Decomposition of aliphatic α-fluorodinitro compounds in the liquid phase

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The decomposition of compounds $Y[CH_2C(NO_2)_2X]_2$ ($X = NO_2$ and F; $Y = CH_2C(O)O$ and OCH_2O) in the liquid phase (melt, solution) was found to proceed *via* the same mechanism (homolytic cleavage of the C—N bond) as in the gas phase. Some stabilizing effects of the O_β atom and independence of the gas evolution rate constant (measured by the yield of final products) on the number of the $-C(NO_2)_2X$ groups were found and interpreted.

Key words: aliphatic fluoronitro compounds, thermal decomposition.

The study of gas-phase decomposition of aliphatic polynitro compounds has shown[1] that α-fluoro-α,α-dinitroalkanes possess a high thermal stability. Unlike other electronegative substituents at the C_α atom, which strongly decrease the energy of cleavage (D) of the C—N bond, the F atom slightly affects D(C—N) and is equivalent (in this respect) to the H atom or Me group. For example, in structures of the $RC(NO_2)_2X$ type (R is alkyl), D(C—N) = 43 kcal mol^{-1} at X = NO_2, Cl, Br, and I and 47—48 kcal mol^{-1} at X = F, H, and Me. At 100 °C, compound $RCF(NO_2)_2$ is more stable than $RC(NO_2)_3$ by 10^3 times. By the thermal stability, the α-fluoro-α,α-dinitromethyl group in aliphatic compounds exceeds nitramine, nitroester, and azide groups and, hence, it is considered as a promising structural element for the development of thermostable high-energy compounds.[2,3]

However, the conclusion about the high stability of fluoroderivatives is based only on the data obtained by the study of vapor. The validity of this conclusion for the condensed state should be verified. In the liquid phase, a deviation from the homolytic decomposition (cleavage of the C—N bond) and the appearance of the polar or ionic mechanism are possible. For example, based on the data on the manometric probe (the volume of the gas evolved during 48 h at 100 °C), the author of Ref. 4 has concluded that the decomposition of compounds of the $ROCH_2C(NO_2)_2F$ type (similar to nitroalkanes) with the O atom at the β-carbon atom (O_β) occurs with sufficiently high rates through the dissociation stage:

$$ROCH_2C(NO_2)_2F \longrightarrow ROCH_2^+ + {}^-C(NO_2)_2F. \quad (1)$$

The stabilities of compounds $X(NO_2)_2CCH_2OCH_2OCH_2C(NO_2)_2X$, where X = F and X = NO_2, differ by only 10 times (instead of 10^3 according to the prognosis for the gas phase).

However, results of discrete experiments, such as a manometric probe, are not always reliable, since they can depend, *e.g.*, on the presence of unstable or catalytic admixtures. More stringent conclusions on the mechanism and rates of decomposition require a detailed kinetic study.

Therefore, in this work, we studied the decomposition of compounds
$F(NO_2)_2CCH_2CH_2COOCH_2C(NO_2)_3$ (**1**),
$(NO_2)_3CCH_2CH_2COOCH_2C(NO_2)_2F$ (**2**),
$(NO_2)_3CCH_2OCH_2OCH_2C(NO_2)_3$ (**3**),
$(NO_2)_3CCH_2CH_2COOCH_2C(NO_2)_3$ (**4**),
$F(NO_2)_2CCH_2OCH_2OCH_2C(NO_2)_2F$ (**5**), and
$F(NO_2)_2CCH_2CH_2COOCH_2C(NO_2)_2F$ (**6**)
in a wide temperature range in melts and solutions. The structures of these substances were chosen in such a way that the effect of substituents F_α and O_β on the decomposition could be checked.

Experimental

Compounds **1**—**6** were synthesized according to procedures described previously.[5,6]

Crystalline compounds **1**—**4** and **6** were purified by recrystallization. Compound **5**, which is a high-boiling liquid, was distilled *in vacuo* (0.2 Torr) at 130 °C.

Decomposition reactions were carried out in a melt at a ratio of the sample weight to the volume of the reaction vessel (m/V) of 10^{-2}—10^{-4} g cm^{-3} or in a 1—5% solution of *m*-dinitrobenzene. Kinetic measurements were carried out by the manometric method. In solutions and at high temperatures in the melt, the reactions were performed to a degree of decomposition >70%. The rate constants (k) were calculated from the slope of kinetic curves in the coordinates of the first-order equation. The molar yield of gaseous products at complete decomposition was determined under the same conditions. At low temperatures, the k values were determined from the times of reaching the 1% degree of decomposition. To

