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Effect of Additive Polyfunctional Substituents on the Thermal Decomposition Rate of R^1,R^2,R^3-Nitromethanes

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Abstract—Kinetics of thermal decomposition of polyfunctionally substituted nitromethanes has been studied by manometric method as well as IR and chromato-mass spectrometry. Activation parameters of the rate-limiting stage of C–NO_2 homolysis have been determined. The rate constant and the activation energy are correlated with additive steric constants of the substituents; this enables prediction of reactivity (thermal stability) of the unstudied mononitrocompounds which decompose with the break of C–NO_2 bond.

Keywords: derivatives of nitromethane, kinetics, thermal decomposition, reaction mechanism, correlation

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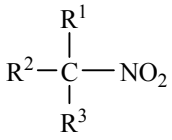
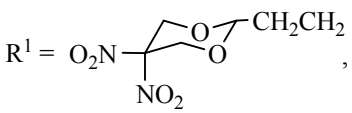
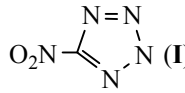
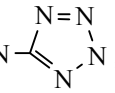
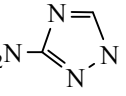
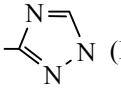
Study of thermal decomposition kinetics of various nitrocompounds with relation to their structure is of great applied and fundamental interest. Extending the previously reported results [1, 2], herein we studied the influence of substituents structure on the rate and activation energy of thermal decomposition of polyfunctional nitrocompounds **I**–**VII** (Scheme 1).

Thermal decomposition of compound **II** in the temperature range 160-180ºC and compound **VI** at 160ºC described by the first-order rate equation up to conversion of 45–50%. Changing of the ratio of substance mass to reaction volume m/V from 2×10^{-4} to 28×10^{-4} g/cm^3 had virtually no effect on the reaction rate constant at 160°C. Similarly, the rate constant was independent of the ratio of the reaction vessel surface to its volume S/V ranging between 2.8 and 4.9 cm^{-1} (in the cases of decomposition of compounds **II** and **VI**). Those observations evidenced about homogeneous mechanism of decomposition of compounds **II** and **VI**, not complicated by chain processes at the reaction vessel walls. Addition of

Scheme 1.

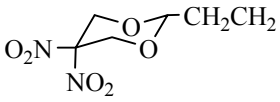


R^1 =  , R^2 = Br, R_3 =  (**I**); R^2 =  , R^3 = Cl (**II**);

R^2 = Br, R_3 =  (**III**); R^2 = Cl, R^3 =  (**IV**); R^2 = Cl, R^3 = Br (**V**);

$R^2 = R^3$ = Cl (**VI**); $R^1 = C_6H_5$, R^2 = F, R^3 = H (**VII**).

Table 1. Kinetic parameters of thermal decomposition of polyfunctionally substituted nitromethanes in solutions of dibutyl phthalate (compounds **II, VI**) and 1,3-dinitrobenzene (compounds **I, III–V**)[a]

Comp. no.	R^1	R^2	R^3	T, °C (range)	E_a, kJ/mol	log A	$k_{160°C}$, s^{-1}	$\Delta S^{\neq}_{160°C}$, J mol^{-1} K^{-1}	$-\Sigma E_s$ [4]	Conditions
I		Br	O_2NTetr	150–170	161.5	15.34	7.25×10^{-5}	37.3	8.32	Solution
II		Cl	O_2NTetr	160–180	165.0	15.37	2.94×10^{-5}	37.8	7.69	Melt
				160–180	165.3	15.36	2.64×10^{-5}	37.6	7.69	Solution
III		Br	O_2NTr	160–180	165.6	15.30	2.12×10^{-5}	36.5	7.57	Solution
IV		Cl	O_2NTr	160–200	169.1	15.35	8.99×10^{-6}	37.5	6.94	Solution
V		Cl	Br	160–200	169.3	15.26	6.91×10^{-6}	35.7	6.88	Solution
VI		Cl	Cl	160–200	173.5	15.33	2.53×10^{-6}	37.1	6.25	Solution
VII	C_6H_5	F	H	220–260	189.1	15.47	4.59×10^{-8}	39.7	3.25	Gas

[a] O_2NTetr – 5-nitro-1,2,3,4-tetrazol-2-yl, O_2NTr – 3-nitro-1,2,4-triazol-1-yl.

gaseous decomposition products, forming at decomposition degree 20–25%, to the initial compound **VI** in melt at 160°C did not alter the rate-limiting stage rate constant; hence, the products don't react with the initial compound.

