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## Kinetics of Thermal Decomposition of 3,7-Dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane

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**Abstract**—The kinetics of thermal decomposition of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane has been studied in solid phase and in solution. The mechanism, kinetic parameters of decomposition, and activation parameters of the rate-limiting step have been determined.

**Keywords:** dinitrotetraazabicyclo[3.3.1]nonane, cyclic nitramines, octogen, thermal decomposition, activation parameters

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3,7-Dinitro-1,3,5,7-tetraazabicyclo[3.3,1]nonane is an intermediate product of nitrolysis of urotropine into 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (octogen), and the yield of octogen is mainly determined by the vield of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane [1]. It should be noted that while the kinetics and mechanism of thermal decomposition of secondary nitramines have been investigated for more than 70 years [2], thermal decomposition of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane has been scarcely studied [3], and the available data are not sufficient for reliable conclusions on the structural and kinetic features or the decomposition mechanism as well as safety issues. In view of the above, we studied the kinetics of thermal decomposition of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane in different states: in solid phase and in solutions in dibutyl phthalate and dinitrobenzene.

Thermal decomposition of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane in solid state proceeded with acceleration and was expressed by the S-shaped kinetic curves (Fig. 1). Variation of the ratio of the reaction vessel surface to its volume (S/V) did not affect the rate and the kinetic equation of decomposition, evidencing absence of heterogeneous reaction on the walls of the vessel as well as of chain processes. At the same time, 20-fold increase in the ratio of the compound loading to the vessel volume (m/V), although shortening the induction period, had practically no effect on the rate of decomposition during the induction period. Therefore, the decomposition of 3,7-dinitro-1,3,5,7tetraazabicyclo[3.3.1]nonane occurred exclusively in the condensed phase, and smooth increase in the rate of decomposition at the acceleration step was due to autocatalytic interaction of the decomposition products, in particular, nitrogen dioxide, with the starting substrate. The initial rate and the induction period were not affected by the variation of the size of the crystals within the 0.01–0.2 mm range (Fig. 2). That was also indicative of the fact that the topochemical effects practically did not affect the acceleration of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane decomposition. In the case of octogen ( $\beta$ -form) **3** the final volume of gaseous decomposition products was larger because here the intracrystalline solvent also evolved which was captured by 3,7-dinitro-1,3,5,7-tetraazabicyclo [3.3.1]nonane during crystallization (Fig. 2) [4].

The kinetic curves of thermal decomposition of 3,7dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane in 2 wt % solutions in dibutyl phthalate and dinitrobenzene differing in the dielectric constant ( $\epsilon$  6.4 and 20.6, respectively) revealed slightly pronounced S-shape, typical of secondary nitramines. The thermal decomposition in dibutyl phthalate and dinitrobenzene



**Fig. 1.** Kinetics of thermal decomposition of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane: (*1*) 140, (*2*) 150, (*3*) 160, (*4*) 170, and (*5*) 180°C.

solutions was faster than in the solid state (Table 1) and, in general, faster than for other cyclic nitramines given for comparison in Table 1.

At first glance, one could assume that accumulation of nitramine groups in the ring should have favored the acceleration of the substrate decomposition, as has been observed for aromatic nitro compounds. However,



**Fig. 2.** Effect of the crystal size on thermal decomposition of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane at 160°C,  $m/V = 4.2 \times 10^{-4}$  g/cm<sup>3</sup>: (1) ground (freshly prepared); (2) ground (aged); and (3) non-ground.

the data for compound 1 (Table 1) showed an opposite trend: the decomposition was sharply decelerated in comparison with 3,7-dinitro-1,3,5,7-tetraazabicyclo-[3.3.1]nonane. For solid compound 1, the rate was decreased by ~62 times. At the same time, the eightmembered cyclic nitramine octogen which can exist as polymorphic crystalline modifications differing in the ring conformation (compounds 1–4), was the most

