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Kinetics of thermoinitiated oligomerization of 3,3´-(2,4,6-triethyl-1,3-phenylene)bis(5-methyl-1,2,4-oxadiazole)

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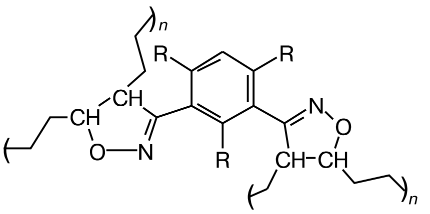
The crystal structure of 3,3´-(2,4,6-triethyl-1,3-phenylene)bis(5-methyl-1,2,4-oxadiazole), which models the cross-linking fragment of polynitriles by benzodinitrile oxides, was determined by X-ray diffraction analysis. The kinetic regularities of its thermoinitiated oligomerization were studied by isothermal calorimetry and spectrophotometry. The process proceeds with self-acceleration, and the Arrhenius dependences of the initial and maximum reaction rates were determined. The reaction accelaration is determined by an increase in the viscosity of the reaction medium. Possible mechanisms were proposed for oligomerization.

Key words: 3,3´-(2,4,6-triethyl-1,3-phenylene)bis(5-methyl-1,2,4-oxadiazole), X-ray diffraction analysis, kinetics, thermoinitiated oligomerization, dynamic calotimetry, NMR spectroscopy, mass spectrometry.

The method of low-temperature curing of rubbers with dinitrile oxides[1] was further developed[2—4] after sterically shielded benzodinitrile oxides of the $(R)_3$—C_6H—$(CNO)_2$ type stable at room temperature were synthesized. The wide use of this efficient method of curing depends on the thermal stability of the isoxazoline ring formed as a fragment (FR) of transversal cross-linking upon the addition of dinitrile oxides to olefins.



FR

Earlier,[5] when studying the thermal stability of the compound obtained in the reaction of benzodinitrile oxide with ethylene and modeling the fragment of transversal cross-linking, we found that the N—O and C—C bonds are cleaved in the isoxaline cycle and the final products, *viz.*, dinitrile $(R)_3$—C_6H—$(CN)_2$ and acetaldehyde, are formed. The kinetic parameters were determined, and the mechanism for the reaction of cross-linkage decomposition was proposed.

The purpose of this work is to study the kinetics of the thermal transformation of 3,3´-(2,4,6-triethyl-1,3-phenylene)bis(5-methyl-1,2,4-oxadiazole) (**I**). Compound **I** models the fragment of transversal cross-linkage formed in the reaction of benzodinitrile oxide with polymers containing nitrile groups.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 3500 instrument (working frequencies 500 and 125 MHz, respectively; solvent DMSO-d_6 + CCl_4 (25 vol.%); internal standard Me_4Si). The starting compound **I** (sample **1**) was studied. The products of its thermal transformation were studied at different stages: after 68 h of heating at 150 °C (sample **2**) and after 24 h of heating at 182 °C (sample **3**). Signal assignment was based on the values of chemical shifts, shapes of multiplets, comparison of integral intensities of the signals, and HSQC 13C-1H experiments.

The mass spectrometric analysis of the thermal transformation products of compound **I** was conducted on an LCSM 2020 instrument (Shimadzu, Japan) using electrospray with ionization of a solution of the reaction products in acetonitrile.

The kinetics of thermal transformation of compound **I** was studied on a DAK automated differential microcalorimeter[6] in glass sealed ampules ($V \approx 2$ cm^3) having no cold part, which made it possible to keep all transformation products in the reaction zone. If not specially indicated, a weighed sample of the studied substance was 50 mg at temperatures in a range of 148.8—201.6 °C.

Manometric measurements were carried out on a setup developed and made at the Institute of Problems of Chemical Physics (Russian Academy of Sciences), which allows one to work under the pressure in the reaction vessel from 0 to 40 atm and at temperatures from 20 to 350 °C.

The absorbance of solutions of the reactions products in chloroform was measured at the wavelength 330 nm on a Spec-

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ord-40 UV/VIS instrument. The absorption regions of solutions of compound **I** and products of its thermal transformation in chloroform did not coincide. The initial regions of the kinetic curves of product accumulation were plotted using the ampule method by the results of determination of the absorbance of solutions of the products, and the reaction rate constants were calculated. In each measurements, the concentration of the solution based on initial compound **I** was $3 \cdot 10^{-4}$ mol L^{-1}. This method does not allow one to study the reaction at large conversions, since products with differed molar absorption coefficients appeared with an increase in the reaction conversions.

