

Kinetics and mechanism of thermal decomposition of nitropyrazoles

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The decomposition of mono-, di-, and trinitropyrazole derivatives in the condensed state was studied by the manometric method. The reaction rate depends on the number and position of nitro groups in the pyrazole cycle and on the polarity of the medium and aggregate state of the substance. The activation energy of the initial non-catalytic stage of decomposition E_1 decreases on going from mono- to trinitropyrazoles from 142 to 132 kJ mol⁻¹, and the pre-exponential factor is 10^{9±0.5} s⁻¹. In a diphenyl solution the decomposition rate is lower than that in the melt, and this difference decreases with increasing in the number of nitro groups in the molecule. For the decomposition of trinitropyrazole in the solid state, E_1 decreases by 10 kJ mol⁻¹. All these facts are explained in terms of the mechanism, according to which the reaction occurs as the oxidation of the adjacent carbon atom by the nitro group and proceeds *via* a strongly polar cyclic transition state.

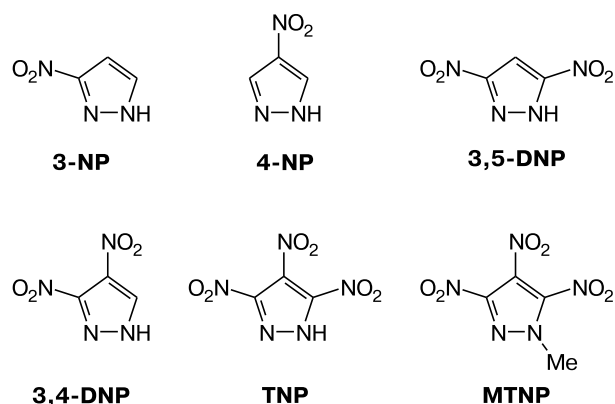
Key words: nitropyrazoles, dinitropyrazoles, trinitropyrazoles, decomposition in condensed phase, kinetics, mechanism, power-consuming compounds.

One of trends of the modern development of the chemistry of high-energy compounds is the synthesis and study of the physicochemical properties of nitro derivatives of NH-azoles, including pyrazoles.^{1–9} In the most part of cases, the thermal stability of nitropyrazoles was evaluated by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) on the basis of their temperature of decomposition onset. Only several studies^{6–9} are devoted to the kinetics of thermal decomposition of nitropyrazoles using TG and DSC in a flow of inert gases, *i.e.*, under the conditions that do not exclude evaporation of the studied substance. Therefore, the kinetic parameters obtained under these conditions can be insufficiently exact and need additional checking. The quantum chemical calculations^{6,7} of probable pathways of the initial state of decomposition simulate the process in the gas phase rather than in the condensed one and do not cover all possible primary decomposition stages and, hence, can also be considered as preliminary. This work is devoted to the study of the kinetics of thermal decomposition of mono-, di-, and trinitropyrazoles in the condensed phase under isothermal conditions using the highly sensitive manometric method. This made it possible to determine the kinetic parameters of decomposition in the condensed phase and the influence of the properties of the solvent on these parameters. As a result, the probable

mechanism of the initial thermolysis stage was proposed and substantiated.

Experimental

3-Nitropyrazole¹⁰ (**3-NP**), 4-nitropyrazole¹⁰ (**4-NP**), 3,5-dinitropyrazole¹¹ (**3,5-DNP**), 3,4-dinitropyrazole¹¹ (**3,4-DNP**), 3,4,5-trinitropyrazole^{1,2} (**TNP**), and 1-methyl-3,4,5-trinitropyrazole^{1b,2} (**MTNP**) were used as objects of the study.



The kinetic studies were carried out using a manometric system designed for the pressure to 100 atm.¹² The reactor was a sealed glass tube 0.5–5.0 mL in volume equipped with a cres-

cent-like membrane with a pointer and placed into a heated metallic body connected to a vacuum pump or a cylinder with compressed air and had a transparent window for the observation of pointer deviations. The pressure was measured by the compensation method. This procedure makes it possible to perform experiments at high temperatures in almost any solvents and to measure the decomposition kinetics at high degrees of filling the vessel with the substance.

