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Thermal Decomposition of 5-Nitraminotetrazole[*] of 3-Azolylamino-2-polyfluorobenzoylacrylates

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Abstract—Thermal decomposition of 5-nitraminotetrazole in solid phase and diluted solutions in aprotic solvents was investigated. The kinetic and thermodynamic parameters of the process were established. A mechanism of unimolecular decomposition was assumed including isomerization into the nitroguanyl azide followed by decomposition of he azide function.

Thermal decomposition of energy-reach tetrazoles is treated in a great many studies summarized in reviews [1, 2] and in a book [3]. However the thermal decomposition of 5-nitraminotetrazole (**I**) is insufficiently understood. A single publication considered this topic but without kinetic data [4].

We report here on the kinetics of the thermal decomposition of compound I in the solid phase and in solution in inert aprotic solvents. The study of thermal decomposition in a diluted solution in a solvent of low polarity where is absent the braking effect of the crystal lattice to a certain extent simulates the gas phase conditions and provides a knowledge on the true reactivity of compound **I**.

Decomposition of compound **I** in the solid state under isothermal conditions at temperature over 100°C frequently resulted in an explosion. Nonetheless in some cases we succeeded in recording kinetic curves of S-form (Fig. 1). Thermogram of compound **I** decomposition under dynamic conditions is presented in Fig. 2: the starting temperature of decomposition is 125°C, vigorous decomposition at 132°C.

The thermal decomposition of compound **I** in 1% solution in dibutyl phthalate (DBP) and dibutyl sebacate (DBS) follows the law of first order reaction up till 70–80% conversion. The change in solution concentration from 0.5 to 5% did not affect the rate of decomposition indicating that the process was unimolecular.

Maximum amount of gaseous decomposition products at the process in solid phase is equal to 3 moles, and in solution 2.4–2.6 moles per 1 mole of initial compound **I**.

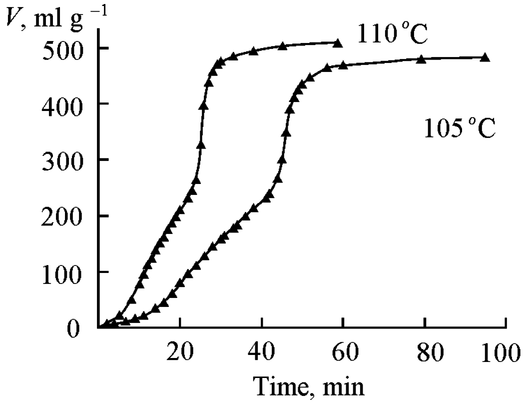

Fig. 1. Kinetic curves of thermal decomposition of compound **I** in the solid phase at m/V 3×10^{-4} g cm^{-3}.

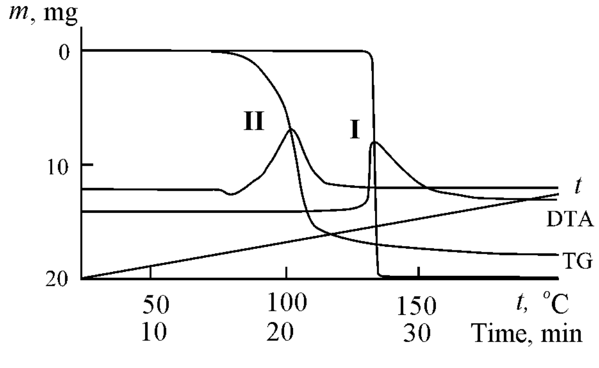

Fig. 2. Thermogram of 5-nitraminotetrazole (**I**) and nitroguanyl azide (**II**) decomposition. Heating rate 5 deg min^{-1}, sample 20 mg. Differential thermogravimetric curves are shown.