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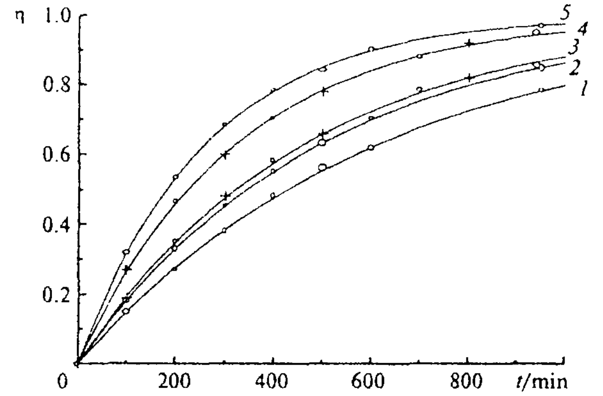


Fig. 1. Kinetic curves of decomposition of TNE (*1*) and trinitroethanol derivatives **1**—**4** (*2*—*5*) at 160 °C. The data for the melt are designated by the circle, and the sign "+" indicates the solution; η is conversion.

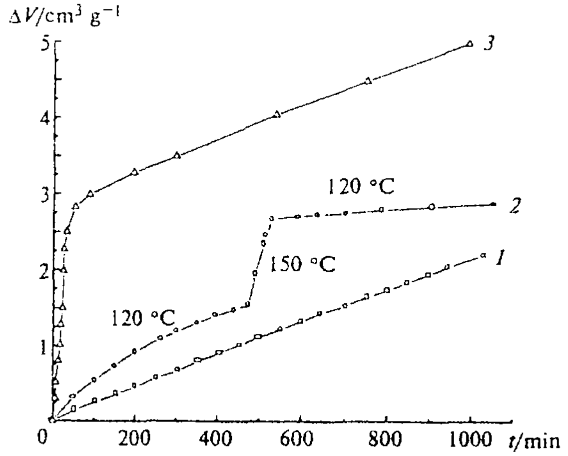


Fig. 2. Initial regions of kinetic curves of decomposition of compound **5** in the melt: *1*, purified sample at 160 °C; *2* and *3*, sample before purification: *2*, subsequent decomposition at different temperatures, *3*, at 160 °C. ΔV is the volume of gaseous products reduced to standard conditions (0 °C, 760 Torr).

increase the accuracy of measurements of the relative stability of different substances (or the same substance under different conditions), the decomposition was carried out simultaneously in the same thermostat. This method eliminated the main source of error, temperature variation, in determination of k by the manometric method.

Results and Discussion

The kinetic curves of decomposition of compounds **1**—**4** and 1,1,1-trinitroethane (TNE) as the reference substance (Fig. 1) show that these compounds can be arranged in the following series: TNE ≈ **1** > **2** > **3** > **4**, which is strictly fulfilled at temperatures below 190 °C. The paired tests indicate that at high temperatures, compound **5** is more stable than **6**. The decomposition of **1**—**4** and **6** is described satisfactorily by a first-order equation. The rate constants of decomposition in the melt and solutions are equal, and autocatalytic processes are absent, which is characteristic of decomposition of polynitroalkanes. In the case of compound **5**, the initial regions of the kinetic curves at low temperatures have shapes indicating the decomposition of unstable admixtures: high rates and the first order at a low conversion (Fig. 2). Dopant process are not catalytic and, therefore, the thermal treatment results in removal of unstable admixtures from compound **5**. At 160 °C, admixtures are consumed already during heating of the substance, after which all samples have the same rates of decomposition. Two-times distillation *in vacuo* at 130 °C also results in complete purification of **5** from unstable admixtures.

The kinetic parameters of decomposition of **1**—**6** are presented in Table 1 along with the data for TNE (melt) and 1-fluoro-1,1-dinitroethane (FDNE) in the gas phase for comparison.

Table 1. Kinetic parameters of decomposition of compounds **1**—**6**

Compound	Medium	Temperature interval/°C	E /kcal mol^{-1}	lg(A/s^{-1})	k(150 °C) /s^{-1}	W^a	ϕ^b
1	Melt	130—193	41.5	16.47	$1.1 \cdot 10^{-5}$	1.3	4.6
2	Melt	130—193	41.5	16.75	$2.0 \cdot 10^{-5}$	2.4	4.7
3	Melt	120—185	41.4	16.50	$1.3 \cdot 10^{-5}$	1.6	9.2
	Melt ^{c}	150—185	41.5	16.50	$1.2 \cdot 10^{-5}$	1.4	—
4	Melt	120—175	41.4	16.60	$1.6 \cdot 10^{-5}$	1.9	9.0
	Melt ^{c}	140—200	41.4	16.65	$1.8 \cdot 10^{-5}$	2.1	9.5
5	Melt	160—200	46.7	16.50	$2.3 \cdot 10^{-8}$	2.1	8.0
6	Melt	140—200	47.0	16.88	$3.4 \cdot 10^{-8}$	3.1	8.0
$MeC(NO_2)_3$ (TNE)	Melt		42.6	16.93	$8.3 \cdot 10^{-6}$		
$MeC(NO_2)_2F$ (FDNE)	Gas		47.8	16.70	$1.1 \cdot 10^{-8}$		

[a] Ratio of rate constants k(150 °C)/k_{ref}. For compounds **1**—**4**, $k_{ref} = 8.3 \cdot 10^{-6}$ s^{-1} (data for TNE in the melt[7]); for **5** and **6**, $k_{ref} = 1.1 \cdot 10^{-8}$ s^{-1} (data for PDNE in the gas phase[1]).