Table 1. Kinetic parameters of thermal decomposition of cyclic nitramines

	Compound	Solid state				Solution				
Comp. no.		E <sub>a</sub> , kJ/mol	log A	$k_{180^{\circ}} \times 10^{5},$ s <sup>-1</sup>	References	$E_{\rm a}, \rm kJ/mol$	log A	$k_{180^{\circ}} \times 10^{5},$	Solvent	References
1	Octogen	158.6	11.20	0.082	[5]	187.9	15.00	0.22	Dinitrobenzene	[5]
2	Octogen (δ-form)	158.9	11.30	0.095	[6]					
3	Octogen (β-form)	150.6 280.3	10. 80 25.00	0.280 0.048	[7] [8]					
4	Octogen (α-form)	171.5 159.0	12.60 10.80	0.067 0.029	[9] [6]					
5	N,N-Dinitropiperazine					155.6	12.00	0.12	Nitrobenzene	[11]
6	Hexogen	165.3 167.4 217.6	11.70 11.30 19.10	0.043 0.010 0.103	[5] [6] [5]	166.1 167.5	14.30 14.62	1.42 2.04	Dinitrobenzene Dibutyl phthalate	[5] [10]
7	Pentogen					155.9	13.60	4.23	Dinitrobenzene	[11]
8	Bicyclooctane	210.2	18.00	0.058	[12]	170.0 165.0	13.77 14.96	14.79 8.65	Dinitrobenzene Dibutyl phthalate	[12] [12]
9	3,7-Dinitro-1,3,5,7-tetra- azabicyclo[3.3.1]nonane	172.9	15.64	5.08		151.6 150.6	13.71 13.62	17.06 18.10	Dibutyl phthalate Dinitrobenzene	

Townstature %C	Degree of conversion 0/	Products of decomposition, mol %						
Temperature, C	Degree of conversion, 76	N <sub>2</sub>	N <sub>2</sub> O	СО	CO <sub>2</sub>			
160	10	0.98	96.19	0.90	1.93			
160	20	0.69	96.47	0.83	2.01			
160	50	0.64	95.57	1.09	2.69			
160	75	0.66	93.94	1.29	4.11			
160	100	0.64	91.87	2.39	5.10			
150	10	0.68	96.32	0.83	2.18			
150	20	0.46	96.55	0.76	2.23			
170	100	0.95	88.22	2.87	7.94			

 Table 2. Composition of non-condensing gaseous products of thermal decomposition of 3,7-dinitro-1,3,5,7-tetraazabicyclo 

 [3.3.1]nonane in solid state

stable. The decomposition rate constant was varied by approximately an order of magnitude depending on the conformation of the ring. As follows from the data in Table 1, the most thermally stable modification was the tightly packed  $\beta$ -form of octogen, taking the conformation of twisted ring in which one pair of adjacent nitro groups was located on the same side of the average plane of the ring, and the other pair was located on the other side. The structure of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane, analog of octogen, in the crystal was similar to the  $\beta$ -modification of octogen, and the N-nitramine groups in the molecule were almost planar [13, 14].

Theoretically, three conformations are possible for the molecule of 3,7-dinitro-1,3,5,7-tetraazabicyclo-[3.3.1]nonane: *chair-chair* (**A**), *chair-boat* (**B**), and *boat-boat* (**C**), differing in the type of angular deformations and nonvalent interactions (Scheme 1). In the crystal, the *chair-chair* conformation (**A**) is realized, in which the nitramine groups have pyramidal structure (deviation of the amine nitrogen from the plane of its surrounding  $\gamma = 26^{\circ}-24^{\circ}$ ) and the CNC



angles in the ring are of 113°-118°, approximately the same as in the  $\alpha$ -form of hexogen (an intermediate in the synthesis of octogen) but lower than in the molecule of octogen (121°-125°). Many intramolecular contacts are shortened in the molecule of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane. The distance between the oxygen atoms and the adjacent methylene carbon atoms is 2.62–2.69 Å [13], which is less than the sum of the van der Waals radii of carbon and oxygen atoms (3.16 Å). Besides, there are some short intermolecular C···O contacts in the structure of 3.7dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane crystals (3.2-3.3 Å). In general, it could be concluded that the structure of bicyclo[3.3.1]nonane was much more rigid than that of cyclooctane, and the conversion of the ring was substantially hampered. Let us notice that, according to the conformational simulations, the structures of the *chair-boat* and *boat-boat* type are substantially less favorable, and low barriers of the formation make such conformations practically unstable. The above reasoning could explain the low thermal stability of 3,7-dinitro-1,3,5,7-tetraazabicyclo-[3.3.1]nonane, its rate constant of thermal decomposition being ~18 times higher than that of the β-conformer of octogen.

