Kinetics of the thermal decomposition of bis(2,2-dinitropropyl)-*N*-fluoroamine

B. L. Korsunskii[a]* and A. G. Korepin[b]

[a]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156
[b]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (095) 265 5714

The kinetics of the thermal decomposition of bis(2,2-dinitropropyl)-*N*-fluoroamine are studied in the liquid phase. The reaction is autocatalytic in a melt. In dilute solution, the reaction rate is described by the first-order law. It is tens of times faster in polar sulfolan than in weakly polar dimethyl phthalate. A mechanism of the decomposition involving the formation of a cyclic transition state at the first, limiting stage of the process is suggested.

Key words: fluoroamines, thermal decomposition; nitrocompounds; kinetics.

Bis(nitroalkyl)amines represent a wide class of power-consuming compounds. The study of their thermal decomposition shows that their reactivities depend strongly on the structures of the molecules.[1,2] This work is devoted to the study of the kinetics of the thermal decomposition of bis(2,2-dinitropropyl)-*N*-fluoroamine (BDFA). There are data on the thermolysis of BDFA in the literature,[3—5] but similar works on monofluoroamines are scarce, although some data on the mechanism of the decomposition of *N*-fluoroazoxy derivatives are available.[6]

Experimental

Bis(2,2-dinitropropyl)-*N*-fluoroamine (m.p. 82—83 °C) was synthesized and purified according to the procedure described previously.[7] The kinetics of the liquid-phase decomposition of BDFA were studied *in vacuo* by the manometric method by the amount of gas evolved, using glass membrane Bourdon manometers (the volume of the reaction vessel was 80 mL), and in air by the mass loss (an automatic ATV-14M thermobalance was used).

Results and Discussion

Figure 1 demonstrates that the thermal decomposition of BDFA has a pronounced autoaccelerating character. Similar regularities are observed in the gravimetric experiments, and it turns out that the main reaction products are gaseous and ~96 % of the mass of the sample is lost in the decomposition. The reaction is accelerated by the additions of acids (Fig. 2) and especially strongly, by the additions of bases (Fig. 3). When the decomposition occurs in dilute solutions, no autoacceleration is observed, and the process is described by a first-order equation with high accuracy. The corresponding kinetic parameters are presented in Table 1.

The data in Table 1 show that the kinetics of the reaction studied depend substantially on the nature of the solvent: the decomposition is more than an order of magnitude faster in polar sulfolan (dielectric constant (ε) is 42 at ~20 °C) than in weakly polar dimethyl phthalate (ε = 8.5). A similar dependence on the polarity of the medium is typical of heterolytic processes and

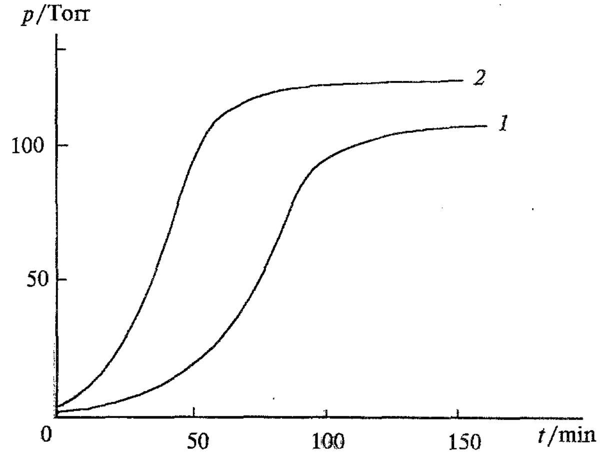

Fig. 1. Kinetics of the thermal decomposition of bis(2,2-dinitropropyl)-*N*-fluoroamine (20 mg) in a melt at 150 °C (*1*) and 160 °C (*2*).

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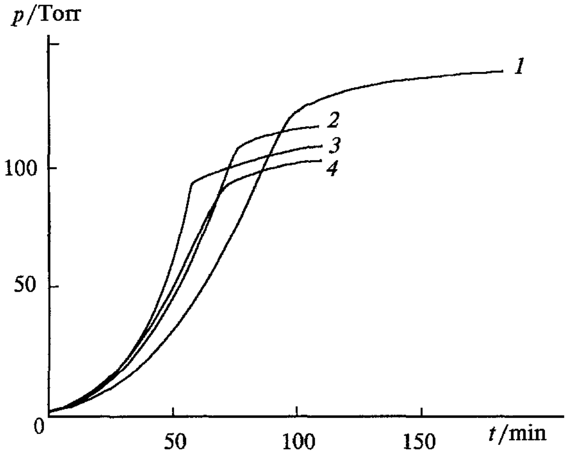


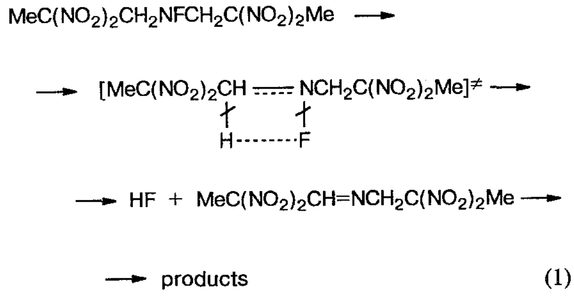
Fig. 2. Kinetics of the thermal decomposition of bis(2,2-dinitropropyl)-*N*-fluoroamine (20 mg) in the absence (*1*) and in the presence of picric acid (*2—4*) at 160 °C. Content of the acid/mg: *1,* 0; *2,* 0.6; *3,* 1.2; *4,* 2.2.