In order to eliminate the effect of crystal lattice on the thermolysis rate constant, decomposition kinetics of the of compounds **I–VI** was further studied in dilute (2–2.5 wt%) solutions in inert solvents: dibutyl phthalate (ε = 6.4) and 1,3-dinitrobenzene (ε = 20.6). The experiments revealed that neither the solution concentration nor the solvent dielectric constant influenced the rate constant; that indirectly confirmed the homolytic decomposition mechanism. Up to conversion of 45–48% (as estimated from the gas evolution) the reaction rate followed the first-order rate equation.

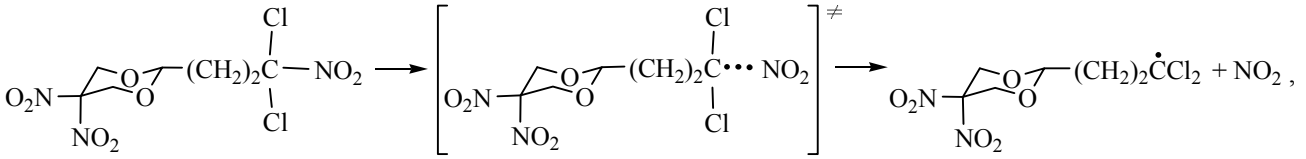
In contrast to compounds **I–VI**, decomposition of compound **VII** was studied in the gas phase. Preliminary checks of the effect of chain process inhibitors (toluene or cyclohexane) at the rate constant has shown that at equal proportion of the vapor pressure of the substance and inhibitor (1 : 1 or 1 : 1.2) the rate constant is independent of the initial pressure. The influence of S/V studied in the spherical Bourdon's manometer with volume from 650 to 4.3 cm^3, also stuffing of reactionary vessel with glass capillaries was used. This changed S/V from 0.52 to 9.1 cm^{-1}. The rate constant of inhibited decomposition of **VII** at S/V = 0.52–0.54 cm^{-1} differed from that determined by extrapolation of $k_{inh} = f(S/V)$ to $S/V = 0$ [3]. Therefore, decomposition of compound **VII** was studied at S/V = 0.52–0.55 cm^{-1}; under those conditions the reaction was homogeneously and obeyed the first-order rate equation.

Activation parameters of thermal decomposition of compounds **I–VII** are collected in Table 1 along with steric constants of the substituents [4].

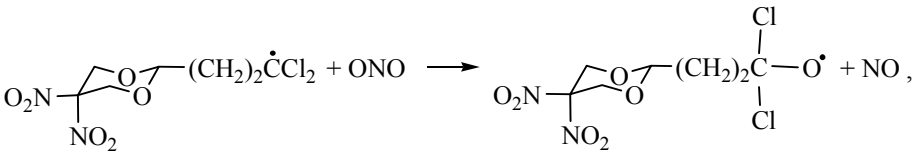
Noteworthy, kinetic parameters of thermal decomposition of compound **II** in melt and in dibutyl phthalate solution were close. In the cases of all the compounds **I–VII**, the determined preexponential factor was practically the same (ranged from 15.3 to 15.5). At the same time, the activation energy increased from 161 to 189 kJ/mol in the **I–VII** series, the rate constant at 160ºC decreasing by more than three orders of magnitude. Hence, enthalpy term made the major contribution into the rate constant, the entropy term being less important. The same applied to the previously studied homolytic mechanism of thermal decomposition of other nitrocompounds [1, 2].

Qualitative composition of thermal decomposition products of selected compounds is shown in Table 2 (compound **VI**: melt, 160°C, and conversion of 7–10%; compound **VII**: gas phase, 200°C, and conversion 15–20%).

Taking into account the products composition and the activation parameters of the reaction, the following mechanism of compound **VI** thermolysis was derived by analogy with trichloronitromethane [5] and 1,1-dichloro-1-nitroethane [6] [Eqs. (1)–(10)].



(1)



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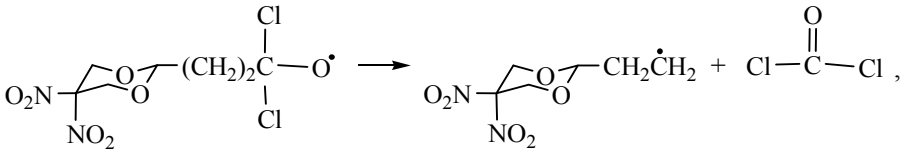
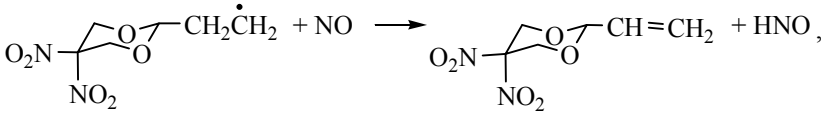


(3)