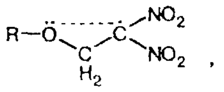
[b] Molar yield of gaseous products.

[c] Solution in *m*-dinitrobenzene (0.3%).

The kinetic parameters of decomposition of compounds **1**—**4**, which starts from trinitromethyl groups, are typical, as a whole, of decomposition of 1,1,1-trinitroalkanes. However, there are some small but noticeable distinctions related to the effect of the O_β atom and the presence of two functional groups in the molecule.

Compound **1** is the most stable in the series of **1**—**4**. As compared to TNE, the kinetics of its decomposition is characterized by a somewhat higher rate, but lower values of activation energy (E) and pre-exponential (A). The decrease in E by 1 kcal mol^{-1} is related to the induction effect of the O_β atom or an increase in the carbon chain length. It is known[8] that trinitropropane and trinitrobutane decompose more rapidly than TNE; however, the decrease in A can be explained only by the influence of the O atom of the ester group. This conclusion follows from the comparison of the kinetics of decomposition of **1** and **2**. The rates of decomposition of compound **2**, in which the acid fragment undergoes decomposition rather than the alcohol fragment, are twofold higher than those of decomposition of **1**. In this case, a decrease in the activation energy, as compared to that of TNE, is not compensated by a decrease in A.

The positive effect of the O_β atom on the stability can be explained by the spatial interaction of the lone pair of the O atom with the p-orbital of the free electron in the radical



which restricts free rotation about the C—O bond and prevents liberation of retarded (in the initial molecule) internal rotation about the C—C bond when the nitro group leaves, thus decreasing the A value as compared to standard alkyl-derivatives. In esters, as compared to formals, this interaction is weakened due to the electronegative influence of the O atom of the carbonyl group and reflects the A value (see Table 1).

An exciting example of a change in the pre-exponential factor due to the conjugation of the reaction center with the O atom of the ester group (not through the space, but along the chain of covalent bonds) has been presented previously.[9] Two reactions of the same type, rearrangement of 1,5-dienes and isomerization of vinylallyl esters, have different pre-exponential factors. Since the barrier of internal rotation about the C—O bond in esters during the formation of the cyclic transition state is increased (see Ref. 9), only two degrees of freedom of internal rotation are lost (not three as in the case of 1,5-dienes), and hence, the pre-exponential factors of these reactions differ by 0.8 logarithmic unit.

Compound **3** differs from **1** by the fact that it possesses two trinitromethyl groups bound to the O_β atom; therefore, it could be expected that **3** decomposes two times more rapidly than **1**. However, the rate constants of gas evolution for **1** and **3** are almost equal. This can be explained by the fact that the decomposition of **3** to light gaseous products occurs stepwise, in two macroscopic stages.

In compounds **1** and **2**, fast secondary reactions generated during detachment of the nitro group at one side of the molecule do not reach its second end, but terminate approximately in the middle of the molecule. This follows from the fact that the gas evolution from **1** and **2**, which have the stable fluorodinitromethyl group at one side, is twofold lower than that of **3** and **4**, whose decomposition can occur from two ends simultaneously. It is impossible to decompose a long-chain molecule with the trinitromethyl and fluorodinitromethyl groups due to one sequence of fast secondary reactions, which also follows from the mechanism of decomposition of trinitromethyl compounds. The detailed scheme of the mechanism has been considered previously.[10] The extension of this scheme to **1** and **2** suggests that in the primary process of decomposition to light gaseous products, only one half of the molecule, which is bound to the trinitromethyl group, decomposes, and the second half is stabilized as the final products.

A similar route of decomposition, but with the formation of intermediate products rather than final products, is likely valid for compound **3** (Scheme 1).

Scheme 1

$$\mathbf{3} \xrightarrow{2k_1} \mathrm{A} + \mathrm{P}_1$$

$$\mathrm{A} \xrightarrow{k_2} \mathrm{P}_2$$

In Scheme 1, A is a compound of the $RCH_2OCH_2C(NO_2)_3$ type, P_1 and P_2 are gaseous products, and $k_1 = k_2$. At 150 °C, $k_1 = 1.1 \cdot 10^{-5}\ s^{-1}$ (as for **1**).