Synthesis of 3,3´-(2,4,6-triethyl-1,3-phenylene)bis(5-methyl-1,2,4-oxadiazole) (I). Acetonitrile (TU 6-093534-82) (20 mL) was poured to 1.5 g of 2,4,6-triethylbenzene-1,3-dinitrile oxide (**II**) (m.p. 96—98 °C). The solution was kept for 55 days in a dark container at 20 °C. The reaction course was monitored by thin layer chromatography on Silufol UV-254 plates using chloroform as an eluent. The yield of unpurified compound **I** was 1.7 g (85%). Purification was carried out by the chromatographic method (column l = 500 mm, d = 20 mm; silica gel 0.035—0.07 mm, 60 Å, chloroform as an eluent). A white crystalline substance was isolated, m.p. 97—98 °C. ^{1}H NMR (DMSO-d$_6$ + CCl$_4$), δ: 0.874 (t, 3 H, $C\underline{H}_3CH_2$, ^3J = 7.5 Hz); 1.100 (t, 6 H, $C\underline{H}_3CH_2$, ^3J = 7.5 Hz); 2.183 (q, 2 H, $CH_3C\underline{H}_2$, ^3J = 7.5 Hz); 2.413 (q, 4 H, $CH_3C\underline{H}_2$, ^3J = 7.5 Hz); 2.686 (s, 6 H, Me); 7.230 (1 H, Ph). ^{13}C NMR: 12.52 (CH_3); 15.96 ($\underline{C}H_3CH_2$(2)); 16.28 ($\underline{C}H_3CH_2$(1)); 24.76 ($CH_3\underline{C}H_2$(1)); 26.82 ($CH_3\underline{C}H_2$(2)); 124.73, 143.66, 146.40 (Ph); 127,25 (CH, Ph); 167,50 (NCN); 177.59 (NCO).

Table 1. Crystallographic data and parameters of X-ray diffraction experiment for compound **I**

Parameter	I
Empirical formula	$C_{18}H_{22}N_4O_2$
Molecular weight	326.40
Color, habitus	Colorless prisms
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	4
a/Å	8.293(2)
b/Å	12.926(3)
c/Å	17.467(4)
α/deg	93.97(3)
β/deg	102.18(3)
γ/deg	93.59(3)
V/Å	1820.1(6)
d_{calc}/g cm^{-1}	1.191
Crystal size/mm	0.8×0.5×0.2
θ/deg	2.06—25.00
Reflection indices	$-7 \le h \le 1, -15 \le k \le 15,$ $-20 \le l \le 20$
Number of measured reflections	6992
Number of independent reflections	5742 R_{int} = 0.0166
Number of refined parameters	452
Goodness-of-fit	1.066
Number of reflections with $I \ge 2\sigma(I)$	2893
Final R factors (for reflections with $I \ge 2\sigma(I)$	
R_1	0.0819
wR_2	0.2436
Residual electron density /e A^{-3}	0.537

X-ray diffraction analysis of compound I. Colorless crystals well cut as flattened tetragonal prisms were grown from a solution of compound **I** in acetone. The crystallographic data for compound **I** are given in Table 1. X-ray diffraction analysis was carried out on a KM-4 automated four-circle difractometer (KUMA DIFFRACTION) with χ-geometry in the ω/2θ scan mode using the monochromatized Mo-Kα radiation. The structure was solved by a direct method using the SIR92 program[7] followed by a series of calculations of the electron density maps. The positions of hydrogen atoms were geometrically specified and refined in the riding model. The positions and temperature parameters of non-hydrogen atoms in the anisotropic approximation were refined by full-matrix least squares using the SHELXL-97 program.[8]

The CIF file containing the full information on the studied structure was deposited with the Cambridge Crystallographic Data Centre (CCDC 859039, www.ccdc.cam.ac.uk/data_request/cif).

Results and Discussion

According to the X-ray diffraction data, the reaction of compound **II** with acetonitrile affords compound **I** containing 1,2,4-oxadiazole fragments, while no alternative 1,2,5-oxadiazole structures are formed. The general view of molecule **I** is shown in Fig. 1. The crystal is built of two crystallographically independent and similar in structure molecules. The bond lengths in them are the same within inaccuracies and range within values usual for the corresponding values. The molecular packing in crystals is loosened, which is also indicated by the density of the crystals (see Table 1). The ethyl group at the C(6) carbon atom of one of the crystallographically independent molecules has abnormally high thermal vibration coefficients, and the C(17) and C(18) atoms are fixed in two randomly equiprobable positions. The crystal contains no hydrogen bonds and shortened intermolecular contacts.

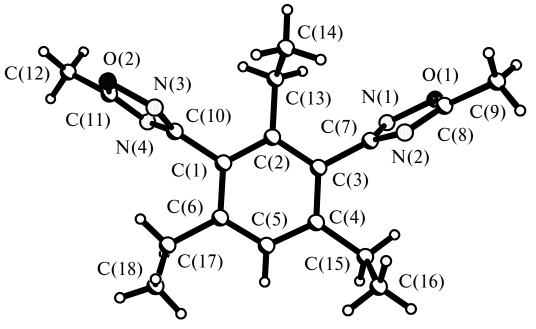

Fig. 1. Molecular structure of compound **I**.

