Thermal decomposition of α-(difluoroamino)polynitroalkanes

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The compounds $RC(NO_2)_2NF_2$ differ little from their nitro analogs, $RC(NO_2)_3$, in stability. They decompose in the gas and liquid phases at identical rates and the decomposition is controlled by cleavage of a $C-NO_2$ bond. For R = NO_2, F, and Me the Arrhenius parameters, E (kJ mol^{-1}) and log (A/s), are: 161.3 and 16.00; 180.2 and 16.20; 168.4 and 16.00, respectively.

Key words: α-(difluoroamino)polynitroalkanes; kinetics of decomposition, reaction mechanism.

α-(Difluoroamino)polynitroalkanes, $RC(NO_2)_2NF_2$, represent a new class of high-energy compounds[1] that are promising for the development of powerful explosives and oxidizing agents for jet fuels. Therefore, the determination of the stabilities of these compounds and an investigation of the mechanism of their thermal decomposition are of interest. In the present work we studied the decomposition of the simplest compounds of this class, *viz.*, $C(NO_2)_3NF_2$ (**1**), $FC(NO_2)_2NF_2$ (**2**), and $MeC(NO_2)_2NF_2$ (**3**) in the gas phase, and **1** and **3** also in the liquid phase. Using these examples we elucidated the characteristic features of the decomposition and found a significant regularity that may make it possible to predict the stability of this class of compounds as a whole.

Experimental

The kinetics of decomposition was studied by the manometric method. The degree of decomposition was 70—100 %. The kinetic curves were processed using a modified Hugenheim method (linearization in $p_t - p_{t+\Delta t}$ coordinates), which does not require that the final pressure p_∞ corresponding to a degree of decomposition of 100 % be known and, moreover, allows this pressure to be determined from any sufficiently long section of the curve. At low temperatures the reaction was arrested when a 5—10 % degree of decomposition was attained. The first-order rate constants were calculated from the time it took for a degree of decomposition of 1 % to be reached. The p_∞ value necessary for the calculations was determined in prolonged runs at higher temperatures. For the gas-phase decomposition, the effects of the initial vapor pressure p_0 (which varied between 15 and 250 Torr), the ratio of the surface area of the vessel to its volume, S/V (0.5—10 cm^{-1}), which was varied by varying the diameter of the vessel or by filling it with glass capillaries, and, in some cases (for compound **3**), of inhibitors of chain processes, NO_2 and I_2, on the reaction rate were studied. For the decomposition of the compounds in the liquid state, the degree of filling of the vessel with the substance, m/V, varied from 0.025 to 0.25 g cm^{-3}, and the rate constants were calculated as for the low-temperature gas-phase decomposition.

When the degree of decomposition is less than 90 %, decomposition of compounds **2** and **3** is described by a first-order equation. The p_∞/p_0 ratio remains practically constant at various temperatures and is 2.9—3.0. In the case of compound **1**, the shape of the kinetic curves is typical for a two-step consecutive process whose second step occurs several times more slowly than the first step (Fig. 1). It is likely that decomposition of compound **1** yields a product that is unstable at the experimental temperature. Decomposition of **1** is described by a first-order equation only when the degree of decomposition is lower than 40—60 %. In this initial step of the process, the p_∞/p_0 ratio decreases from 3.5 to 2.2 as the temperature increases from 140 °C to 175 °C. At the same time, when the second step is completed, the overall gas evolution is $4p_0$. When $S/V > 10$ cm^{-1}, the reaction occurs in one step with a rate constant identical to that observed at low S/V values, and $p_\infty/p_0 = 4p_0$.

The data on the gas-phase decomposition of **1** are presented in Table 1. The studies carried out with compounds **2** and **3** involved similar variation of the experimental conditions. All of the above-listed factors (p_0, S/V, inhibitors, m/V) have no effect on the rates of the processes. The parameters for the Arrhenius equations for the first order reactions of the decomposition of compounds **1**—**3** are listed in Table 2. For comparison, we give the data for pure nitro analogs of **1**—**3**, *viz.*, compounds $RC(NO_2)_3$.