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Table 1. Kinetic parameters of thermal decomposition of compounds **I, II** under various conditions

Compd. no.	Conditions of decomposition	Temperature, °C	$k_{app} \times 10^4$, s^{-1}	E_a, kJ mol^{-1}	log*A*	$\Delta^{\neq}S$,[a] J mol^{-1} K^{-1}
I	Solid phase	105	0.57	–	–	–
	(isothermal)	110	1.40	–	–	–
	1% solution in DBP	110–150	3.44[a]	153	16.9	68
	1% solution in DBS	90–130	2.05[a]	150	16.2	55
II	Melt (dynam.)	75–110	450.7[a]	148	18.4	96
	1% solution in $CHCl_3$	61	0.52	–	–	–

[a] At 120°C.

The apparent rate constants and activation parameters of the thermal decomposition of compound **I** under various conditions are given in Table 1.

For a long time the structure of compound **I** was under discussion: whether it was nitrimine or primary nitramine [5]. Yet this problem is a key to the mechanism of the thermal decomposition of compound **I**. Now it is established that compound I both in solid state [4] and in solution [6] exists in the nitrimine form.

It was presumed in [4] that the initial act of the thermal decomposition of compound **I** was elimination of molecular nitrogen from the tetrazole cycle as showed the change in the IR spectrum at heating of compound **I** (decreased intensity of the absorption bands belonging to the tetrazole ring vibrations at remaining intensity of bands corresponding to nitro group). The nitrimine function in the molecule of compound **I** in its structural parameters is similar to analogous fragment of nitroguanidine, but the latter is stable to about 200°C.

In the gaseous decomposition products at the process carried out in the solid phase were found considerable amounts of NO and CO [4] that was common to the homolytic decomposition of N-nitro compounds at the $N{-}NO_2$ bond followed by redox reactions with NO_2 participation [3]. In the thermal decomposition of compound **I** in 1% solution in DBP the main detected gaseous decomposition product is molecular nitrogen N_2 liberated at complete decomposition in amount ~1 mole per 1 mole of compound **I**. Also was observed evolution of some N_2O and CO_2 (less than 0.1 mole per 1 mole of initial compound **I**). At the same time no NO or NO_2 were detected apparently due to the reaction of the reactive nitrogen oxides with the solvent. Besides the analytical performance of the device used did not permit determination of the other possible gaseous decomposition products, e.g., HCN.

The results obtained in combination with the published data on the mechanism of thermal decomposition of the tetrazole derivatives [1–4] suggest essentially several paths of tetrazole ring opening in compound **I** followed by nitrogen molecule elimination: 1) A homolytic rupture of the least strong nitrogen–nitrogen bond in the molecule. According to X-ray analysis [4] this is the $N^1{-}N^2$ bond. 2) A heterolytic rupture of the $N^1{-}N^2$ bond. 3) An isomerization into 1-azido-*N*-nitroformamidine (nitroguanyl azide) (**II**) and decomposition of the azide function to afford nitrene.

As seen from the presumed scheme that in all cases the probable way to stabilize the intermediate active species is the formation of hypothetical 3-nitriminodiaziridine (**III**).