Table 1. Kinetics of the thermal decomposition of bis(2,2-dinitropropyl)-*N*-fluoroamine in 4% solutions of different polarity

Parameter	k/s^{-1}	
	in sulfolan	in dimethyl phthalate
T/°C:		
130	$2.6 \cdot 10^{-4}$	—
140	$4.3 \cdot 10^{-4}$	—
150	$1.0 \cdot 10^{-3}$	$3.9 \cdot 10^{-5}$
160	$1.8 \cdot 10^{-3}$	$7.0 \cdot 10^{-5}$
170	$2.8 \cdot 10^{-3}$	$1.4 \cdot 10^{-4}$
180	—	$3.3 \cdot 10^{-4}$
190	—	$7.9 \cdot 10^{-4}$
E_a/kJ mol^{-1}	92.0±5.0	123.0±7.9
A/s^{-1}	$10^{8.3\pm0.6}$	$10^{10.7\pm0.9}$

Note: k is the reaction rate constant, E_a is the activation energy, and A is the pre-exponential factor.

reactions occurring *via* a polar transition state, and considerably less typical of radical processes. Therefore, it is reasonable to consider that the formation of the cyclic activated complex (Eq. 1) is the limiting stage of the reaction.



$$\mathrm{MeC(NO_2)_2CH_2NFCH_2C(NO_2)_2Me} \longrightarrow$$

$$\longrightarrow [\mathrm{MeC(NO_2)_2\underset{\underset{H}{\uparrow}}{CH} \cdots \underset{\underset{F}{\uparrow}}{N}CH_2C(NO_2)_2Me}]^{\neq} \longrightarrow$$

$$\longrightarrow \mathrm{HF + MeC(NO_2)_2CH{=}NCH_2C(NO_2)_2Me} \longrightarrow$$

$$\longrightarrow \text{products} \qquad (1)$$

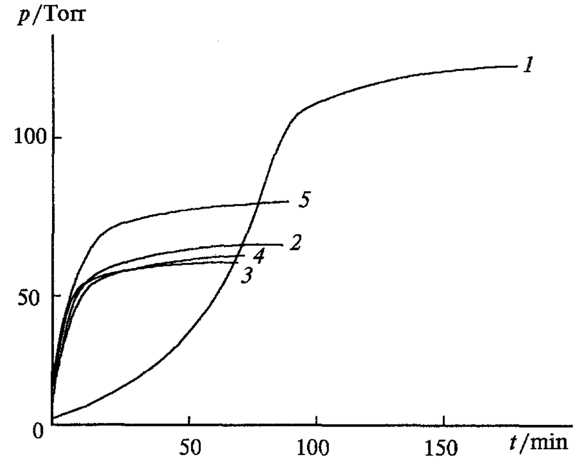


Fig. 3. Kinetics of the thermal decomposition of bis(2,2-dinitropropyl)-*N*-fluoroamine (20 mg) in the absence (*1*) and in the presence of the base, non-symmetric diphenyldimethyl urea, (*2—5*) at 160 °C. Content of the base/mg: *1,* 0; *2,* 0.4; *3,* 1.1; *4,* 1.6; *5,* 2.

This conclusion is confirmed by the low values of the pre-exponential factor, which is characteristic of monomolecular reactions that occur *via* the formation of a cyclic activated complex.[8,9] The important role of the nitro group should be mentioned. Due to its electron-withdrawing capability, the nitro group activates the α-H atom, which participates in the formation of the transition state. The decreased value of the pre-exponential factor is also caused to a certain extent by the fact that the polar transition state is more highly solvated than the less polar initial molecule, which results in negative activation entropy. This is confirmed by the fact that the pre-exponential factor in a sulfolan solution is lower than in less polar dimethyl phthalate. It is pertinent to mention that reaction (1) has also been suggested previously[10] as the primary stage for the explanation of the composition of the products of the transformation of BDFA in an aqueous-alcoholic media, where water is an important participant in the process.