Results and Discussion

The decomposition curves for the studied compounds at the temperatures corresponding to the rate constant of the initial stage $k_1 = 10^{-5}$ – 10^{-6} s $^{-1}$ are shown in Fig. 1. The decomposition of mono- (**3-NP**, **4-NP**) and dinitropyrazoles (**3,4-DNP**, **3,5-DNP**) in the liquid state proceeds *via* the first-order equation or with a weak autocatalysis. Unlike them, the decomposition of trinitropyrazoles **TNP** and **MTNP** occurs with a strong acceleration. The kinetic curves are described by the first-order equation of autocatalysis. The degree of filling of the vessel with the substance ($m/V/g\text{ cm}^{-3}$) exerts no effect on the initial stage but influences the acceleration of the process. At $m/V = 0.01$ the autocatalytic rate constant ~ 100 times exceeds k_1 . For **TNP** and **MTNP**, the gas evolution upon complete decomposition measured at temperatures >170 °C is 570 and 580 cm $^3\text{ g}^{-1}$, respectively. These values were accepted to be a measure of 100% decomposition and used for the calculation of k_1 for the considered compounds from the initial rate at low temperatures.

In a solution of diphenyl chosen as a nonpolar and lowly volatile solvent, the decomposition of all compounds, including trinitro derivatives **TNP** and **MTNP** (Fig. 2), follows the first-order equation.

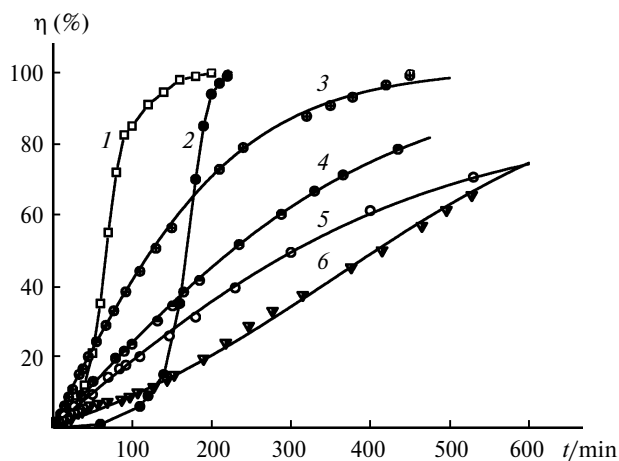


Fig. 1. Comparison of the kinetic curves of decomposition of nitropyrazole derivatives in the liquid state ($m/V = 0.01\text{ g cm}^{-3}$) in the region of rate constants 10^{-5} – 10^{-6} s $^{-1}$: **TNP**, 200 °C (1); **MTNP**, 200 °C (2); **3,4-DNP**, 230 °C (3); **4-NP**, 300 °C (4); **3-NP**, 300 °C (5); and **3,5-DNP**, 250 °C (6).

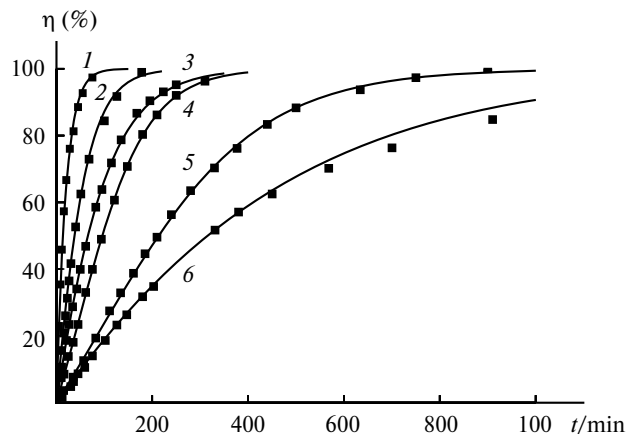


Fig. 2. Kinetic curves of decomposition of **TNP** and **MTNP** in solutions: **MTNP**, diphenyl, 280 °C (1); **MTNP**, diphenyl, 260 °C (2); **TNP**, *o*-dichlorobenzene, 240 °C (3); **TNP**, diphenyl, 240 °C (4); **MTNP**, *o*-dichlorobenzene, 240 °C (5); and **MTNP**, diphenyl, 240 °C (6).

The kinetic parameters of decomposition of all compounds in the liquid phase and in solutions are presented in Table 1. The data for the solid phase for **TNP** are also given. The reproducibility of k_1 determination was 10–15%, and the accuracy of determination of the activation energy was 6 kJ mol $^{-1}$. Figure 1 and Table 2 show that **3-NP** is the most stable compound in the liquid state, and **4-NP** is insignificantly inferior to **3-NP** in stability followed by **3,5-DNP** (dinitropyrazole with the separated nitro groups), then **3,4-DNP** (dinitropyrazole with the adjacent nitro groups), and then **MTNP** and **TNP**.