Results and Discussion

The facts that these reactions obey first-order kinetics and the rate constants do not depend on p_0, S/V, and inhibitors, and that the rates of decomposition in the gas and liquid states are similar imply that the decomposition is a homolytic monomolecular reaction. The great magnitudes of the pre-exponential factors agree with a mechanism that involves dissociation of the molecule into two large moieties, *i.e.*, cleavage of a $C-NO_2$ or $C-NF_2$ bond. The energies of dissociation

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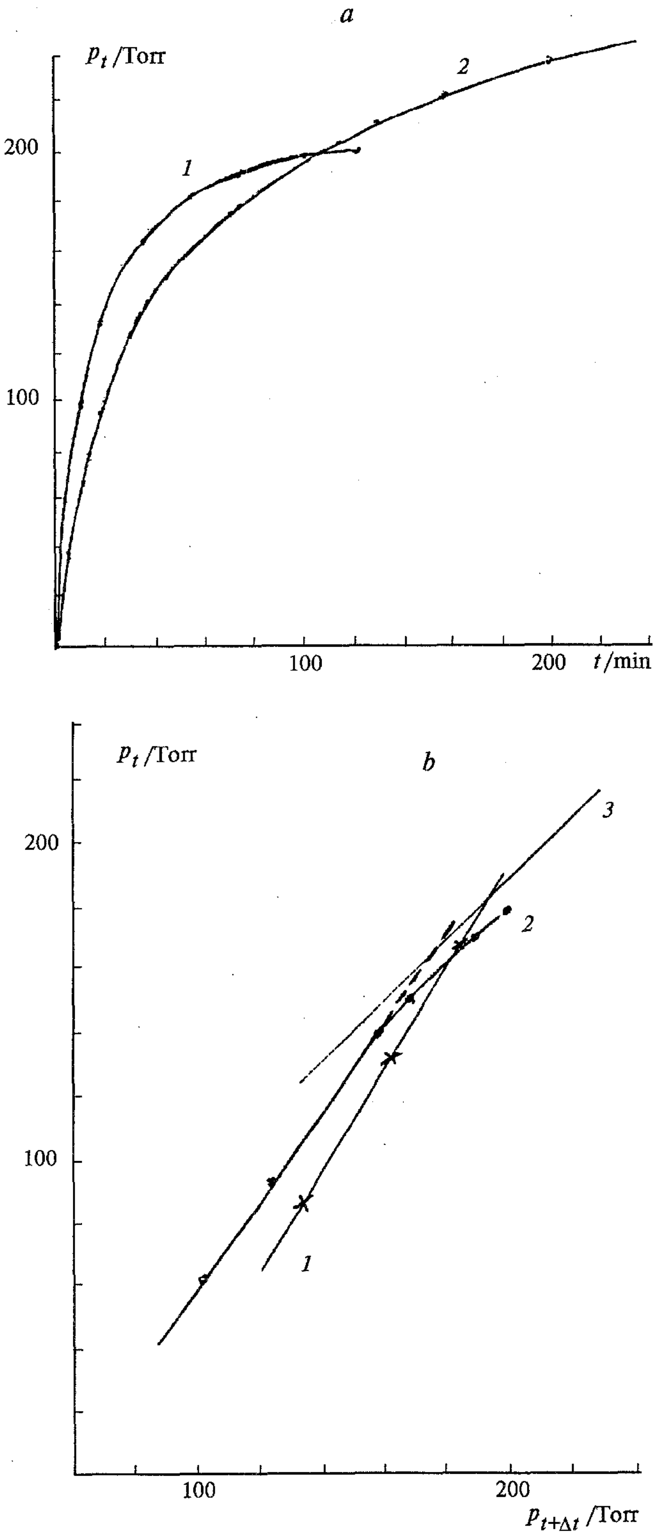


Fig. 1. The kinetic curves (*a*) and linearization in $p_t - p_{t+\Delta t}$ coordinates (*b*): $MeC(NO_2)_2NF_2$, 190 °C, $p_0 = 100$ Torr, $\Delta p_\infty = 195$ Torr, $p_\infty/p_0 = 2.95$, $\Delta t = 10$ min (*1*); $C(NO_2)_3NF_2$, 160.5 °C, $p_0 = 107$ Torr, $\Delta p = 175$ Torr, $p_\infty/p_0 = 2.63$, $\Delta t = 10$ min (*2*); equal pressure lines (*3*).

Table 1. The conditions of the experiments and the rate constants of the first step of decomposition of $F_2NC(NO_2)_3$ in the gas phase

