Mechanism of the primary stages of decomposition of aliphatic nitro- and fluoronitronitramines

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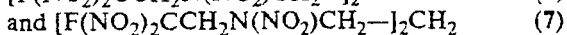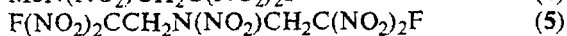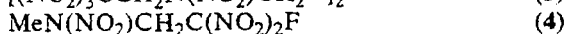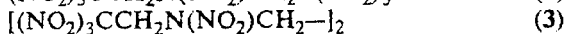*142432 Chernogolovka, Moscow Region, Russian Federation.*
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The primary stage of the decomposition of compounds $RN(NO_2)CH_2C(NO_2)_2X$ is the homolytic cleavage of the $C-NO_2$ bond, at $X = NO_2$ and $N-NO_2$ bond at $X = F$. The inductive effect of substituents decreases the dissociation energies of the $C-N$ and $N-N$ bonds by 1—2 kcal mol^{-1}. Kinetic effects caused by the spatial interaction of groups and by stepwise decomposition of polyfunctional compounds are described.

Key words: nitro compounds, nitramines, thermolysis, interaction of groups, reaction mechanism; kinetics.

Although thermal decomposition of secondary nitramines has been studied in numerous works,[1] these reactions have not been adequately investigated. Many problems concerning the influence of substituents and the medium on the rate and mechanism of decomposition remain unsolved. Decomposition of simple nitramines normally starts with homolytic cleavage of the $N-N$ bond, whose strength depends relatively slightly on the substituents. However, when some substituents, for example an F atom and a carbonyl group[1] or a furazan ring,[2] are present in the α- or β-position with respect to the nitramino group or when the decomposition is carried out in a hydrocarbon medium,[3] its mechanism and rate sharply change. The process is accompanied by intramolecular rearrangements and intermolecular interactions, whose mechanisms are unknown. The kinetics of decomposition of nitro-derivatives of nitramines, which constitute a large group of high-energy compounds, have not been studied either. The molecules of these compounds incorporate two or several reaction centers, which interact and compete with one another in the primary decomposition reactions.

Therefore, in this work, we studied the kinetics and mechanisms of the initial (non-catalytic) steps of thermolysis of trinitromethyl and fluorodinitromethyl derivatives of secondary nitramines in the liquid phase. As typical representatives, we chose the following compounds:

$MeN(NO_2)CH_2C(NO_2)_3$	(1)
$(NO_2)_3CCH_2N(NO_2)CH_2C(NO_2)_3$	(2)
$[(NO_2)_3CCH_2N(NO_2)CH_2-]_2$	(3)
$MeN(NO_2)CH_2C(NO_2)_2F$	(4)
$F(NO_2)_2CCH_2N(NO_2)CH_2C(NO_2)_2F$	(5)
$[F(NO_2)_2CCH_2N(NO_2)CH_2-]_2$	(6)
and $[F(NO_2)_2CCH_2N(NO_2)CH_2-]_2CH_2$	(7)
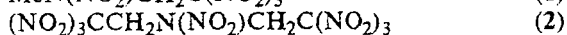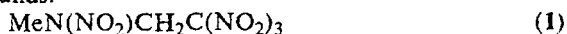
Decomposition of compounds **2**, **3**, and **5** has been studied previously[4] but only under conditions of fast heating. It was found that NO_2 is formed as a primary thermolysis product; however, this fact hardly makes it possible to elucidate the nature of the primary step of decomposition. The kinetic approach appears more promising for this purpose. We carried out a formal kinetic analysis of the decomposition of heterofunctional compounds under isothermal conditions, distinguished the initial step, determined its kinetic parameters, and compared these parameters with known characteristics of the decomposition of monofunctional compounds, *viz.*, nitramines or polynitroalkanes.

For this approach, accuracy of kinetic measurements is an important point. Therefore, the reactions were studied mostly in dilute solutions, *i.e.*, under conditions where the perturbing influences of admixed catalytic or autocatalytic processes is almost entirely eliminated. To analyze the products of decomposition and to elucidate the possible role of intermolecular interactions in the initial stages of the process, some experiments were carried out in the melt.