The following regularities are observed. The decomposition of nitropyrazoles in the liquid state at the initial stage is characterized by an activation energy of 140–160 kJ mol $^{-1}$, the value of which decreases on going from mono- to trinitro derivatives, and by a lowered value of pre-exponential factor $A = 10^{9\pm 0.5}$ s $^{-1}$. For decomposition in diphenyl, k_1 always decreases (with a slight increase of the activation energy), and the highest difference in the values of E in solution and in melt is observed for the mononitro derivatives. For **3-NP** the difference is 20 times, whereas that for **TNP** is only 3 times. In *o*-dichlorobenzene, which is more polar than diphenyl (dielectric constant ϵ of these solvents is 10 and 2, respectively), the decomposition rate increases but does not attain the level of pure **TNP**. The same regularity is observed for **3,4-DNP**, whose decomposition in nitrobenzene ($\epsilon = 35.6$) is 2 times faster than that in diphenyl but is slower than that in the melt.

The unusual change in the rate is observed for the transition of **TNP** to the solid state. For this compound, the decomposition rate does not decrease compared to the liquid phase as it is usual¹³ but increases, and the activation energy decreases by 10 kJ mol $^{-1}$.

All obtained results are consistent with the certain reaction mechanism, which can be derived from an analysis

Table 1. Kinetic parameters of decomposition of nitropyrazoles

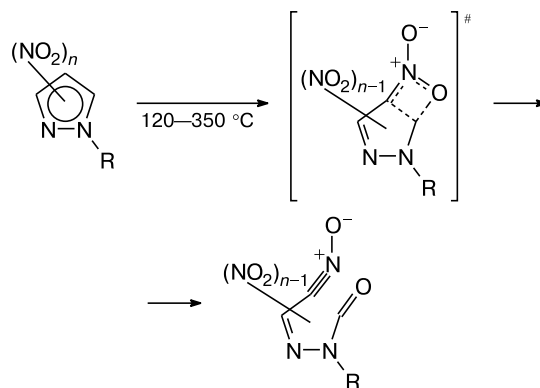
Compound	M.p./°C	Medium	$\Delta T/^\circ\text{C}$	E^* /kJ mol ⁻¹	log(A/s^{-1})	$k_1 \cdot 10^7/\text{s}^{-1}$ (230 °C)
3-NP	175	Melt	250–320	142.7 (132.7) ¹⁰	8.50	3.20
4-NP	162	Diphenyl	280–350	161.8	9.00	0.16
		Melt	280–320	142.3 (92.5) ¹⁰	8.53	5.70
3,5-DNP	168	Diphenyl	280–350	159.6	8.97	0.25
		Melt	230–250	138.1 (86) ⁷	8.80	23
3,4-DNP	87	Diphenyl	280–340	150.7	9.08	2.90
		Melt	200–250	134.0 (106) ⁷	9.50	400
TNP	186	Diphenyl	220–280	144.4	9.40	42
		Nitrobenzene	230	—	—	80
		Melt	190–220	131.8 (121), ⁷ (127.3) ⁶	9.60	830
MTNP	90.8	Diphenyl	220–340	136.5	9.63	290
		<i>o</i> -Dichlorobenzene	230	—	—	370
		Solid phase	120–160	121.7	9.40	—
		Melt	140–200	134.0 (237) ⁸	9.70	618
		Diphenyl	200–280	141.9	9.45	69

* The literature data obtained by TG and DSC are given in parentheses.

of the literature data on the decomposition of unsaturated nitro compounds. On the basis of the quantum chemical calculations of the activation energy for different elementary acts it was concluded¹⁴ that the most probable route of decomposition for nitroethylene and other nitroalkenes in the gas phase is the intramolecular oxidation of the adjacent carbon atom by the nitro group, which proceeds through the polar transition state of the oxazet structure. In the case of the studied nitropyrazoles, this process can be presented by Scheme 1.

This mechanism can also be classified as the intramolecular nucleophilic addition, whose rate should depend on the electron density on the reaction center as that for any heterolytic process and on the dielectric constant of the medium. The conclusion¹⁴ is consistent with a series of experimental data. It was found¹⁵ that the decomposition of 1-methyl-1-nitrostyrene $\text{PhCH}=\text{C}(\text{Me})\text{NO}_2$ affords PhCHO and MeCN . The activation energy of the homogeneous gas-phase decomposition of nitropropene and other nitroolefins is¹⁶ 170 kJ mol⁻¹, which is close to the calculated¹⁴ value. The pre-exponential factor of the decomposition of nitroolefins in the gas phase is 10¹² s⁻¹, which is characteristic of the reactions proceeding *via* the four-membered cyclic transition state.¹⁶

The same mechanism was proposed¹⁴ for the decomposition of 1,1-dinitro-2,2-diaminoethylene $(\text{NO}_2)_2\text{C}=\text{C}(\text{NH}_2)_2$ and *o*-dinitrobenzene and can be considered probable for the nitropyrazole derivatives. The rate constants of radical addition to the double bond of olefins