GC analysis of non-condensing gaseous products of thermal decomposition of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (Table 2) showed that nitrous oxide was the major one, and nitrogen amount was 100–200 times lower, whereas thermal decomposition of hexogen and octogen gives comparable amounts of nitrous oxide and nitrogen [15]. Scheme 2.

$$O_2 N \bigvee_{N=N}^{N} N - NO_2 \longrightarrow \left[ O_2 N \bigvee_{N=N}^{N} N^{\bullet \bullet \bullet} NO_2 \right]^{\neq} \longrightarrow O_2 N \bigvee_{N=N}^{N} N^{\bullet} + NO_2$$
(1)

$$CH_2 = N - NO_2 \longrightarrow CH_2O + N_2O$$
(3)

$$CH_2 = N - CH_2 + NO_2 \longrightarrow CH_2 = N + CH_2O + NO$$
 (4)

$$O_2 N \cdot N \xrightarrow{N}_N N^{\bullet} + NO \longrightarrow O_2 N - N \xrightarrow{N}_N N - NO$$
(5)

$$O_2 N - N \xrightarrow{N} N - NO \longrightarrow CH_2 = N + CH_2 = N - NO + CH_2 = N - CH_2 - NO_2$$
(6)

$$CH_2 = N - NO \longrightarrow CH_2 = N + CH_2O + N_2$$
(7)

$$CH_2 = N - CH_2 - N - NO_2 \longrightarrow CH_2 = N + CH_2O + N_2O$$
(8)

$$CH_2 = N - CH_2 - N - NO_2 \longrightarrow CH_2 = N + CH_2 = N - NO_2$$
(9)

$$CH_2 = N - NO_2 \longrightarrow CH_2 = N + NO_2$$
(10)

$$CH_2O + NO_2 \longrightarrow NO + CO_2 + CO + H_2O$$
(11)

According to the LC–MS analysis data for 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane and condensed products of its thermal decomposition at 5 and 30% conversion, the molecular ion peak in the mass spectrum of the starting 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]-nonane was weak (1.81%), the major peaks being assigned to the fragment ions with m/z 128 (100%) and 142 (64%). For condensed products of the thermal decomposition, the intensity of those peaks was different depending on conversion, and new peaks of fragment and rearrangement ions appeared (m/z 202, 172, 144, 130, 114, 112, 88, 74, 72, 58, 46, 44, 42, 30, 28), suggesting the destruction of the ring during decomposition.

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In view of the above-mentioned and the symbate variation of the activation parameters of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane decomposition in solution, the homolytic mechanism of thermal decomposition could be suggested (also by analogy with

hexogen and octogen), with the rate-determining step being the N–NO<sub>2</sub> bond rupture in one of the rings of the molecule (Scheme 2). For such mechanism, the transition state should be more ordered than the initial one, and the activation energy should be lower than the energy of the weakest N–NO<sub>2</sub> bond (1.375 Å) [15].

The activation entropy of thermal decomposition of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane in a solution at 180°C was as low as 5.75 J mol<sup>-1</sup> K<sup>-1</sup> (dibutyl phthalate) and 4.02 J mol<sup>-1</sup> K<sup>-1</sup> (dinitrobenzene). One could assume that the transition state was close to the initial state due to more rigid structure and the presence of short C···O contacts in the 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane molecule with planar configuration of the nitramine group.

Mechanism (1)–(11) in Scheme 2 adequately explained the formation of gaseous and condensed products of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane

thermal decomposition as well as low activation parameters of the Arrhenius equation in a solution as compared to those of hexogen and octogen (Table 1).

In summary, the kinetic features, activation parameters, and the mechanism of thermal decomposition of 3,7-dinitrotetraazabicyclo[3.3.1]nonane in the solid state and in solutions were determined. It was shown that the acceleration of decomposition was due to autocatalysis by the products of the reaction. The effect of the structure of the 3,7-dinitrotetraazabicyclo [3.3.1]nonane molecule on the rate and the mechanism of thermal decomposition were revealed.

## **EXPERIMENTAL**

3,7-Dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane was synthesized from urotropine dinitrate and acetic anhydride and purified by crystallization from acetone, mp 207°C (205–206°C [1]).

The kinetics of thermal decomposition was studied by manometric method using the Burdon type glass manometer with residual air pressure in the reaction volume of  $10^{-2}$ – $10^{-1}$  mmHg [16]. Gaseous products of decomposition were analyzed using an LKhM-80 chromatograph equipped with Polysorb 1 column. Composition of the condensed products of decomposition was analyzed using a Shimadzu LCMS-2020 chromato– mass spectrometer (solvent: acetonitrile, energy of ionization 70 eV). Rate constants of thermal decomposition were calculated from the starting rates of decomposition. The error in determination of the rate constant did not exceed 6–8%, activation energy was determined with accuracy of ±3–4 kJ/mol.

## CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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