Experimental

All the solids used were purified by recrystallization from ethanol or aqueous acetone. Decomposition reactions were studied by the manometric method. The pressure in the reaction vessel was measured by the compensation method using sensitive sickle-shaped membranes, usually in the range 5—700 Torr with a relative error of <2%. During the experiments, the temperature was maintained with an accuracy of ±0.1 °C using a liquid thermostat filled with a low-viscosity silicone oil.

When the reaction was carried out in solution, *m*-dinitrobenzene, which is a low-melting non-volatile substance, inert toward nitro-compounds and products of their decompo-

sition at 200 °C, was used as the solvent. The melts of the compounds under study in *m*-dinitrobenzene (concentration 0.3—3.0 mol.%) were prepared prior to the experiments, usually at 100 °C.

The kinetic experiments in solutions were carried out until the degree of conversion of the initial compound was 50—100%. The kinetic curves were described satisfactorily by a first-order equation. Decomposition in the melt was studied for nitramines 1 and 2. In this case, the reactions were autocatalytic. The rate of the catalytic (but not of the initial) stage depended on the degree of filling of the vessel with the substance. The kinetic curves were poorly described by the first-order equation of autocatalysis; therefore, the rate constants (k) for the initial step of decomposition were calculated from the time needed to reach a degree of decomposition of 1%. The complete gas evolution (which is conveniently expressed in units of adjusted volume $\Delta V_\infty/N$ cm^3 g^{-1}) corresponding to 100% decomposition was determined at elevated temperatures. Since ΔV_∞ may depend on the temperature and the compositions of the gas products formed at the initial and autocatalytic stages may be different, errors in the determination of k, activation energy E, and preexponential factor A are possible. Therefore, the data obtained for solutions are, in principle, more accurate, and measurements for the rest of the compounds were carried out only in solutions.

For compounds 1 and 2, the ΔV_∞ values equal to 635 and 730 were used in the calculation of k. The stoichiometric coefficients of the reaction (the numbers of moles of gaseous products formed from 1 mole of the initial compound) for compounds 1 and 2 were 6.8 and 12.7, respectively. Large stoichiometric coefficients were also observed for decomposition of all the other compounds. For compound 3 in solution, $\Delta V_\infty = 565$, which corresponds to the evolution of 12 moles of gaseous products.

The manometric procedure chosen provides well reproducible kinetic curves. The experiments showed that the rate constants found in three entries differ by 10—15%, and the maximum error (the greatest deviation from the arithmetic mean) does not exceed 5—7%. For this accuracy of the measurements, 10—12 entries carried out in the temperature range from T to T equal to 40 °C are sufficient for the activation energy to be determined with an accuracy of ±1.0

kcal mol^{-1}. For a smaller number of entries, the error increased to ±1.5 kcal mol^{-1}. The activation energies for the key compounds 1 and 4 and also that for compound 3, for which it was significant to carry out the most accurate comparison with compound 1, were determined with the above-mentioned minimum error.

The products of decomposition of compound 1 were analyzed at 140 °C and at degrees of conversion of 2, 15, and 100%. The products were fractionated by freezing at −78 and −195 °C. Light gases were analyzed by gas chromatography on columns with Paropack Q, and NO$_2$ was determined by colorimetry. The products were identified by IR spectroscopy and by chemical analysis. The yields of gaseous products proved to be identical to within 10—15% and amounted to (in moles per mole of 1): CO, 0.3; CO$_2$, 1.4; NO, 1.0; NO$_2$, 0.2; N$_2$O, traces; N$_2$, 1.25; MeONO$_2$, 1.0; H$_2$O $\cong$ 0.8. Complete decomposition of compound 1 yielded a non-volatile condensed residue (5% w/w) consisting of five products. Due to the small amount of the residue, these products could not be reliably identified. The major compound (65%) was a low-volatility (100 °C/0.1 Torr) liquid, whose elemental composition and IR spectra corresponded most closely to MeN(NO$_2$)CH$_2$C(O)Mc or MeN(NO$_2$)CH$_2$COOMe. The second component in order of the content (15%) was an amino acid, probably, MeHNCH$_2$COOH, which catalyzes the decomposition of compound 1. The rest of the condensed products also contained C=O and N=O bonds and might have been carboxy or nitro derivatives.