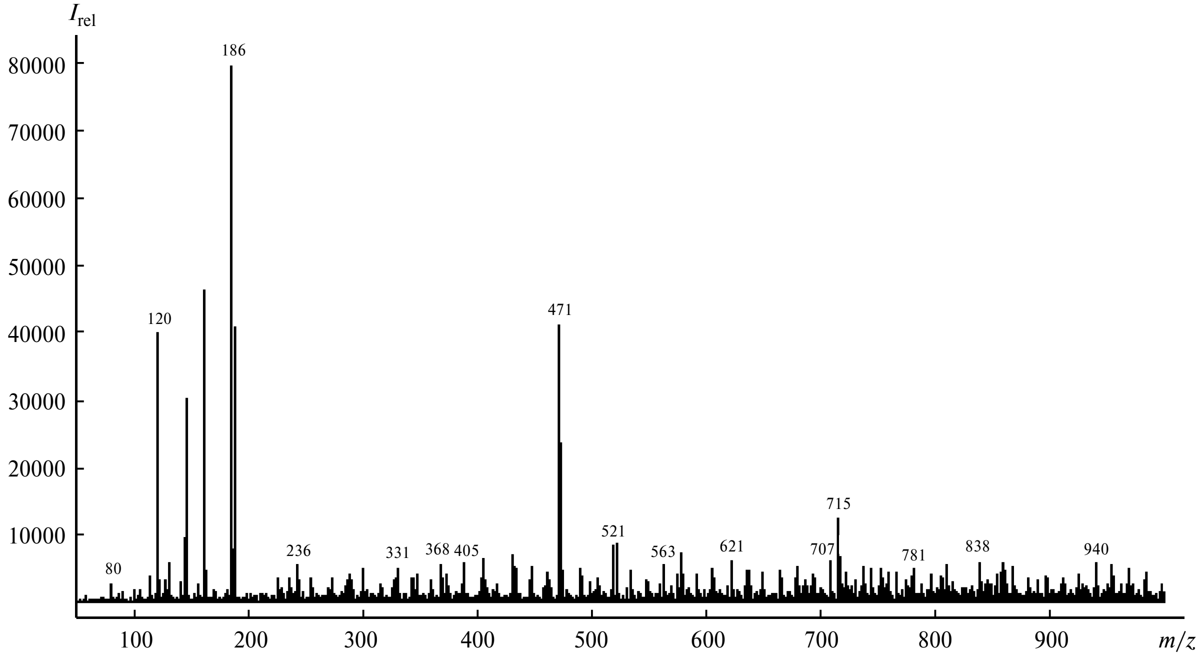

Fig. 2. Fragment of the mass spectrum of the oligomerization products of compound **I** for 170 °C, 48 h.

The study of the kinetics of the thermal transformation of a melt of compound **I** by the manometric method *in vacuo* in the temperature range from 120 to 180 °C at different degrees of filling of the vessels (m/v = = 0.2—0.8 g cm^{-3}) revealed that no gaseous reaction products are formed in the thermal transformation of the linkage, unlike the thermal decomposition of the linkage formed in the reaction of benzodinitrile oxide with ethylene.[5] The studied substance was colored in experiments, indicating the reaction occurrence. As the reaction conversion increased, the transformation products gained a resin-like consistence.

The mass spectrometric analysis of the reaction products showed that the reaction afforded products with the molecular weight up to 3000 atomic units (Fig. 2). The presence of these products can be explained by their thermally initiated oligomerization of cross-linking fragments formed in the reaction of benzodinitrile oxide with nitriles.

The ^{1}H and ^{13}C NMR spectra of transformation products **2** and **3** exhibit signals coinciding with the signals in the spectrum of the starting compound **I** and also weak lines shifted relatively to the corresponding lines of the initial monomer (Fig. 3). Several signals are distinctly seen near each signal that coincides with the signal from compound **I**. Their number and the total intensity for sample **3** are higher than those for sample **2**. The lines remain narrow, indicating a low degree of polymerization. In the ^{1}H NMR spectrum of sample **3**, normalization to the signal 1 H of the overall surface area of the signals in the phenyl region (6.8—7.5 ppm) gives 21 H for the overall surface area of the alkyl signals (0.6—3.1 ppm), which is totally 22 H according to the empirical formula of compound **I** ($C_{18}H_{22}N_4O_2$). It follows from this that the transformation does not involve the benzene ring.