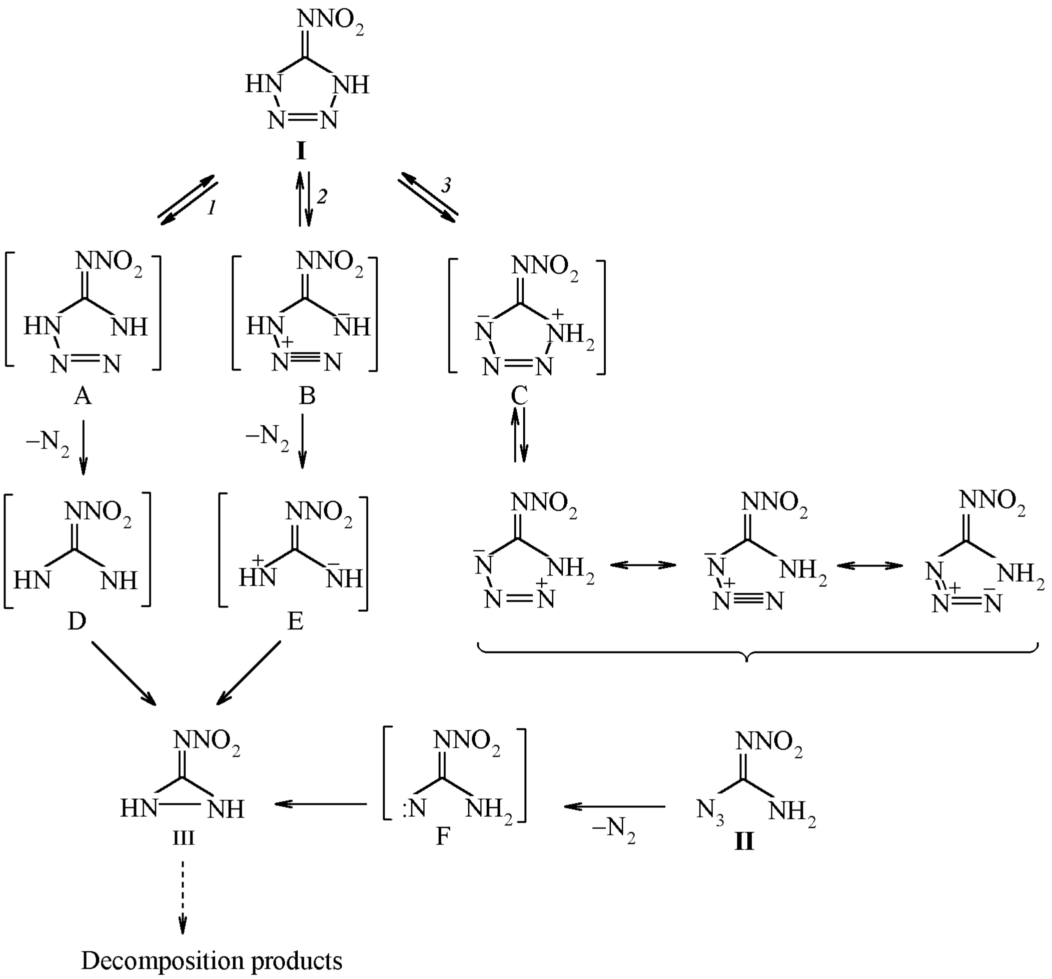
The possibility of diaziridine derivatives formation at the thermal decomposition of tetrazoles was previously considered in [2, 3].

We estimated the thermodynamic effects of the presumed decomposition paths by quantum-chemical calculations along the semiempirical methods MNDO, AM1, and PM3 for molecules **I–III** and also for the probable intermediate species (Scheme 1).

Semiempirical calculations with full geometry optimization give in general fair estimation of the bond angles and planar structure of the molecule of compound **I**; however, the numerical values of some bond lengths considerably differ from the figures obtained by X-ray diffraction analysis (Table 2). According to the calculations the least strong is the $N{-}NO_2$ bond and not $N^1{-}N^2$ in the tetrazole cycle.

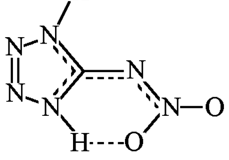
The X-ray data correspond to a crystalline substance, and they take into account the inter-

Scheme 1.



molecular interactions in the crystal lattice whereas the calculations were performed for an individual molecule in the gas phase or in diluted solution disregarding the solvation effect. However the main reason of discrepancy in experimental and estimated bond lengths is apparently another.

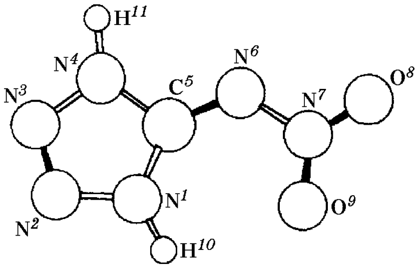
The semiempirical procedures used underestimate the characteristic for nitrimines delocalization of the π-electron density in the nitrimine moiety that results in the shortening of the $N-NO_2$ bond, elongation of the N–O bonds, and averaging of the C–N bond lengths.