Results and Discussion

It follows from the data presented in Table 1 and in Fig. 1 that the rates of decomposition in a dilute solution and in the melt are virtually identical (especially in the case of the most thoroughly studied compound 1); this indicates that the decomposition of these compounds is not accompanied by any side reactions or bimolecular interactions. The rate constant also does not depend on the concentration of the compound in solution.

Table 1. Kinetic characteristics for the decomposition of nitronitramines

Com-pound	Medium	T/°C	E /kcal mol^{-1}	log$A$/s^{-1}	k/s^{-1} at 150 °C	ω^*
1	Solution	130—180	40.3	16.70	$7.6 \cdot 10^{-5}$	9.1
	Melt	90—140	40.4	16.74	$7.4 \cdot 10^{-5}$	8.9
2	Solution	110—165	36.1	15.06	$2.6 \cdot 10^{-4}$	31.3
	Melt	110—150	36.8	15.59	$3.8 \cdot 10^{-4}$	45.8
3	Solution	130—180	40.7	16.80	$5.9 \cdot 10^{-5}$	7.0
4	Solution	175—210	40.5	14.90	$9.5 \cdot 10^{-7}$	5.3
5	Solution	170—210	39.8	14.92	$2.3 \cdot 10^{-6}$	12.8
6	Solution	160—210	40.0	15.29	$3.3 \cdot 10^{-6}$	18.0
7	Solution	160—210	42.3	16.20	$2.2 \cdot 10^{-6}$	12.2
CH$_3$C(NO$_2$)$_3$	Melt		42.6	16.93	$8.3 \cdot 10^{-6}$	
R$_2$NNO$_2$	Solution		41.1	14.50	$1.8 \cdot 10^{-7}$	
CH$_3$C(NO$_2$)$_2$F	Gas^5		47.7	16.70	$1.1 \cdot 10^{-3}$	

Note. For 1—3, $k_{ref} = 8.3 \cdot 10^{-6}$ s^{-1} (the data for 1,1,1-trinitroethane in the melt[6]); for 4—7, $k_{ref} = 1.8 \cdot 10^{-7}$ s^{-1}, the typical value for decomposition of a planar nitramine group.[7] * The ratio of the rate constant of decomposition of the compound under study (k) to that of the reference monofunctional compound (k_{ref}) at 150 °C.
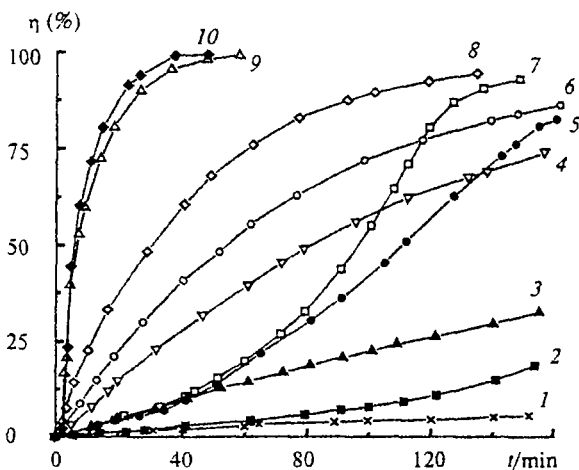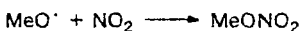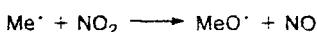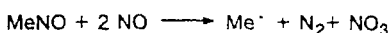
Fig. 1. Examples of kinetic curves of gas evolution during decomposition of compounds 1 and 2: compound 1, solution, 130 °C (*1*); 1, melt, 130 °C (*2*); 2, solution, 130 °C (*3*); 1, solution, 155 °C (*4*); 2, melt, 130 °C (*5*); 2, solution, 145 °C (*6*); 1, melt, 140 °C (*7*); 1, solution, 165 °C (*8*); 2, solution, 165 °C (*9*); 1, solution, 180 °C (*10*).