Run	T /°C	The diameter of the vessel /cm	S/V /cm^{-1}	p_0 /Torr	p_∞/p_0	k/s^{-1}
1	109.5	3	2	63	3.50 (accepted)	$1.26 \cdot 10^{-6}$
2	110.0	3	2	113	The same	$8.30 \cdot 10^{-7}$
3	119.8	3	2	245	»»	$4.74 \cdot 10^{-6}$
4	130.0	3	2	68	»»	$1.18 \cdot 10^{-5}$
5	130.0	3	2	157	»»	$1.50 \cdot 10^{-5}$
6	130.0	3	2	16	»»	$1.45 \cdot 10^{-5}$
7	140.0	3	2	15	3.30	$3.51 \cdot 10^{-5}$
8	140.0	12	0.5	15	3.10	$3.33 \cdot 10^{-5}$
9	140.0	3	2	132	3.52	$3.35 \cdot 10^{-5}$
10	140.3	3	2	142	3.56	$3.30 \cdot 10^{-5}$
11	160.5	3	2	107	2.63	$3.83 \cdot 10^{-4}$
12	160.3	3	2	62	2.58	$3.25 \cdot 10^{-4}$
13	160.5	3	2	30	2.50	$4.30 \cdot 10^{-4}$
14	160.0	3	2	20	2.67	$4.08 \cdot 10^{-4}$
15	160.0	12	0.5	109	2.40	$4.02 \cdot 10^{-4}$
16	160.0	12	0.5	20	2.50	$4.22 \cdot 10^{-4}$
17	160.7	5 (with filling)	10	154	4.33	$4.00 \cdot 10^{-4}$
18	169.5	3	2	140	2.39	$8.24 \cdot 10^{-4}$
19	174.5	3	2	180	2.30	$1.45 \cdot 10^{-3}$

Table 2. The kinetic parameters of thermal decomposition of α-(difluoroamino)polynitroalkanes and their nitro analogs*

Compound	State	T/°C	E/ kJ mol^{-1}	log(A/s)	k/s^{-1} (100°C)
$F_2NC(NO_2)_3$	Gas	110—175	161.3	16.00	$2.7 \cdot 10^{-7}$
	Liquid	80—90	162.1	16.40	$5.2 \cdot 10^{-7}$
$FC(NO_2)_2NF_2$	Gas	170—220	180.2	16.20	$1.0 \cdot 10^{-9}$
$MeC(NO_2)_2NF_2$	Gas	170—190	168.4	16.00	$2.7 \cdot 10^{-8}$
	Liquid	120—140	168.4	16.00	$2.7 \cdot 10^{-8}$
$C(NO_2)_4$	Gas		160.0	16.30	$8.1 \cdot 10^{-7}$
	Liquid	80—110	156.7	15.50	$3.8 \cdot 10^{-7}$
$FC(NO_2)_3$	Gas	178—236	175.6	15.40	$6.9 \cdot 10^{-10}$
$MeC(NO_2)_3$	Gas	160—210	181.0	17.11	$6.2 \cdot 10^{-9}$
	Liquid	100—140	178.5	16.93	$9.1 \cdot 10^{-9}$

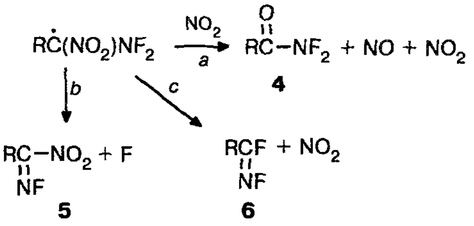
* For the data on polynitroalkanes, see Refs. 2 and 3.

of the C—NF_2 bonds in compounds **1—3** are[1] 188.1, 199.9, and 208.2 kJ mol^{-1}, respectively, *i.e.*, they are much greater than the activation energies observed. On the other hand, the kinetic parameters and absolute rates of decomposition of compounds **1—3** do not differ from those of the nitro analogs $RC(NO_2)_3$ within the limits of experimental error (the accuracy of the determination of activation energy was 6 kJ mol^{-1}) (see Table 2). Therefore, one may conclude that decomposition of compounds **1—3** occurs *via* cleavage of C—NO_2 bonds, rather than C—NF_2 bonds. The effect of an α-NF_2 group on the strength of a C—NO_2 bond is equivalent to that of a nitro group. In other words, the replacement of one nitro group in $RC(NO_2)_3$ by NF_2 does not result in a change in the mechanism or the rate of decomposition. This fact can be used for predicting the rates of decomposition of α-(difluoroamino)polynitro compounds using the data for more easily available nitro compounds that have been studied in more detail.[4]

By analogy with the previous studies,[5,6] three main pathways for the transformation of the $RC^{\bullet}(NO_2)NF_2$ radicals formed in the first step of the decomposition of $RC(NO_2)_2NF_2$ can be considered: oxidation (*a*), ejection of F (*b*), and rearrangement with abstraction of NO_2 (*c*) (Scheme 1).

At temperatures around 150 °C, compound **4** and, especially, compounds **5** and **6** should be stable final products in the case when R = Me and F, or unstable intermediate products when R = NO_2. This probably accounts for the fact that decomposition of **1** occurs in two consecutive steps. Reactions *b* and *c*, unlike *a*, should have activation barriers, and their relative role with respect to the roles of *a* and other oxidation reactions yielding large quantities of gases should increase when the temperature increases. This may account for the decrease in the p_{∞}/p_0 ratio in the first step of the decomposition of **1** when the temperature increases.

Scheme 1



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