



Thermal Decomposition of Azidonitramines

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Abstract: The kinetic laws and mechanism of the thermal decomposition of azidonitramines in gaseous phase, melt, and in solutions are discovered. Homolysis is established to be the first order reaction, the limiting stage has Arrhenius's parameters $E_a = 144.8-166.5 \text{ kJ mole}^{-1}$, $\lg A = 13.53-14.97$, what is not adequate for monofunctional alkylazides and alkylnitramines. The thermolysis of azidogroup initiates the decomposition. Nitraminogroup in β - or α -position to azidogroup increases the decomposition rate by 1-2 orders correspondingly as compared with δ -position.

Keywords: thermal decomposition, nitramines, azidonitramines

Introduction

Azidonitramines are known to be high energetic compounds [1-3]. They have two explosophoric groups, where the thermal decomposition can be initiated. To elucidate which of groups initiates the thermal decomposition and their reciprocal influence on thermostability, the kinetic laws and mechanism of thermal decomposition of azidonitramines with the general formula $\text{N}_3\text{CH}_2[\text{N}(\text{NO}_2)\text{CH}_2]_n\text{R}$, where $n=1$ $\text{R}=\text{H}$ (**1**), CH_2CN (**2**), N_3 (**3**), $\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{N}_3$ (**4**), $n=2$ $\text{R}=\text{N}_3$ (**5**), $n=3$ $\text{R}=\text{N}_3$ (**6**), also $(\text{N}_3\text{CH}_2\text{CH}_2)_2\text{NNO}_2$ (**7**), and $\text{N}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{N}(\text{NO}_2)\text{CH}_3$ (**8**) were studied. Thermolysis was studied both in gaseous and in melt and in solution of dibutylphthalate (DBP).

Experimental Methods

Azidonitramines (**1-8**) were synthesized by known methods [1-3] and purified by distillation or crystallization. According to the chromatographic data they contained 99.5-99.6% of the main substance.

The thermal decomposition kinetics was studied by a manometric method using a Bourdon's manometer, the initial pressure in the reaction vessel was 10^{-1} - 10^{-2} mm of mercury. The kinetics of compounds (**2**) and (**6**) were studied also by ampoule method according the nitrogen dioxide formation using photoelectrocolorimeter [4].

The r.m.s. error in determination of the first order rate constants was no more than 6% and no more than 10%, if the rate constants was found from the initial decomposition rates. The error for activation energy did not exceed 0.4 kJ mol^{-1} and 0.05 units of logarithm for pre-exponential factor.

The gaseous decomposition products were analyzed qualitatively on LKhM-72 chromatograph (the temperature of the active coal column $140 \text{ }^\circ\text{C}$) and on Specord 75 IR spectrometer. The condensed products were analyzed on mass-spectrometer MKh-1303 (ionization energy 60 eV, emission current 2 mA, the temperature of ions source $150 \text{ }^\circ\text{C}$) and on chromato-mass-spectrometer MKh-1312 (the temperature of the column with squalane $80 \text{ }^\circ\text{C}$, the temperature of effusion cell $100 \text{ }^\circ\text{C}$).

Results

The thermal decomposition of azidonitramines in gaseous and liquid phase followed the first-order equation of reaction for conversions of 40-50% excepting of compounds (**2**) and (**4**) which kinetic curves are S-shaped (Figure 1). Kinetic curves for the nitrogen dioxide formation during thermolysis of (**2**) and (**6**) have the same shape form. Decomposition in gaseous and liquid phases was not complicated by the chain and heterogeneous processes because decomposition rate was not influenced by either the initial pressure of substance vapour (within the limits 30-200 mm of mercury) or ratio of substance mass to reaction volume, m/V ($2.4 \cdot 10^{-3}$ - $7.7 \cdot 10^{-4} \text{ g cm}^{-3}$) and the reaction vessel surface ($S/V=1.9$ - 9.2 cm^{-1}) or chain processes' inhibitors (toluene, phenol, xylene, nitrogen oxide). Carbon oxide, nitrogen oxide and gaseous decomposition products did not change the rate, but addition of decene increased the rate constant (Figure 2). It may be explained by interaction of azidogroup with double bond in decene [5]. The solvent's dielectric permittivity (biphenyl, $\epsilon = 2.53$, dibutylphtalate, $\epsilon = 6.44$;

dinitrobenzene, $\varepsilon = 20.6$) and substance's concentration in solution (2-25%, mass) did not change the decomposition rate practically.