The first-order kinetics of irreversible decomposition of a complex polyfunctional compound can correspond to a one-step monomolecular reaction, a nonbranched chain process, or a sequence of transformations with the rate-determining first step. Since stoichiometric coefficients are large, the first of these possibilities can be immediately ruled out. Chain mechanisms of decomposition of aliphatic polynitro-compounds are never observed.[5] They are impossible, because the products of thermolysis always contain large amounts of NO and NO_2, which are inhibitors of free-radical processes. Hence, only the third variant remains, *viz.*, a sequence of transformations, whose rate its limited by the first step. The non-integer stoichiometric coefficient is in agreement with the following sequence of processes: some intermediate compounds are converted according to several pathways characterized by different stoichiometric coefficients (see, for example, Scheme 1), and, therefore, the stoichiometric coefficient for the overall reaction is fractional.
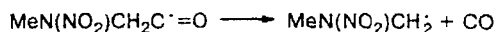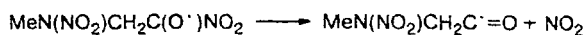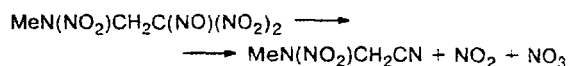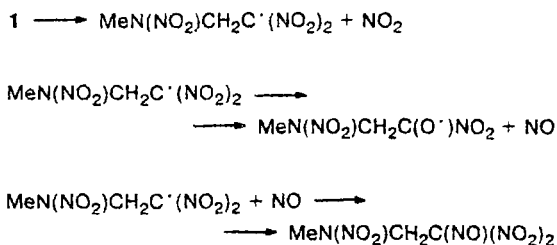
Scheme 1

$1 \longrightarrow MeN(NO_2)CH_2C^\cdot(NO_2)_2 + NO_2$

$MeN(NO_2)CH_2C^\cdot(NO_2)_2 \longrightarrow$
      $\longrightarrow MeN(NO_2)CH_2C(O^\cdot)NO_2 + NO$

$MeN(NO_2)CH_2C^\cdot(NO_2)_2 + NO \longrightarrow$
      $\longrightarrow MeN(NO_2)CH_2C(NO)(NO_2)_2$

$MeN(NO_2)CH_2C(NO)(NO_2)_2 \longrightarrow$
      $\longrightarrow MeN(NO_2)CH_2CN + NO_2 + NO_3$

$MeN(NO_2)CH_2C(O^\cdot)NO_2 \longrightarrow MeN(NO_2)CH_2C^\cdot=O + NO_2$

$MeN(NO_2)CH_2C^\cdot=O \longrightarrow MeN(NO_2)CH_2^\cdot + CO$

$MeN(NO_2)CH_2C^\cdot=O + NO_2 \longrightarrow$
      $\longrightarrow MeN(NO_2)CH_2COO^\cdot + NO$

$MeN(NO_2)C^\cdot H_2 + NO_2 \longrightarrow MeN(NO_2)CH_2O^\cdot + NO$

$MeN(NO_2)CH_2COO^\cdot \longrightarrow MeN(NO_2)C^\cdot H_2 + CO_2$

$MeN(NO_2)CH_2COO^\cdot + RH \longrightarrow$
      $\longrightarrow MeN(NO_2)CH_2COOH + R^\cdot$

$MeN(NO_2)CH_2O^\cdot \longrightarrow MeN^\cdot(NO_2) + CH_2O$

$CH_2O + NO_2 \longrightarrow CO + CO_2 + H_2O + NO$

$MeN^\cdot(NO_2) + NO_2 \longrightarrow MeNO + NO + NO_2$

$MeNO + 2 NO \longrightarrow Me^\cdot + N_2 + NO_3$

$Me^\cdot + NO_2 \longrightarrow MeO^\cdot + NO$

$Me^\cdot + NO_3 \longrightarrow MeONO_2$

$MeO^\cdot + NO_2 \longrightarrow MeONO_2$

The first-order rate constant found experimentally should apparently be attributed to the first step of this sequence provided that all the subsequent reactions are fast. Thus, the mechanism of the thermolysis of compounds **1—7** can be analyzed using the kinetic data listed in Table 1.