Nonetheless the calculation in PM3 approximation reproduces the experimental formation enthalpy in the gas phase for nitrimines (nitroguanidine) and tetrazoles [1]. Yet the bond lengths for N–N bonds in compound **I** calculated by PM3 method stronger deviate from the experimental values than those obtained by MNDO and AM1 procedures.

Although nitrimine **III** contains a three-membered cycle it is not a thermodynamically extremal molecule (Table 3). Its formation enthalpy (PM3) is virtually the same as for compound **I**, and considering its quite common bond lengths (MNDO, AM1) molecule **III** may be regarded as relatively stable. Unlike compound **I** the molecule of compound **III** is not planar. This quality does not favor delocalization of the electron density and results in elongation of the $N-NO_2$ bond, thus leading to conclusion that the latter is probably cleaved at further thermolysis. Therewith it is possible to understand the finally

Table 2. Bond lengths (*l*, Å) and bond angles (φ, deg) in a molecule of 5-nitraminotetrazole (**I**), calculated by MNDO, AM1, and PM3 procedure, and data of the X-ray diffraction analysis



l or φ	MNDO	AM1	PM3	X-ray analysis [4]
N^2–N^3	1.257	1.263	1.252	1.275
N^3–N^4	1.352	1.355	1.379	1.347
N^1–N^2	1.354	1.351	1.380	1.360
C^5–N^1	1.400	1.422	1.404	1.335
N^1–H^{10}	1.010	1.002	0.997	–
C^5–N^4	1.403	1.420	1.402	1.337
C^5–N^6	1.326	1.344	1.335	1.344
N^4–H^{11}	1.008	0.995	0.994	–
N^6–N^7	1.381	1.385	1.409	1.331
N^7–O^8	1.205	1.198	1.201	1.255
N^7–O^9	1.219	1.216	1.223	1.235
$O^9{\wedge}H^{10}$	2.574	2.314	2.508	–
$N^2N^3N^4$	109.5	110.1	109.6	108.0
$N^1N^2N^3$	109.6	109.8	109.7	107.7
$N^2N^1C^5$	109.9	109.8	109.4	109.9
$N^2N^1H^{10}$	120.8	123.7	121.6	–
$C^5N^1H^{10}$	129.3	126.5	129.0	–
$N^1C^5N^4$	100.9	100.6	101.8	104.1
$N^1C^5N^6$	138.0	134.0	136.2	135.7
$N^4C^5N^6$	121.0	125.3	122.0	120.2
$C^5N^4N^3$	110.0	109.5	109.5	110.3
$N^3N^4H^{11}$	122.0	122.9	121.6	–
$C^5N^4H^{11}$	127.9	127.5	128.9	–
$C^5N^6N^7$	123.0	120.5	124.4	114.4
$N^6N^7O^8$	115.2	116.2	116.5	115.3
$N^6N^7O^9$	121.8	121.7	118.0	124.1
$O^8N^7O^9$	122.9	122.1	125.5	120.7
ΔH_f^0, kJ mol^{-1}	350.20	595.84	400.28	252.29[a]

[a] Formation enthalpy for solid phase [7].

observed composition of the thermolysis products obtained from compound **I** in the process carried out in the solid state.

The enthalpy diagram calculated by PM3 procedure for various pathways of compound **I** decomposition is shown in Fig. 3. As seen, the pathways and *2* are virtually equivalent, and the most thermodynamically feasible pathway of the thermal decomposition occurs through the azidomethine-tetrazole isomerization (*3*). The difference in formation enthalpy of intermediates A, B, and C is insignificant. Since we did not perform the search for the saddle point on the potential energy surface, and the formation enthalpy for A, B, and C species were found at the optimal geometry thereof, therefore strictly speaking the assumed intermediates cannot be regarded as transition states of the reaction, and the difference between formation enthalpies of initial compound **I** and the A, B, C species cannot be considered as activation energy. It is presumable that the cyclic intermediate species B is close to the transition state by its geometry unlike the A, B species where the possibility of free rotation of the fragment –NH–N–N around C–N bond provides a structure with maximally removed from each other nitrogen atoms N^1 and N^2. The rotation of the fragment –NH–N–N in A and B species in order to obtain a planar structure with a minimal distance between N^1 and N^2 atoms significantly increases the enthalpy of such structure (more than by 100 kJ mol^{-1}). Yet the formation enthalpy difference between initial compound **I** and intermediate C (128.2 kJ mol^{-1}) is of the same order of magnitude as the experimental activation energy (Table 1).