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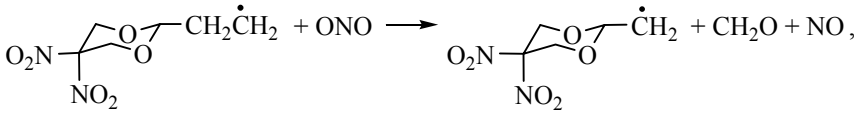
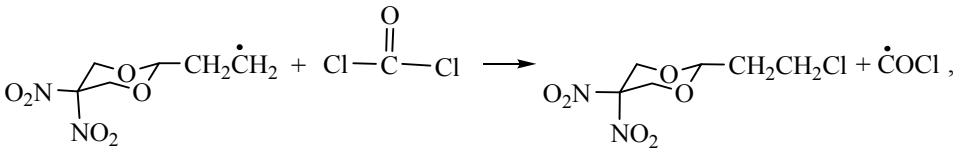


(5)



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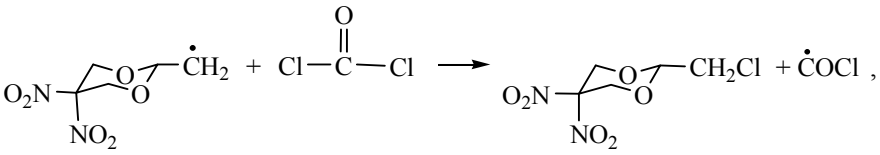
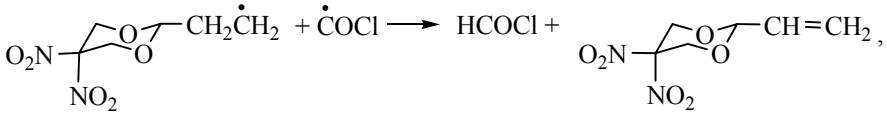


(7)



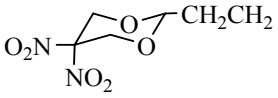
(8)

$$2HNO \rightarrow N_2O + H_2O, \quad (9)$$

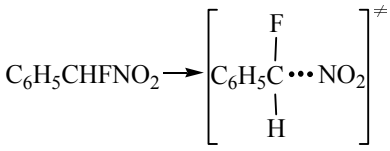
$$CH_2O + NO_2 \rightarrow CO + NO + H_2O. \quad (10)$$

At first glance, reaction initiated at carbon atom of *gem*-dinitromethyl group in 1,3-dioxane ring could be expected to compete with the major pathway of compounds **I**–**VI** thermolysis. However, we previously demonstrated that *gem*-dinitromethyl group in 1,3-dioxane ring was more stable under the experiment conditions [7]. Rate constant of its decomposition (solution in dibutyl phthalate, 160°C) was of 4.9×10^{-7} s^{-1}, about 5 times lower than that in the case of compound **VI**. Hence, thermolysis of compounds **I**–**VII** apparently occurred via homolysis of the C–NO_2 bond in *gem*-dihalogenonitromethyl group. In parti-

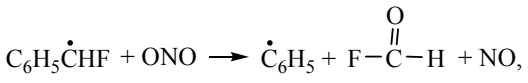
Table 2. The main thermal decomposition products of compounds **VI** and **VII**

Comp. no.	R^1	R^2	R^3	Products
VI		Cl	Cl	$R^1CH{=}CH_2$, $R^1CH_2CH_2Cl$, R^1CH_2Cl, $Cl_2C{=}O$, $HClC{=}O$, NO, N_2O, CH_2O, CO, H_2O
VII	C_6H_5	F	H	$C_6H_5{-}C_6H_5$, C_6H_5NO, $HFC{=}O$, NO

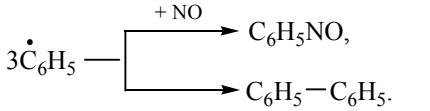
cular, conversion path of compound **VII** was represented by Eqs. (11)–(14).



$$\rightarrow C_6H_5\dot{C}HF + NO_2, \quad (11)$$



(12)



(13)

(14)

Note also that in the cases of compounds **I** and **II** homolysis of the N^2–N^3 bond with tetrazole ring opening could be a rate-limiting reaction stage [8]. Such mechanism was operative at higher temperature, and at 160°C (dibutyl phthalate solution) the rate constant was of 5.8×10^{-7} s^{-1} [9], about two orders of magnitude lower than those reported in Table 1.