The activation energies of the decomposition of trinitroalkanes and secondary nitramines are close, whereas the preexponential factors are appreciably dissimilar. In the former case, they always exceed 10^{16} s^{-1}, while in the latter case, they are seldom greater than $10^{14.5}$ s^{-1}. Thus, decompositions of a trinitromethyl group and of a nitramino group can be distinguished from each other only based on the rate constants, which, unlike the *E* values, are measured with high accuracy and can differ by a factor of 60 for monofunctional compounds. The effects of substituents, an increase in the number of reaction groups in polyfunctional compounds, and simply the errors in determination of *E*

distort the relationship between the Arrhenius parameters characterizing the cleavage of the C—N and N—N bonds but not between the corresponding rate constants. Thus an error in the determination of E is always counterbalanced by a change in A (false compensation effect), which has only a minor influence on the difference between the rate constants.

From a comparison of the magnitudes of rate constants k and preexponential factors A, it follows that decomposition of compounds 1—3 begins with trinitromethyl groups.

In the case of compounds 4—7, the easiest way of choosing between the decomposition of nitramino and fluorodinitromethyl groups is to use the E_a values for the reaction. The rates of decomposition of these groups at the temperatures used in our experiments differ by approximately an order of magnitude, and their E_a differ by 6 kcal mol^{-1}, which is much greater than the experimental error. The data for compounds 4—7 presented in Table 1 (low E values and moderate A values) unambiguously indicate that decomposition of these compounds begins with nitramino groups.

By comparing the groups of compounds 1—3 and 4—7 one can see that the ratio of the rate constants for key compounds 1 and 4 is equal to 95, *i.e.*, it is larger than that in the case of monofunctional compounds, and that the smallest ratio (between compounds 3 and 6) is 30. The rates of decomposition of compounds 3 and 6 are 7 and 18 times, respectively, greater than those for the reference monofunctional compounds. Thus, a comparison of the groups of compounds 1—3 and 4—7 leads to the conclusion that decomposition of polyfunctional compounds 1—3 involves the less stable trinitromethyl group.

The results obtained here make it possible to identify a number of fine effects concerning the rate and mechanism of decomposition of the compounds studied.

Compound 1 is 10 times less stable than 1,1,1-trinitroethane, because the C—N bond in it is ~2 kcal mol^{-1} less strong. This difference can be fully attributed to the inductive influence of the β-nitramino group on the decomposition of the C(NO$_2$)$_3$ group.

Using the views on the secondary reactions accompanying decomposition of trinitroalkanes reported in the literature[5] and the data on the transformations of the methylnitramine radical MeN·NO$_2$ in an oxidative NO and NO$_2$ medium,[8] the detailed mechanism of the decomposition of compound 1 can be represented by Scheme 1. This scheme provides a qualitative explanation of the composition of the thermolysis products formed from 1 including the high yield of methyl nitrate and the absence of N$_2$O. It is relatively unlikely that the same products are formed upon the primary cleavage of the N—N bond in compound 1. Detailed schemes of the fast chemical reactions that accompany decomposition of secondary nitramines have not yet been reliably established. However, it is known[1] that decomposition of these compounds always yields N$_2$O or stable *N*-nitroso-

derivatives, which have not been detected among the products of decomposition of 1. Thus, the homolytic mechanism proposed for decomposition of 1, according to which dissociation of the C—N bond is the first step of the process, is quite justified.

The CO and CO$_2$ resulting from the thermolysis of 1,1,1-trinitroalkanes are formed from the α-C atom. This carbon atom passes into nitrile or carboxyl groups to only a small extent. The β-C atom is not oxidized at the C—H bonds and enters into the composition of stable compounds in combination with some groups such as OH, NO$_2$, or ONO$_2$.[5] In compounds like 1, the β-C atom also undergoes complete oxidation due to the low strength of the C—N bond in H$_2$C·—NNO$_2$R (see Scheme 1). Subsequently, the nitramino group is destroyed, and the reaction stops only at the δ-C atom. Partial oxidation in excess NO$_2$ yields stable nitro ester. At temperatures of decomposition of nitro esters, they are converted into alcohols and carboxylic acids or undergo more extensive oxidation at the δ-C atom.