It is characteristic that the activation parameters of the thermal decomposition of BDFA and of the corresponding *N*-nitrosoamine, bis(2,2-dinitropropyl)-*N*-nitrosoamine, for which the possibility of decomposition *via* a cyclic transition state is discussed,[2] nearly coincide, which indicates that they have common mechanisms. It is also noteworthy that *N,N*-difluoroamines[11] and *N*-fluoroazoxy compounds[6] related to BDFA can decompose *via* a similar mechanism (although a six-membered activated complex is formed in the latter case), and the kinetics of the decomposition of difluoroamines also depend on the polarity of the medium.

In addition to the mechanism presented above (see Eq. (1)), decomposition according to a pure heterolytic E1 mechanism *via* the splitting of the N—F bond can be assumed (a similar mechanism for difluoroamines has been discussed[11]). We do not rule out this possibility, which, in fact, does not strongly contradict Eq. (1) (the F^- anion formed at the first stage and probably entering into the composition of the ionic pair accepts a proton and is transformed into HF). Nevertheless, we consider the E1 mechanism to be improbable, because it is difficult to assume that the ionic reaction occurs readily in a relatively weak polar medium such as dimethyl phthalate.

Finally, one more class of related compounds, *N*-nitro-*N*-fluoroamines, can also decompose *via* the formation of cyclic activated complexes to yield HF, although the authors of several works[12,13] believe there may be a parallel radical channel. The mechanism of the thermal decomposition of *N*-nitro-*N*-fluoroamines as a whole is complicated and in many respects unclear.[14]

As can be seen from Fig. 1, the decomposition of BDFA in the liquid phase (melt) occurs with pronounced autoacceleration: the maximum reaction rate is 10 to 20 times greater than the initial rate, depending on the temperature of the medium. When BDFA is diluted and dissolved, no autoacceleration is observed and the decomposition kinetics are described by a first-order equation. The data obtained make it possible to conclude that the character of the process is autocatalytic. It should be emphasized that this is the first example of autocatalysis for the thermal decomposition of bis(nitroalkyl)amines.

The mechanism of the autocatalysis is rather complicated and cannot be analyzed in detail at present. Therefore, we restrict ourselves to general ideas. In the simplest case, the kinetics of the autocatalytic reaction are described by the following equation:

$$d\alpha/dt = k_1(1-\alpha)^l + k_2\alpha^m(1-\alpha)^n, \qquad (2)$$

where α is the degree of conversion; k_1 and k_2 are the rate constants of the non-catalytic and catalytic reactions, respectively; *l, m,* and *n* are the corresponding reaction orders. Since the first-order equation is fulfilled in dilute solutions, it can be considered that $l = 1$. It turns out that as the reaction occurs, *i.e.*, as α increases, the specific rate of the process $(d\alpha/dt)\cdot(1-\alpha)^{-1}$ at first increases and then decreases sharply after reaching a maximum. This is possible only in the case when $n \geq 2$ (assuming that *m* and *n* are integers). At the same time, Fig. 1 shows that the inflection point corresponding to the maximum reaction rate is reached at $\alpha \approx 2/3$.

It is easy to show that in order to reach the maximum rate of conversion at $\alpha > 0.5$, the condition $m > n$ must be fulfilled and thus, $m \geq 3$. We were unable to calculate the kinetic data obtained at $l = 1$, $m = 3$, and $n = 2$. This means that either *m* and *n* indeed are still higher or Eq. (2) is not fulfilled at all, which is more probable. In particular, it is likely that not one particle (according to Eq. (2)), but several different autocatalytic particles are involved in the reaction. In fact, the formation of nitrogen oxides is typical of the thermal decomposition of nitrocompounds in the condensed phase. They yield nitrous acid when they are dissolved in an initial substance and react with water (which is also a typical product of the thermal decomposition of nitrocompounds). Apparently, an acidic medium, which is formed in the case of BDFA due not only to nitrous acid, but to hydrofluoric acid as well (see Eq. (1)), causes the autocatalysis of the thermal decomposition. This conclusion is confirmed by the data on the catalytic effect of picric acid on the reaction studied (see Fig. 2). In addition, it has been experimentally confirmed that hydrogen fluoride reacts with difluoroamines even at room temperature.[11] It should also be mentioned that difluoroamines are able to react both with nucleophilic and electrophilic reagents due to their amphoteric nature.[15] Bis(2,2-dinitropropyl)-*N*-nitrosoamine, which is related to BDFA, decomposes without autocatalysis.[2] This also confirms that the fluoroamine group is the reaction center for the acidic catalysis of the decomposition of the BDFA molecule.

When looking at the effect of a base (diphenyldimethyl urea) on the decomposition of BDFA, one should consider the direct reaction of the base with the initial substance rather than the acceleration, because the kinetic law of the reaction changes in the presence of a base (see Fig. 3). This result is expected, because it is known that many nitrocompounds are unstable toward bases. In addition, nucleophilic reagents readily dehydrofluorinate difluoroamines,[15,16] and BDFA should behave in a similar way. Let us also note that the acceleration of the thermal decomposition of difluoroamines under the action of urea and other bases has been observed.[11]

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