Scheme 1

R = H, Me; $n = 1-3$

in the absence of steric hindrances correlate with the energy of electron localization,¹⁷ which approximately depends, in turn, on the C=C bond length.¹⁸ The C=C bond length in ethylene is 1.33 Å, the shortest bond between the carbon atoms in pyrazole is 1.38 Å, and that in benzene is 1.45 Å. Intramolecular oxidation occurs easily in nitroethylene ($E = 192$ kJ mol⁻¹, $A = 10^{12.1}$ s⁻¹) and does not occur in nitrobenzene.¹⁶ Instead of this, nitrobenzene decomposes *via* the radical mechanism with NO_2 group elimination ($E = 292$ kJ mol⁻¹, $A = 10^{17.3}$ s⁻¹)¹⁶. Taking into account that the pre-exponential factors of the radical and molecular decomposition differ by five orders of magnitude,

we can conclude that the activation energy of intramolecular oxidation in nitrobenzene exceeds 250 kJ mol^{-1} .

The situation is fundamentally different in the case of *o*-dinitrobenzene. The decomposition of this compound proceeds only *via* the molecular mechanism¹⁶ with the parameters $E = 205 \text{ kJ mol}^{-1}$, $A = 10^{12.9} \text{ s}^{-1}$. The reason of the change of the mechanism is the activation of the oxidation process for the *ortho*-arrangement of the nitro groups. According to the C—C bond length, pyrazole is closer to ethylene than to benzene. Therefore, it can be assumed that the mononitropyrazole derivatives decompose according to the intramolecular oxidation type and the activation energy of this process somewhat exceeds 200 kJ mol^{-1} . This conclusion is valid for the gas phase only.

In the case of di- and trinitropyrazoles, an additional factor favoring intramolecular oxidation appears due to the adjacent nitro groups. Due to the induction and resonance effects, each nitro group induces a decrease in the electron density on the carbon atom bound to the nitro group, which facilitates its attack by the adjacent nitro group and decreases the activation energy. Thus, the observed decrease in the activation energy in a series of the mono-, di-, and trinitro derivatives can be explained, at

least partially, by the intramolecular electronic effects of the nitro groups on the electron density distribution on the carbon atoms of the ring.

In the liquid phase, the rate of reactions proceeding through the polar transition state depends on the polarity of the medium. If the transition state is more polar than the initial compound, then the solvation by medium molecules would result in the stabilization of the transition state, a decrease in the activation energy, and an increase in the reaction rate. The solvation effect decreases with temperature, which results in a relative decrease in the process rate and a decrease in the apparent activation energy and pre-exponential factor. Thus, the low values of A ($\sim 10^9 \text{ s}^{-1}$), which are not typical of processes with the four-centered cyclic transition state,¹⁹ can be explained by the influence of the medium on the reaction proceeding through the polar transition state.

The decrease in the difference of the decomposition rates in a diphenyl solution and in the melt of the substance itself, which is observed on going from mono- to trinitro derivatives of pyrazole, corresponds to an increase in the dipole moment of the substance with an increase in the number of nitro groups and, hence, a decrease in the