The calculation of the observed rate constant k_{obs} of complete gas evolution under the condition that $P_1 = P_2$ has been performed previously,[10] and it has been shown that the kinetic curve of total evolution of gaseous products at the first and second stages ($P_1 + P_2$) corresponds to a first-order curve and $k_{obs} = k_1$. Experiments with compound **3** (k_{obs} is close to k_1 rather than to $2k_1$) confirm this general conclusion, which follows from Scheme 1: for compounds with two equivalent reaction centers, the rate constants of decomposition of the starting compound and formation of the final products differ by two times.

Compound **4** contains the trinitromethyl alcohol and acid fragments, which are present separately in molecules **1** and **2**. The decomposition of molecule **4** proceeds from two ends, the gas evolution is twofold higher than that in the case of **1** and **2**, and the rate constant with respect to the yield of products is higher than that for **1**, but lower than that for **2**.

It can be assumed by analogy to **3** that the decomposition of **4** occurs stepwise, and intermediate stages have the same rate constants as the reactions of decomposition of **1** and **2** (Scheme 2).

Scheme 2

$$\mathbf{1} \xrightarrow{k_1} 4.5\ P_0$$

$$\mathbf{2} \xrightarrow{k_2} 4.5\ P_0$$

$$\mathbf{4} \xrightarrow{k_1} \mathbf{A} + P_1$$

$$\mathbf{4} \xrightarrow{k_2} \mathbf{B} + P_2$$

$$\mathbf{A} \xrightarrow{k_2} P_3$$

$$\mathbf{B} \xrightarrow{k_1} P_4$$

In this case, $k_1 = 1.1 \cdot 10^{-5}$ s^{-1}, $k_2 = 2.0 \cdot 10^{-5}$ s^{-1} (at 150 °C), intermediate **A** has a structure of the $RCH_2CH_2C(NO_2)_3$ type with the trinitromethyl group in the acid residue, and intermediate product **B** is similar to $ROCH_2C(NO_2)_3$, *i.e.*, contains the trinitromethyl group in the alcohol residue.

The calculation of the kinetic curves under the condition that $P_1 = P_2 = P_3 = P_4 = 4.5\ P_0$, where P_0 corresponds to the isolation of 1 mole of products, is presented in Fig. 3. The rate constant calculated from the overall curve *4* ($1.54 \cdot 10^{-5}$ s^{-1}) coincides with the experimental curve.

The difference between formals and esters is distinctly seen for compounds **5** and **6**. The effect of the O atom of the ester group on the reaction rate is small in absolute value, and liquid compounds **5** and **6** are close in stability to PDNE vapor. They possess an activation energy equal to the dissociation energy of the C—N bond in dinitroalkanes and a value of the pre-exponential factor characteristic of the decomposition of polynitroalkanes. No properties of reaction (1) are observed as in the case of compounds **1**—**4**.

Thus, the decomposition of ethers and esters of 2,2,2-trinitro- and 2-fluoro-2,2-dinitroethanol in the liquid phase occurs according to the standard mechanism for polynitro compounds, *i.e.*, through the homolytic dissociation of the C—N bond. The F_α substituent stabilizes the molecule considerably, and the O_β atom only insignificantly affects the reaction rate, resulting in a simultaneous decrease in both the activation energy and the pre-exponential factor. In compounds with two reaction groups, the decomposition occurs stepwise, the accumulation of the final products obeys a first-order equation, but occurs with a lower rate constant than that of the primary decomposition of the starting compound.

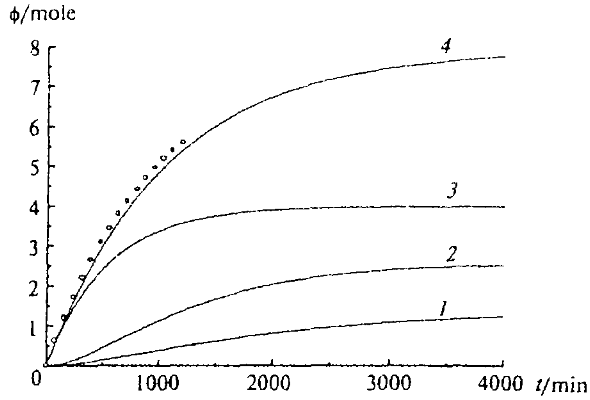


Fig. 3. Kinetic curves of evolution of gaseous products at intermediate stages of decomposition of compound **3** at 150 °C (the curves were calculated by Scheme 2): *1*, P_4; *2*, P_3; *3*, $P_1 + P_2$; *4*, overall curve $P_1 + P_2 + P_3 + P_4$. Experiment is indicated by points.

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