For the phenyl protons, the overall surface area of the changed signals in sample **3** is 45% and that of the unchanged signals is 55%. This is approximately* consistent with the estimate for the Me groups: about 40% for the changed groups (δ 1.55—2.14) and about 60% for the unchanged groups (δ 2.70±0.1). In the spectrum of sample **2** with a lower conversion, the singlet at δ 1.76 (δ ^{13}C 23) has the highest intensity (~3%). The singlet is retained in the spectrum of sample **3**, but now the Me group at δ 2.12 (15%) prevails. Two other sufficiently intense methyl signals at 2.05 and 1.76 ppm are observed (10% each). Weaker signals are also present. The estimation by the CH_3 triplet and CH_2 quartet of the single ethyl group gives 46 and 48% for the unchanged signals. Taking into account that the measurement inaccuracy is ~5% in this case, the total estimate for the ratio of unchanged and changed groups is 45±5/55±5%. Thus, no changes in chemical shifts and, hence, in the chemical environment occurred during the transformation for 50% of groups in sample **3**.

The kinetics of the thermal transformation of compound **I** was studied in detail using the method of isothermal calorimetry, which has no drawbacks characteristic of manometric and spectrophotometric procedures of the re-

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* The estimate is approximate, because the sum of surface areas (5.73) is smaller than 6 H, *i.e.*, some signals do not fall to the isolated integration regions.

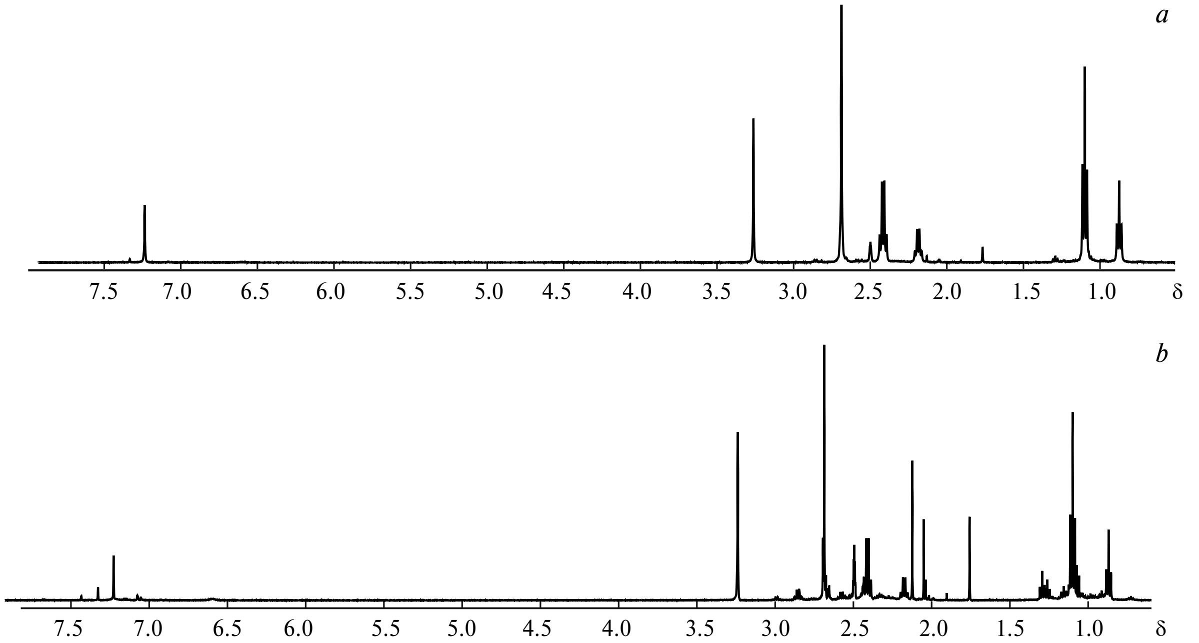


Fig. 3. ^{1}H NMR spectra for samples **2** (*a*) and **3** (*b*). For assignment, see the description of the spectrum of compound **I** in text. Signal δ 2.5 is DMSO-d_5, and δ 3.26 is a water admixture in the solvent.

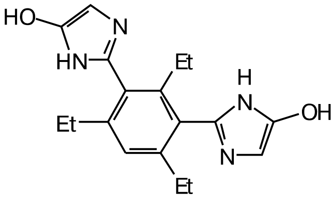
action occurs with a heat effect that differs from zero. Figure 4 shows the dependences of the heat release rates in the oligomerization of **I** at different temperatures on the current heat of the process, which is directly proportional to the reaction conversion.

$$Q = \int_0^t (\mathrm{d}Q/\mathrm{d}t)\mathrm{d}t.$$

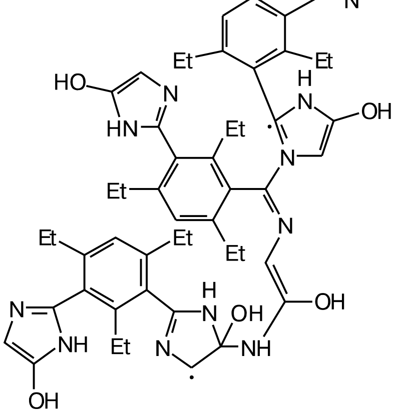
The total heat of the process Q_0 determined by the numerical integration of the time dependence of the heat release rate is about 940 J g^{-1}.