Previously we demonstrated that reactivity of α-halogenodinitro-compounds correlated with additive steric constants of the substituents [2]. We studied the same dependence of thermolysis rate of compounds **I**–**VII** and revealed that the rate constant [Fig. 1, Eq. (15)] and the activation energy [Fig. 2, Eq. (16)] were perfectly correlated with the steric constants of the substituents.

$$\log k_{160^\circ C} = -(0.628\pm0.014)\Sigma E_s - (9.425\pm0.095), \quad (15)$$
$$r = 0.999;\ S_y = 0.137;\ n = 7,$$

$$E_a = (5.44\pm0.07)\Sigma E_s + (206.93\pm0.51), \quad (16)$$
$$r = 0.999;\ S_y = 0.70;\ n = 7.$$

The observed correlation coincided with the suggested homolytic mechanism of thermolysis of compounds **I–VII**, the rate-limiting stage being break of the C–NO_2 bond in the alkyl fragment of the molecule.

In order to verify the derived correlations, we calculated kinetic parameters of thermolysis of some mononitrocompounds and compared them with the corresponding reference data [10–12]; the results are collected in Table 3. In most cases the observed deviation was comparable to the experiment accuracy.

EXPERIMENTAL

Compounds **I–VII** were produced and purified by well-known methods [13], contained 99.3–99.6% of the major component (chromatography data).

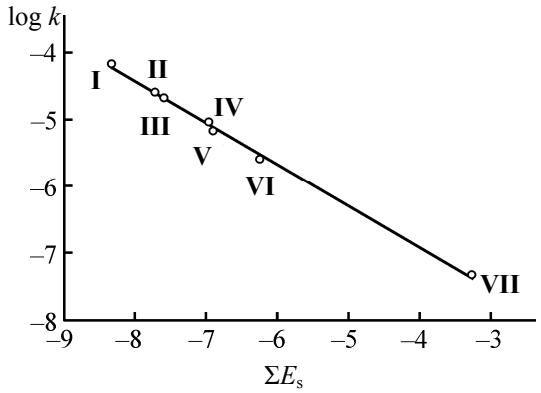


Fig. 1. Rate constant of thermal decomposition of compounds **I–VII** (160°C) as function of steric constants of the substituents.

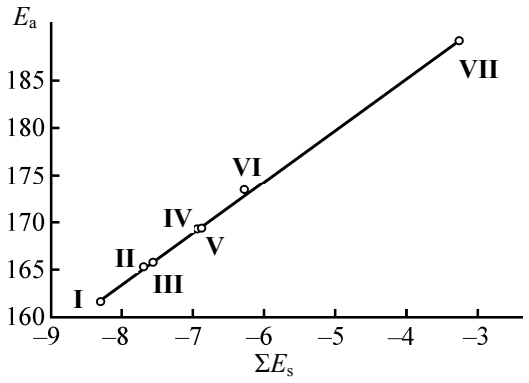


Fig. 2. Activation energy of thermal decomposition of compounds **I–VII** as function of steric constants of the substituents.

Table 3. Experimental and calculated kinetic parameters of selected mononitro- and dichloronitrocompounds

Compound	Experiment		ΣE_s	Calculated according to Eqs. (15), (16)		Deviation, %		Reference
	E_a, kJ/mol	$\lg k_{160°C}$		E_a, kJ/mol	$\log k_{160°C}$	ΔE_a	$\Delta(\log k_{160°C})$	
$CH_3CCl_2NO_2$	178.5	–6.310	–5.62	176.4	–5.896	1.18	6.6	[10]
$C_2H_5CCl_2NO_2$	178.9	–6.428	–5.69	176.0	–5.852	1.62	9.0	[10]
$C_6H_5CH_2NO_2$	176.4	–7.527	–3.57	187.5	–6.293	6.3	4.6	[10]
Cl_3CNO_2	156.5	–4.311	–8.43	161.1	–4.131	2.83	4.2	[11]
CH_3NO_2	227.2	–13.064	3.72	227.2	–11.761	0	9.9	[12]

Thermal decomposition kinetics was studied by manometric method using glass Bourdon's manometer [2] at residual air pressure in a reactionary vessel of 10^{-2}–10^{-1} mmHg. Rate constants were calculated by the Guggenheim method using the first-order rate equation. The related error of kinetic parameters determination did not exceed 10% (rate constant), 0.4 log units (pre-exponential factor), and 6 kJ/mol (activation energy).

Gaseous decomposition products were analyzed using the UR-10 infrared spectrometer equipped with the KBr gas cuvette. Condensed products were analyzed using the MX-1312 effusion chromatomass spectrometer; the experimental parameters were as follows: Squalane capillary column temperature 50–80°C, effusion chamber temperature 100°C, detector temperature 100°C, injector temperature 120–150°C, residual pressure 1.3–1.5 mmHg, emission current 20 μA, accelerating voltage 55 V, cathodic current 9.35 μA.

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