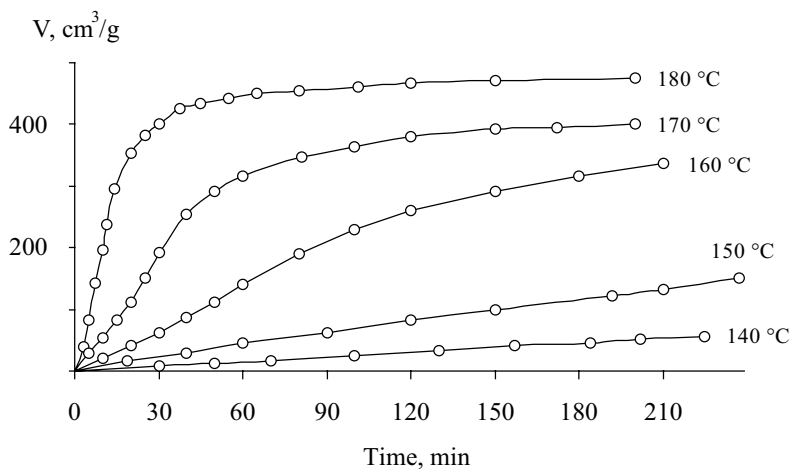


Figure 1. Kinetic curves of thermal decomposition of compound (5) in melt.

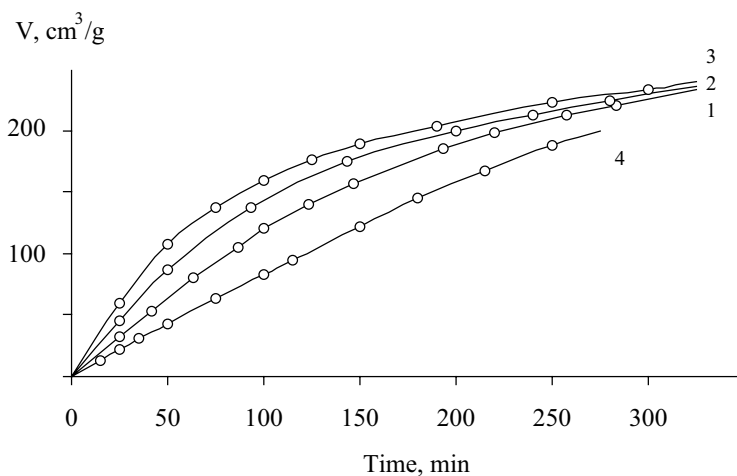


Figure 2. Volume of gas evolved versus time for the compound (1) in the presence of decene, mole/mole (at 150 °C): 1 – 0.5; 2 – 1; 3 – 2; 4 – without decene.

The kinetic and thermodynamic parameters for azidonitramines are listed in Table 1.

Table 1. Kinetic and thermodynamic parameters of thermal decomposition for azidonitramines (**1-8**)

No.	Compounds	Thermolysis condition	T, °C	E_a , kJ mol ⁻¹	lg A	$k_{160^\circ\text{C}}$, 10 ⁵ , s ⁻¹	$\Delta S_{160^\circ\text{C}}^\ddagger$, J(mol K) ⁻¹
1	N ₃ CH ₂ N(NO ₂)CH ₃	gas phase solution	130-170 140-180	157.0 147.3	14.24 13.53	10.49 6.52	+16.3 +2.7
2	N ₃ CH ₂ N(NO ₂)CH ₂ CH ₂ CN	melt solution NO ₂ accumulation	140-180 140-180 140-180	152.7 150.2 167.8	14.22 13.96 15.05	6.60 6.21 0.64	+15.9 +10.9 +31.8
3	N ₃ CH ₂ N(NO ₂)CH ₂ N ₃	melt solution	130-170 140-180	152.3 144.8	14.85 13.90	29.16 23.61	+27.9 +9.8
4	N ₃ CH ₂ [N(NO ₂)CH ₂] ₂ N ₃	melt solution	110-150 130-170	151.0 145.2	14.92 13.74	28.14 23.16	+29.3 +6.7
5	[N ₃ CH ₂ N(NO ₂)CH ₂] ₂	melt solution	130-170 140-170	151.9 152.7	14.33 14.26	12.05 6.77	+18.0 +16.7
6	N ₃ CH ₂ [N(NO ₂)CH ₂] ₃ N ₃	melt solution NO ₂ accumulation	136-170 136-170 150-180	149.8 146.0 168.1	14.47 13.88 15.75	25.86 20.00 3.37	+20.7 +9.4 +45.2
7	(N ₃ CH ₂ CH ₂) ₂ NNO ₂	melt solution	150-190 150-190	162.3 161.9	14.97 14.80	2.54 1.80	+30.3 +27.0
8	N ₃ (CH ₂) ₂ OCH ₂ N(NO ₂)CH ₃	solution	170-210	166.5	14.16	0.12	+14.8
9	(NCCH ₂ CH ₂) ₂ NNO ₂ [5]	melt solution	215-250 210-250	182.7 172.9	14.89 13.92	0.008 0.012	+7.0 +2.5