According to calculation the open-chain azidomethine structure **II** is by 44.1 kJ mol^{-1} more energetically feasible than the isomeric tetrazole structure **I**. In the solid state was experimentally obtained the opposite result: The formation energy of compound **II** was by 46 kJ mol^{-1} greater than that of compound **I** [7]. This fact may be due to considerable difference in the energy of crystal lattices of compounds **I** and **II**. The sublimation heat of compound **I** estimated as a difference between the experimental formation enthalpy for the solid state and that in the gas phase calculated by PM3 method amounts to 148 kJ mol^{-1} and is similar to the experimental value determined for nitroguanidine, 142.7 kJ mol^{-1} [8]. For compound **II** this value is notably smaller (58 kJ mol^{-1}).

The mechanism *3* is also in agreement with the following fact. The N^1–N^2 bond according to the X-ray analysis is the least strong in molecule **I**; nevertheless, its length (1.360 Å) is on the same level as N–N bonds in such compounds as hexogen and octogen [9]. The considerably smaller thermal stability of compound **I** compared with the latter substances both in the solid phase and in solution

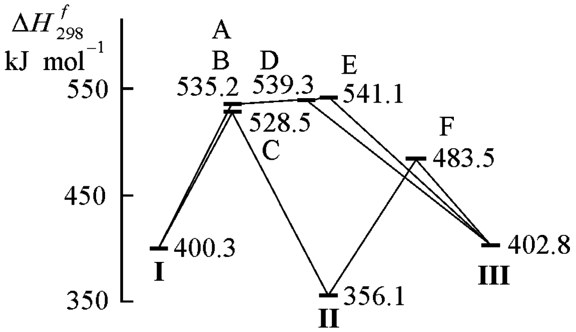


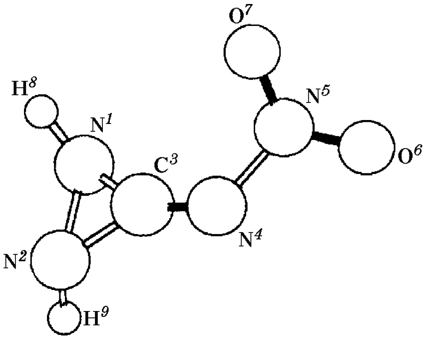
Fig. 3. Enthalpy diagram of various thermolysis pathways of compound **I** calculated along semiempirical quantum-chemical method PM3. The designation of compounds is given according to the scheme.

cannot be rationalized within the framework of the mechanisms *1–2* since the primary act of the secondary nitramines thermolysis is just the homolysis of the N–N bond [3], and the energies of intermolecular interactions in hexogen, octogen, and compound **I** are relatively close in values [8].

It was mentioned in [10] that at thermal decomposition of compound **II** in chloroform or petroleum ether alongside the gaseous decomposition products arose insoluble in the above solvents but water-soluble residue that was not further studied. In order to check whether this residue is the presumed compound **III** we studied the thermal decomposition of compound **II** in 1% chloroform solution. The residue formed was unambiguously identified as compound **I**. From 1 mole of compound **II** at full conversion forms up to 0.7 mol of compound **I**. The quantity of the gaseous decomposition products amounts to 1 mole per 1 mole of the decomposed substance. The kinetics of gas liberation is described with an equation of the first order process. The apparent rate constant of the reaction is given in Table 1.