To explain the value of the heat of the process, let us assume that the main route of the thermal transformation of compound **I** is its exothermic isomerization with the formation of imidazole derivative **III** followed by its oligomerization with the cleavage of one of the N—C bonds in the heterocycle to form a biradical. Further any end of the biradical adds to the double bond of the heterocycle to form a growing biradical oligomer, for example, with structure **IV**.

The pattern of oligomerization at one of two heterocycles of the molecule was exemplified. A similar process of radical oligomerization involves the second imidazole cycle of the compound formed by isomerization. If the oligomerization proceeds *via* the proposed mechanism, the quaternary C atoms are formed in the oligomer structure of the products observed in the NMR spectrum. The recombination of two ends of the oligomer biradical results in chain termination and macrocycle formation, whereas the recombination of ends of the adjacent biradicals elongates the substance chain.



III



IV

The heat of isomerization of two oxadiazole cycles to the imidazole derivative calculated using the MOPAC (PM3) program is approximately 330 kJ mol^{-1} for the initial compound. The heat of the formation of the polyimidazole derivative by the replacement of the C=N double bond by two ordinary C—N bonds is –3 kJ mol^{-1}. The heat for the replacement of the C=C double bond by the C—C ordinary bond and C—N ordinary bond is 41 kJ mol^{-1}. Totally, the calculated heat effect with allowance of the

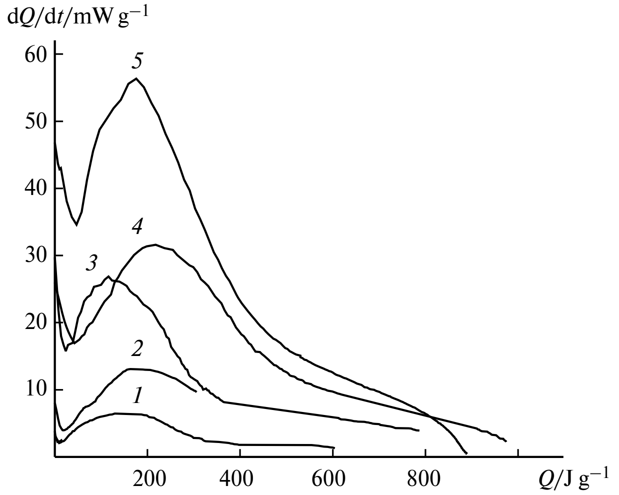
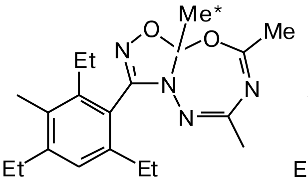


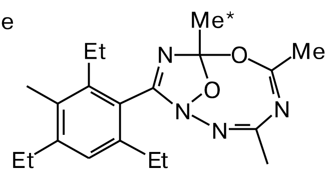
Fig. 4. Heat release rates dQ/dt in the oligomerization of compound **I** *vs* current heat of the process Q at 176.1 (*1*), 180.6 (*2*), 191.4 (*3*), 197.3 (*4*), and 201.6 °C (*5*).

calculation inaccuracy is close to that observed experimentally.

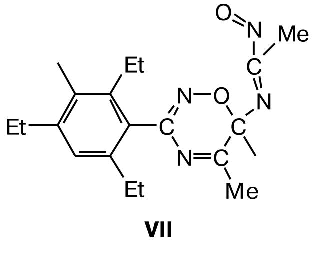
The formation of linkages of different types is proposed as additional parallel routes of compound **I** transformation also capable of increasing the weight of the reaction products. The most probable route can be the cleavage of the N(2)—O(1) bond and the addition of the formed biradicals to the C(5)—N(4) or C(3)—N(2) double bonds of the 1,2,4-oxadiazole cycles, which should result in the formation of a fragment of conjugated seven- and five-membered heterocycles. Of numerous possible variants of addition, thermochemical concepts allow fragments **V—VI** and fragments **VII** to take place. Fragments **VII** contain the six-membered heterocycle obtained from two five-membered heterocycles *via* the mechanism with the formation of an intermediate carbene accompanying by the C(3)—N(2) bond cleavage in the heterocycle followed by the insertion of carbene with the C(3) atom at the C(5)—O(1) bond in the second heterocycle and the addition of the NO group by the nitrogen atom to the C(5) carbon atom.