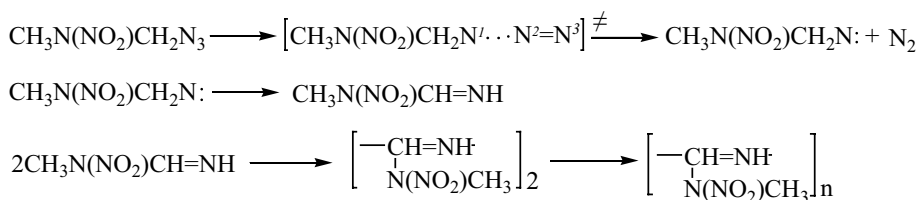
The decomposition rate in melt was 1.2-2.1 times more than for solutions. It may be caused by the interaction of initial molecules with each other or with decomposition products. Besides that decomposition rate of monoazidocompounds (**1**, **2**) is less than of compounds with two azidogroups in molecule (**3**, **4**, **6**).

The decomposition products of compound (**1**) in melting phase were studied in more detail at different conversion degrees. It has been noticed that intensity of azidogroup's absorption band in the region 2130 cm⁻¹ decreases while conversion degree increases. The intensity of nitraminogroup's absorption peaks (1540-1300 cm⁻¹) was practically constant. Only the molecular nitrogen and imine CH₃N(NO₂)CH=NH were fixed in products of 1-2% conversion by IR- and mass-spectroscopy. The nitrogen dioxide appeared in products of more deep conversion (5-10%), when composition of decomposition products became enough complicated. Thus, the molecular ions with m/e 206 [CH₃N(NO₂)CH₂N]₂⁺, 103 [CH₃N(NO₂)CH=NH]⁺, 45 [CH₃NO]⁺, 43 [CH₃NCH₂]⁺, 29 [CH₂NH]⁺, 28 [N₂]⁺ and their splinter ions were discovered in mass-spectra of decomposition products.

In effusiochromatograms of decomposition products (conversion 2-5%), besides initial compound (1), it was found four peaks with mass 58 $[-CH_2-NH-]_2$, 87 $[-CH_2-NH-]_3$, 103 $[CH_3N(NO_2)CH=NH]$, and 129 $[-N(CH_3)-CH_2-]_3$. For compound (2) the peaks with mass 53 (CH_2CHCN) , 58 $[-CH_2-NH-]_2$, 87 $[-CH_2-NH-]_3$ were registered and 4 peaks else, which did not reproduce from experiment to experiment. When the conversion of compounds (1, 2) was 80-90%, the gaseous phase had N_2 , N_2O , NO , NO_2 , H_2O , CO , CO_2 , HCN , and condensed phase consisted from oligomer (polymer), included $[-CH_2NH-]$ and $[-N(CH_3)CH_2-]$ fragments mainly.

Discussion and Conclusions

The observed kinetic laws, activation parameters and composition of decomposition products of alkylazidonitramines (1-8) can be best explained in the framework of radical decomposition mechanism with primary break of N^1-N^2 bond in azidogroup. It can be written as example for compound (1)



The nitrene's formation was proved by the experiments on the decomposition of compound (1) in carbon oxide and nitrogen oxide excess. The absorption band of azidogroup (2130 cm^{-1}) disappeared and absorption bands of isocyanate (2200 cm^{-1}) and nitrosoamine (1550 cm^{-1} , 1450 cm^{-1}) groups appeared in IR-spectra at the complete conversion.

The special experiment was conducted for determination of kinetics of NO_2 formation during decomposition. The Arrhenius parameters of compounds (2), found by nitrogen dioxide evolution, are more than corresponding manometric data, and the rate constants are one order less (Table 1). This fact may be explained by the most thermostability of nitraminogroup. The independent experimental data confirm this (compounds (9) [5], Table 1). The monofunctional alkylnitramines are one order more stable than monofunctional alkylazides. However, alkylazidonitramines are 2-3 orders less stable than monofunctional alkylazides [6, 7] and alkylnitramines [5, 8]. It may be explained by intermolecular

interaction of azide and nitramine groups leading to decrease two-bonding character of N¹-N² bond in azidogroup. The interaction weakens if azide and nitramine groups are connected by ethylene bridge, for example, compound (7). In this case rate constant was 4 times less than for compound (3). In compound (8) azidogroup and nitramine group are connected by the four member chain, so they decompose independently, and the rate constant of compound (8) is similar to monofunctional alkylazides.

In conclusion, we note that accumulation of nitramine groups in the molecule (compounds (3), (4), (6)) does not lead to change of azidonitramines' thermostability. However, if nitramine and azido groups are neighbour (transition from δ - to α -substitution) the rate of azidogroup's decomposition increases by two orders because of steric and induction interaction of neighbouring groups inside of molecule.

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