bond in the tetrazole ring.

Scheme 1.



The activation energy of the rate-determining stage is marginally dependent on the substrate nature, being of about E_{av} 175.9 kJ/mol, but the difference in the pre-exponential factors attains 0.42 log unit. On the other hand, these findings may be treated as an insignificant decrease of the energy of activation and simultaneous increase of the pre-exponential factor in the **I**–**VIII** series, indicating increase of the translational activation entropy and its contribution to the logarithm of the decomposition rate constant (Scheme 1).

It is known that thermal decomposition of azides [7, 8] as well as of nitro compounds [9] involves a semirigid transition state in which rocking vibrations of the starting molecule are not transformed into free rotation but only decrease their frequency. Therefore, increased entropy of activation and, correspondingly, pre-exponential factor in the thermal decomposition of methyl azide (**IX**, see table) as compared to the normal value ($10^{13.0}$ s^{-1}, $\Delta S^{\neq} = 0$) are related solely to the reduced frequency of bending vibrations of the $CH_3N^1–N^2$ and $N^1–N^2N^3$ bonds associated with the $N^1–N^2$ bond being broken. Elongation of the $N^2–N^3$ bond in 2-methyl-5-phenyl-tetrazole in the transition state is accompanied by decrease of the bending vibration frequency of that bond and release of free rotation around the $N^2–N^3$ bond, as well as by decrease of the torsion vibration frequency (up to free rotation) of the methyl group at the reaction center N^2. All these factors contribute to the activation entropy of the thermal decomposition and to the pre-exponential factor and thus provide understanding of the observed difference in the pre-exponential factors for compounds **I**–**IX** (see table).

A linear relation was found between logarithm of the rate constant of thermal decomposition of substituted 5-phenyltetrazoles and the Hammett substituent constant σ (see figure):

$$\log k_{200°C} = (0.530 \pm 0.031)\sigma - (4.224 \pm 0.014);$$

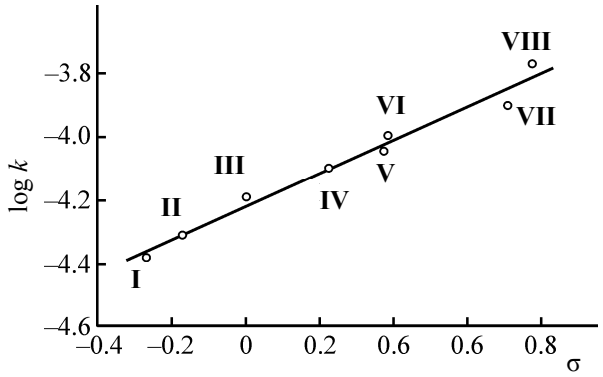
$$r = 0.988;\ S_y = 0.083;\ n = 8.$$

The low ρ value (0.530) indicated a weak sensitivity of the thermal decomposition of substituted 5-phenyltetrazoles to the electronic properties of the substituents.

Activation parameters of thermal decomposition of compounds **I**–**IX**

Comp. no.	R	Conditions	Temperature range, °C	E_a, kJ/mol	log A	$k_{200°C} \times 10^5$, s^{-1}	$\Delta S^{\neq}_{200°C}$, J mol^{-1} K^{-1}	σ
I	*p*-OCH_3	Solution	170–210	177.2	15.18	4.11	33.6	–0.268
II	*p*-CH_3	Solution	200	–	–	4.87	–	–0.17
III	H	Gas[a]	170–210	177.0	15.30	5.70	35.9	0
		Solution	170–210	176.1	15.25	6.39	35.0	
IV	*p*-Cl	Solution	200	–	–	7.89	–	0.227
V	*m*-Cl	Solution	170–210	175.7	15.35	8.91	36.9	0.373
VI	*m*-Br	Solution	170–210	175.5	15.38	10.04	37.5	0.391
VII	*m*-NO_2	Solution	180–200	174.8	15.40	12.56	37.8	0.71
VIII	*p*-NO_2	Solution	170–210	174.5	15.50	17.07	39.7	0.778
IX	CH_3N_3	Gas[b]	155–200	170.7	14.45	4.00	19.6	

[a] Data from [5]. [b] Data from [6].



Log $k_{200°C}$ as function of the substituent constant σ.

In conclusion, it was interesting to compare the thermal stability of the substrates in view of conformation of the azido group which was linear in methyl azide and "bent" in 2-methyl-5-phenyltetrazole on the basis of the conformational activation energy. The latter could be estimated as follows. The average value of log*A* was of 14.88; so to obtain the experimental values log $k_{200°C}$ = −4.244 (**III**) and log $k_{200°C}$ = −4.398 (**IX**) for the thermal decomposition in the gas phase, the energies of activation should be of 173.2 and 174.6 kJ/mol, respectively. The difference in the activation energies was as low as 1.4 kJ/mol, comparable with their determination accuracy. Therefore, we concluded that thermal stability of compounds **I**–**VIII** ("bent" azido group) and **IX** (linear azido group) were almost the same.

EXPERIMENTAL

Compounds **I**–**VIII** were synthesized as described in [10] and were purified by fractional crystallization. The products purity was confirmed by thin-layer chromatography on Silufol UV-254 plates. The substrates used in the kinetic study were chromatographically pure, containing 99.5–99.7% of the main component.

Kinetics of thermal decomposition was studied under static conditions via the manometric method using manometer of Bourdon's type [11] under a residual air pressure of 10^{-2} to 10^{-1} mmHg. Temperature was maintained constant within ± 0.5°C. The rate constants were calculated using the first-order kinetic equation according to Guggenheim's method [12]. The error in determination of the rate constants was below 6–7%. The mean-square error of the activation energy determination was of 2.1 kJ/mol, and that of log *A* determination was of 0.05 log unit.

Molecular nitrogen evolved during thermal decomposition of 2-methyl-5-phenyltetrazoles was quantified by gas chromatography using an LKhM-80 instrument (Polisorb-1 column, 18–20°C).

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