V



VI



VII

Possible heats of the reaction for the discussed structures were estimated using the data on the energies of the cleaved and formed bonds in the reactants and products.

Structures **V** and **VI** are formed through the cleavage of one double C=N bond and one ordinary N—O bond and formation of ordinary bonds C—N, N—N, and C—O. The heat of the reaction will be $Q = E_{\text{C—N}} + E_{\text{N—N}} + E_{\text{C—O}} - E_{\text{C=N}} - E_{\text{N—O}} = 305 + 163 + 360 - 613 - 157 = 58$ kJ mol^{-1}, being approximately 20% of the value observed in experiment. The formation of structure **VII** occurs due to the cleavage of one double C=N bond and ordinary N—O and C—O bonds and the formation of ordinary bonds C—C and C—N and one double bond N=O. The heat of the reaction should be $Q = E_{\text{C—C}} + E_{\text{C—N}} + E_{\text{N=O}} - E_{\text{C=N}} - E_{\text{N—O}} - E_{\text{C—O}} = 348 + 305 + 621 - 613 - 157 - 360 = 150$ kJ mol^{-1}, being approximately 50% of the experimental one. Based on the calculated heats, one can assume a small contribution from the parallel reactions corresponding to the formation of structures **V—VII** to the overall rate of heat release.

The possibility of parallel processes is consistent with the NMR spectral data. For the groups with the changed chemical shift, the Me groups of the oxadiazole cycle exhibit the highest effect (from δ 2.69 to 1.76). This is explained, most likely, by the transformation of the C(5) carbon atom into the quaternary atom and indicates in favor of the formation of cross-linkage structures of types **V** and **VI**. In these structures, one of the methyl groups retains the initial chemical environment, while another (Me*) changes it, which explains an approximately equal ratio of the changed and unchanged groups in the polymer. The structures of types **V**, **VI**, and **VII** also agree with the appearance of lines in the carbon spectrum that are characteristic of quaternary carbon atoms with electronegative substituents (δ 110—117).

The dependences of the heat release rate on time and current heat of the processes are complicated. The observed initial region of decreasing heat release rate, beginning from the release of about 8 J g^{-1} of heat, which corresponds to ~1% reaction conversion, is exchanged first by a region of rate increasing to the release of ~190 J g^{-1} (~20% reaction conversion) and then by a region of decreasing heat release rate to the complete cessation of the process. To elucidate the problem about a relationship of the decrease in the heat release rate in the initial region to the thermal transformation of a more reactive admixture if any in the starting sample **I**, we carried out experiment at 176.1 °C interrupting the reaction at the minimum of the rate, isolating the initial substance from the reaction mixture, and repeating the reaction. The curve of heat release rate for the thermal transformation of compound **I** isolated from the reaction mixture is identical to that of the heat release rate of the initial compound **I**. Therefore, the initial region of heat release rate characterizes the reactivity of intrinsic oxadiazole **I**. It also could be assumed that the initial region is related to the equilibrium transformation of one conformation of the substance into another. However, experiment at 170.5 °C with interrupting of the reaction at the minimum of the heat release rate and cooling of the sample to ~20 °C with the purpose to shift the conformational equilibrium to the initial position followed by the repeated placing the ampule into the calorimeter to continue the reaction did not confirm this assumption. After the ampule was heated, the same heat release rate that was observed before interrupting experiment was detected. The regular decrease in the rate at the initial region at the lowest boundary of the temperature range (176.1 °C) was observed within 75 min and at the upper boundary (201.6 °C) within 20 min. Additional studies are needed to reveal a reason for such a decrease in the rate.

Assuming that the isomerization of oxadiazole **I** to the imidazole derivative followed by oligomerization to form the polyimidazole derivative as the major reaction that explains the observed thermal effect of the reaction, the kinetic scheme of the process will consist of the following stages.

(1) Chain generation:

— 1,2,4-oxadiazole derivative transforms into the imidazolol derivative;

— cleavage of the imidazole ring at the ordinary N—C bond to form the biradical.

(2) Chain propagation:

— interaction of the biradical with the free valence on the nitrogen atom with the C=N double bond of the imidazole ring results in the formation of the free valence on the C atom of the heterocycle and an increase in the biradical length by one structural unit;

— similar chain generation reactions occurs beginning from another end of the biradical with the free valence at the C atom.

(3) Chain termination:

— reactions of closure of macrobiradical end with free valences at the nitrogen and carbon atoms to form macrocycles with N—C, N—N, and C—C bonds. These reactions lead to the formation of a network (cross-linked) polymer. An increase in viscosity decreases the probability of collision of the biradical ends to form the macrocycle, which corresponds to a decrease in the chain termination rate constant and results in the observed increase in the rate of oligomerization of the starting compound.