Thus in the chloroform medium was observed not only decomposition of azide **II**, but also a concurrent with decomposition isomerization into tetrazole **I** that being insoluble in chloroform and more thermally stable than compound **II** was removed from the reaction.

Table 3. Bond lengths (l, Å) and bond angles (φ, deg) in a molecule of 3-nitriminodiaziridine (**III**) calculated by MNDO, AM1, PM3 methods



l or φ	MNDO	AM1	PM3
N^2–C^3	1.425	1.416	1.422
N^1–C^3	1.427	1.416	1.427
C^3–N^4	1.276	1.288	1.280
N^1–N^2	1.432	1.416	1.560
N^2–H^9	1.020	1.014	0.994
N^1–H^8	1.020	1.013	0.995
N^4–N^5	1.417	1.426	1.470
N^5–O^6	1.204	1.195	1.119
N^5–O^7	1.210	1.205	1.208
O^7–H^8	3.620	3.289	3.634
$N^1C^3N^2$	60.3	60.0	66.4
$N^2C^3N^4$	144.3	146.7	142.6
$N^3C^3N^4$	155.3	153.2	150.8
$N^1N^2C^3$	59.9	60.0	56.9
$C^3N^2H^9$	116.1	117.9	120.6
$N^1N^2H^9$	112.0	113.0	115.0
$N^2N^1C^3$	59.8	60.0	56.6
$C^3N^1H^8$	116.5	118.7	120.2
$N^2N^1H^8$	111.9	113.3	114.5
$C^3N^4N^5$	119.0	119.3	124.5
$N^4N^5O^6$	116.3	116.0	115.6
$N^4N^5O^7$	119.0	120.4	116.7
$O^6N^5O^7$	124.5	123.6	127.6
ΔH^0_f, kJ mol^{-1}	417.47	480.89	402.84

In decomposition proceeding along the scheme

$$\text{tetrazole} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{azidoazomethine}$$

$$\xrightarrow{k_2} \text{decomposition products}$$

the relation between the experimental rate constants (k_{app}) and rate constants k_1, k_{-1}, and k_2 can be deduced with the use of the method of quasistationary concentrations [3, 11]:

$$k_{\text{eff}} = k_1 k_2/(k_{-1} + k_2).$$

Quasi-steady state condition: $k_1 << k_{-1} + k_2$.

Since the thermal stability of azidoazomethine **II** is far less than that of tetrazole **I** (mp 80, temperature of decomposition start 75, vigorous decomposition at 100°C) (Table 1, Fig. 2), then $k_1 << k_2$. The published data on kinetics of azidoazomethines cyclization [12], in particular concerning compound **II** [13], permit a statement $k_1 << k_{-1}$; thus the quasi-steady state condition is fulfilled.

We should note in conclusion that the unimolecular thermal decomposition of tetrazole **I** presumably occurs through a limiting stage of reversible isomerization into azidoazomethine **II** with subsequent decomposition of the azide function through probable intermediate formation of diaziridine **III**.

EXPERIMENTAL

Compounds **I, II** were synthesized by the known procedures [14]. The kinetics of thermal decomposition of compound **I** in solution and in solid phase were measured manometrically [15]. The decomposition of compound **II** in chloroform was studied by volumetric method. The decomposition of compounds **I, II** under dynamical conditions was measured on derivatograph Q-1500D. Gaseous products were analyzed on chromatograph LKhM-80 (column packed by sorbent Polysorb-1, 18–20°C). IR spectra were registered from KBr pellets on Fourier spectrometer Nicolet IMPACT-400.

The rate constants of decomposition in solutions were calculated according to the equation of the first order process, and for decomposition in the solid phase from the initial decomposition rate. The error in determination of the rate constants does not exceed 10%, the error in estimation of the activation energy was no more than 0.4 $kJ\,mol^{-1}$, and that of the logarithm of the preexponential factor no more than 0.05 log. unit. The procedure of estimation of kinetic parameter from derivatography data was described in [16]. Quantum-chemical calculations were carried out with the use of CS MOPAC-93 software.

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