The above-presented scheme of secondary reactions can be applied to compounds 2 and 3. It can be assumed that in the case of compound 2, the whole molecule immediately decomposes to light gaseous products in a sequence of rapid secondary reactions, while the destruction of 3 occurs in two steps: after the rate-determining abstraction of one of the nitro-groups, a part of the molecule up to the δ-position is oxidized *via* fast secondary reactions, whereas the rest of the molecule is converted into intermediate A of the RCH$_2$(NO$_2$)NCH$_2$C(NO$_2$)$_3$ type, where R = CN, CH$_2$OH, COOH, CH$_2$ONO$_2$, or CH$_2$NO$_2$.

Comparison of the rates of decomposition of compounds 1 and 3 (see Table 1) reveals the following feature that seems strange at first glance. Compound 1 contains one trinitromethyl group acting as the reaction center, while compound 3 contains two groups of this kind. It might be expected that 3 would decompose twice as fast as 1. However, the gas evolution rate constant found for the decomposition of 3 is far from being twice larger than that observed for 1; conversely, it is even somewhat smaller. This can be explained by the fact that decomposition of 3 occurs stepwise *via* intermediate A, whose structure was considered above. The essence of the stepwise decomposition becomes clear from Scheme 2. The first step of the decomposition of compound 3 is characterized by a rate constant which is twice as large as that for compound 1. This step involves the cleavage of one of the trinitromethyl groups, and, in addition to gaseous products, it yields a condensed intermediate A in which the second C(NO$_2$)$_3$ group is retained. Decomposition of this intermediate is the second step of the process, and its rate is half that observed in the case of 3.

The curves of gas evolution were calculated assuming that the first and the second reactions yield equal amounts of gaseous products $P_1 = P_2 = 6\ P_0$ (P_0 corresponds to the evolution of 1 mole of gaseous products) and $k_1 = k_2$

Scheme 2

$$3 \xrightarrow{2k_1} A + P_1 \tag{1}$$

$$A \xrightarrow{k_2} P_2 \tag{2}$$

$= 7.6 \cdot 10^{-5}$ s^{-1} (as in the case of 1). It can be seen from Fig. 2 that the calculated gas evolution curve closely simulates a first-order reaction and nearly coincides with the experimental curve for the decomposition of compound 3. The rate constant calculated from the overall curve of gas evolution is $7.6 \cdot 10^{-5}$ s^{-1}, *i.e.*, it coincides with k_1 and is somewhat larger than the observed rate constant for decomposition of 3 $(5.9 \cdot 10^{-5}$ s$^{-1})$. Complete agreement between the calculated and experimental curves was obtained for $P_1 = 5\ P_0$, $P_2 = 7\ P_0$. This result makes it possible to draw the following conclusion. The rate constant for gas evolution in the stepwise decomposition of compounds with two reaction centers is approximately identical to that for compounds with one decomposition center.

Yet another unexpected fact that can be discovered by comparing the rates of decomposition of compounds 1 and 2 (see Table 1 and Fig. 1) is the following. The decomposition of 2 is characterized by a lower activation energy and occurs at a substantially higher rate than decomposition of 1. This difference between compound 2 and compounds 1 or 3 can be explained by the field effect, which has been observed previously for structural analogs of 2, namely, for pentane derivatives overloaded with nitro groups.[5] Owing to steric restrictions and

electrostatic interactions, the molecule of 2 exists predominantly in a twisted conformation,[9] in which one of the O atoms of the nitramine group approaches the C atom of the $-C(NO_2)_3$ group to a distance of 3.09 Å (which is smaller than the sum of the van der Waals radii of O and C atoms equal to 3.19 Å) and thus stabilizes the free valence in the radical generated on the abstraction of NO_2. This results in a decrease in the E value and, to some extent, in the A value (since free rotation around the C—C bond in the $RCH_2C \cdot (NO_2)_2$ radical becomes hindered).

The rate of decomposition of compound 4 is 5 times higher than the typical rate of decomposition of a planar nitramine group. This is a result of the inductive influence of the $-C(NO_2)_2F$ group on the $-NNO_2-$ group located in the β-position. Note that in compound 1, the effect of the nitramino group on the destruction of $-C(NO_2)_3$ is twice stronger.