The observed dependence of the heat release rate on the reaction depth is determined by both the change in the monomer concentration in the course of the process and the change in the chain termination rate constants due to an increase in the viscosity of the reaction mixture when oligomer molecules are formed. To distinguish the influence of the increasing viscosity of the medium on a complex of constants of oligomerization stages, the dependence of the specific reaction rate $(\mathrm{d}\eta/\mathrm{d}t)/(1-\eta)^{1.5}$ on the reaction depth η was analyzed:

$$\eta = \int_0^t (\mathrm{d}Q/\mathrm{d}t)\mathrm{d}t \Big/ \int_0^\infty (\mathrm{d}Q/\mathrm{d}t)\mathrm{d}t,$$

where $\mathrm{d}\eta/\mathrm{d}t = (\mathrm{d}Q/\mathrm{d}t)/Q_0$ is the process rate, and $(\mathrm{d}Q/\mathrm{d}t)$ is the heat release rate (Fig. 5).

The formation of oligomer already at small depths of conversion increases the viscosity of the reaction medium and, as a consequence, decreases the termination rate constant, which is limited by the diffusion rate of oligomer radicals. As a result, the oligomerization rate increases in the range of 1—20% reaction depth. At high depths of conversion, an increase in the viscosity of the system results in the situation where the rate of monomer diffusion to the oligomer radical becomes the rate-determining step for the chain propagation reaction, which formally leads to a decrease in the chain propagation rate constant and, finally, to a decrease in the ratio of the chain propagation rate constant to the square root of the chain termination rate constant. The oligomerization rate constant determined by this ratio and the monomer concentration also begins to decreases from a certain depth of conversion.

The experiment at 192.3 °C in which an equal weight of the oligomer reaction products was added to the starting compound **I** confirms the conclusion about the substantial influence of the viscosity of the reaction medium on the polymerization rate (Fig. 6). The addition of the product increases the initial heat release rate by 3.7 times. Then the rate only decreases during the process. The heat of the thermal transformation of oxadiazole **I** in the presence of the reaction product does not differ from that for the thermal transformation of the pure compound.

The degree of acceleration remains almost unchanged when the ratio of the weighed sample to the free volume of

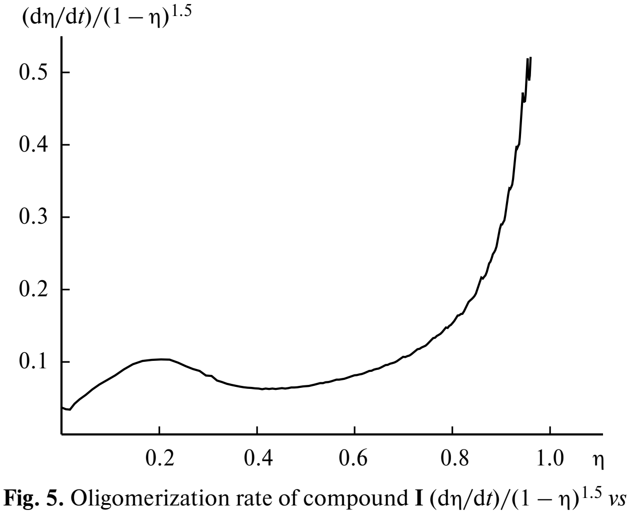


Fig. 5. Oligomerization rate of compound **I** $(\mathrm{d}\eta/\mathrm{d}t)/(1-\eta)^{1.5}$ *vs* reaction conversion η at 192.3 °C.

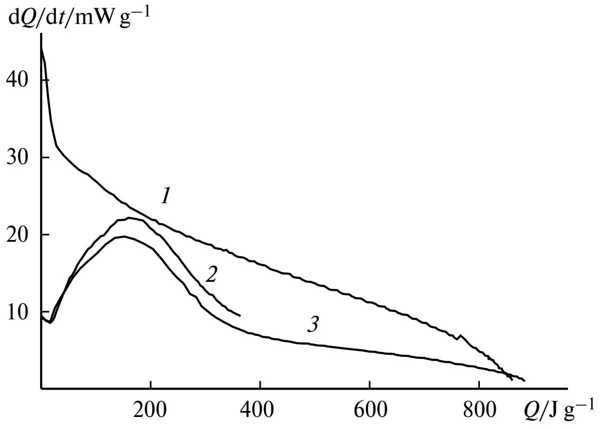


Fig. 6. Heat release rate dQ/dt in the oligomerization of compound **I** *vs* current heat of the process Q at 192.3 °C for the initial oxadiazole **I** with an additive of the thermal transformation product (*1*) for pure oxadiazole **I** at weight samples $m = 0.05$ (*2*) and 0.1 g (*3*).

the ampule (m/V) changes twofold (see Fig. 6). Therefore, the rate increase is related to the change in the properties of the condensed phase only.