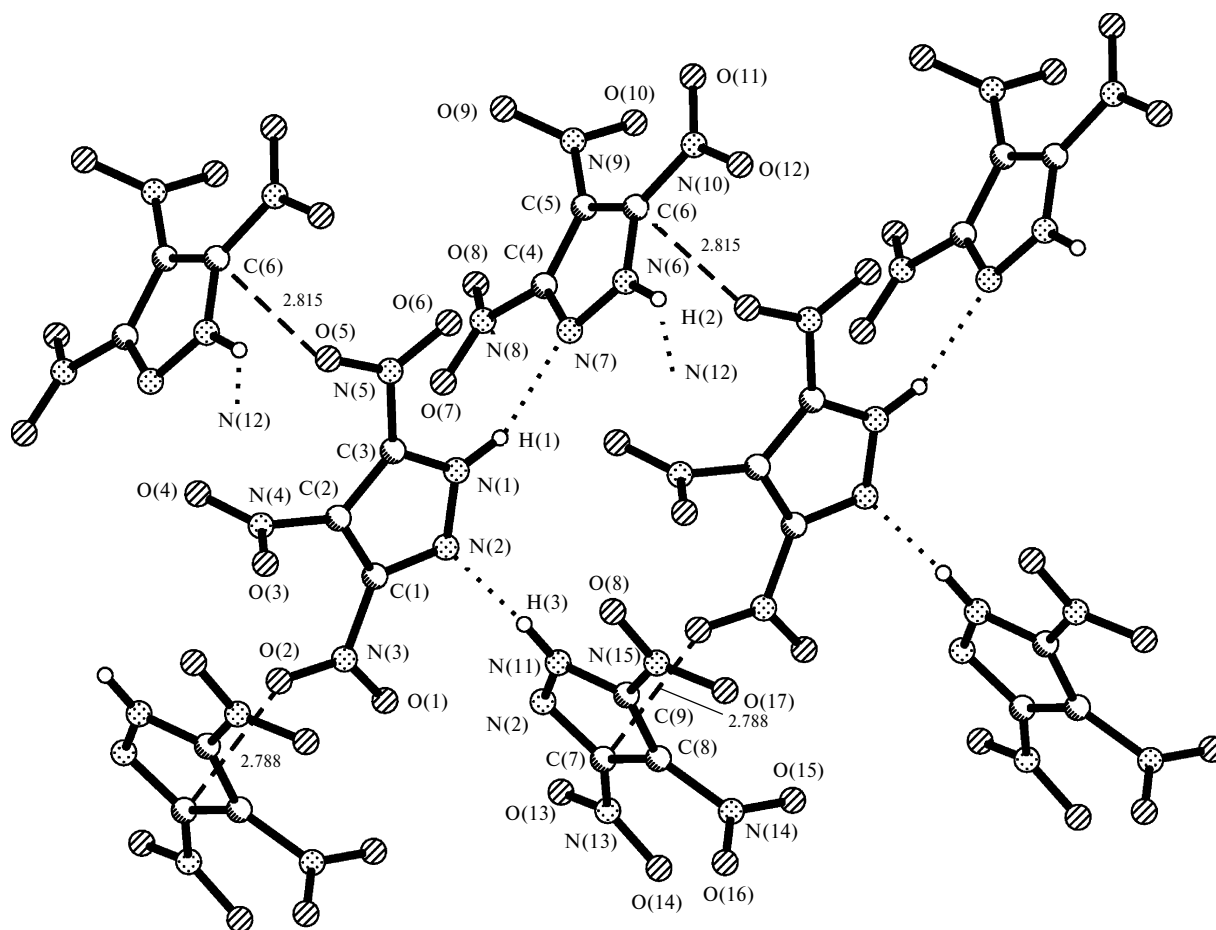


Fig. 3. Fragment of the TNP crystal packing with hydrogen bonds and shortened intermolecular contacts $(\text{NO}_2)\text{C}\dots\text{ON}(\text{O})\text{C}$.

difference of polarities of the initial compound and transition state.

The higher decomposition rate in melts of **3,4-DNP** and **TNP** compared to their solutions in *o*-dichlorobenzene or nitrobenzene means that di- and trinitropyrazoles have a high permittivity than these solvents.

In the theoretical section of the work,⁶ based on the quantum chemical calculations of the energy barriers of the initial elementary steps of **TNP** decomposition, the authors preferred the protons transfer to the oxygen atom of the adjacent nitro group. However, as shown experimentally, the replacement of hydrogen by the methyl group does not dramatically change the process rate. The channel of intramolecular oxidation was not considered.⁶

In the case of **TNP** with m.p. 186 °C, the decomposition rate was measured in the liquid state, solution, and solid state. It turned out that a reciprocal phenomenon is observed for **TNP** instead of a decrease in the decomposition rate that usually occurs upon the liquid–crystal phase transition¹³ (see Table 1). The X-ray diffraction data^{2,3} were used to explain a reason for this increase in the decomposition rate. The X-ray diffraction data show that the crystal of this compound is penetrated by chains of shortened contacts between the oxygen atoms of one molecule and carbon atoms of another molecule (Fig. 3). This distance between the O(5) oxygen atom of the nitro group in one molecule and the C(6) carbon atom of another molecule is 2.915 Å, which is less than the sum of the van der Waals radii of the O and C atoms (3.3 Å). The contact of this type between the O(2) and C(7) atoms is still shorter: 2.788 Å. It is most likely that the strong intermolecular interactions increase the positive charge on the carbon atoms of the ring and enhance the reactivity of **TNP** in the oxidation reaction, which increases the decomposition of solid **TNP** over the liquid one.

Thus, it can be assumed that the thermal decomposition of the nitropyrazole derivatives starts from the intramolecular oxidation of the adjacent carbon atom by the nitro group. The considered reaction proceeds *via* the strongly polarized cyclic four-membered transition state and, therefore, all factors stabilizing it (substituents of the acceptor type, polarity of the medium, electrostatic intermolecular contacts in the solid phase) increase the decomposition rate.

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