In the case of compound 5, the rate constant is approximately twice higher than that for nitramine 4; this is due to the inductive effect of the two fluoro-dinitromethyl groups. No conformation effects are manifested in compound 5. In this respect, compound 5 differs from its analog, compound 2, in which the nitramino group exerts a strong through-space effect on the cleavage of the C—N bond.

Compounds 6 and 7 contain two nitramino groups each, and the rate constants of their decomposition are 4 and 2 times larger than that for compound 4, respectively. Possibly, decomposition of these compounds proceeds stepwise, and the increase in the rate of the process (especially in the case of 6) is due to the $O...NNO_2$ through-space interaction of the nitramino groups separated by two or three methylene bridges. The intermediate six-or seven-membered cyclic structures needed for this interaction are the most accessible non-strained configurations of atoms linked to one another. In view of this hypothesis, it is of interest to study other polyfunctional nitramines containing the $-N(NO_2)CH_2CH_2N(NO_2)-$ structural fragment.

Thus, in the study of polynitro-substituted nitramines, we found that decomposition of these compounds always starts from the cleavage of those bonds that are the least strong according to the analysis of the corresponding monofunctional compounds. The reaction occurs by a homolytic mechanism that includes the cleavage of the C—N or N—N bonds. The strength of these bonds decreases by 1—2 kcal mol^{-1} as a result of the inductive effect of groups. In addition, in some cases, spatial interactions (field effect, anchimeric assistance), which are impossible in monofunctional compounds, may also be manifested. In the case of compound 2, the occurrence of this effect can be regarded as proven, while for compounds 6 and 7, its role has been assumed. Yet another result of this study is that the kinetic effect of the stepwise decomposition of polyfunctional compounds was demonstrated experimentally as follows. The evolution of the final products imitates first-order kinetics but
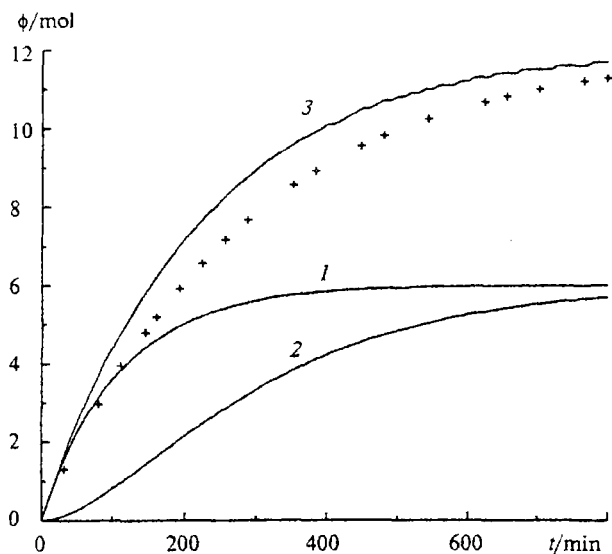

Fig. 2. Kinetic curves for the yield of gaseous products calculated from Scheme 2 (see the text) at $P_1 = P_2 = 6\ P_0$, $k_1 = k_2 = 7.6 \cdot 10^{-5}$ s^{-1}; reaction (1) (*1*); the curve for P_2 (*2*); the overall curve for $P_1 + P_2$ (*3*); the crosslets indicate experimental points $(k = 5.9 \cdot 10^{-5}$ s$^{-1})$.

is characterized by a smaller rate constant than the destruction of the initial compound. The first-order kinetics is retained for this sequence of transformations if the rate constants for the first and the second steps are close to each other and if the final products are independently produced in approximately equal amounts from the initial compound and from the intermediate.

The scheme for stepwise decomposition can be easily adapted to compounds containing three or four identical reaction groups, and it can be used to interpret numerous published data on the kinetics of decomposition of polyfunctional compounds of various classes (organic azides, nitramines, nitro esters, difluoroamines, polynitro compounds) including explosives: hexogen, octogen, nitroglycerol, PETN, trinitrotriazidobenzene, *etc.*

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