The dependences of the specific reaction rate $(d\eta/dt)/(1-\eta)$ on the reaction depth for the experiments considered above (see Fig. 6) are compared in Fig. 7. In both experiments, the initial region of the rate drop is observed. The distinction is that for the thermoinitiated oligomerization of pure compound **I** an increase in the viscosity of the reaction mixture increases the specific rate already at small depths of conversion. The subsequent rate drop after the maximum of the transformation of compound **I** is achieved is related to a decrease in its current concentration. Two facts are noteworthy when comparing the dependences of the specific rates. First, the repeated increase in the specific reaction rate is observed when the reaction conversions higher than 0.5 are achieved in experiment with pure compound **I**. A similar increase in the specific rate from the indicated conversion is also observed when the reaction product is added to the initial compound **I**. It can be assumed that at these reaction conversions an increase in the specific rate is determined by a significant decrease in the chain termination rate constant along with a continuing increase in the viscosity of the reaction medium. Second, the difference in specific rates between the transformation of pure compound **I** and that with the product additive at the 20% reaction conversion, for which the specific rate for pure compound **I** has a maximum, is only 1.2 times. Therefore, an additive of 25% reaction product to the starting compound **I** should result in the limiting increase in the initial rate of the process.

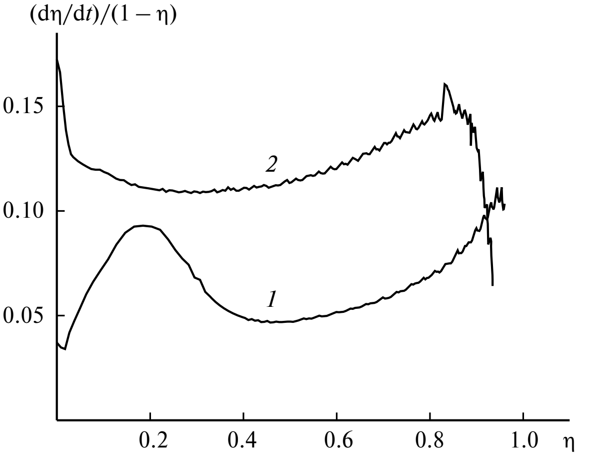


Fig. 7. Specific reaction rate $(d\eta/dt)/(1-\eta)$ *vs* reaction conversion η for the oligomerization of compound **I** (192.3 °C) for the initial oxadiazole **I** (*1*) and with an additive of the oligomerization product (*2*).

The temperature dependences of the initial and maximum heat release rates in the coordinates of the Arrhenius equation and the results on the initial oligomerization rates obtained by the spectrophotometric procedure are presented in Fig. 8.

The scatter in converstions of achieving the maximum rate is not too large (see Fig. 4). This is probably associated with the temperature dependence of the viscosity of the reaction medium: the higher the temperature, the lower the viscosity of the medium and, hence, the maximum rate is attained at greater conversions. The study of the temperature dependence of the maximum rate of the process is probably suitable for an analysis of the possibility to retain the oligomerization mechanism at the initial stage and during the development of the process.

The results on the initial reaction rate determined using two procedures are well consistent. The value of 101.2±8.8 kJ mol^{-1} was obtained for the activation energy, and the logarithm of the pre-exponential factor was 6.6±1.0 (s^{-1}). Within the experimental error, the initial

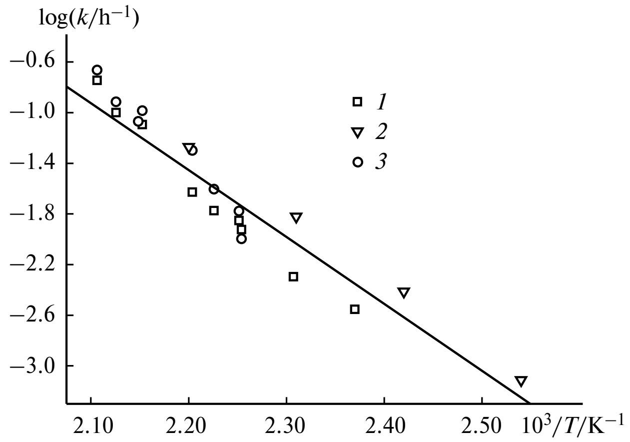


Fig. 8. Logarithm of the oligomerization rate of compound **I** *vs* reciprocal temperature. The initial rate was determined by calorimetry (*1*) and spectrophotometry (*2*); the maximum rate was determined by calorimetry (*3*).

and maximum rate have the same activation energy and the pre-exponential factor differs by 1.5 times. This can indicate that the oligomerization proceeds *via* the single mechanism in the course of the whole process.

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