Thermal stability of high-energy compounds

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The influence of molecular structure on the stability of high-energy compounds is considered. The kinetic parameters of the decomposition of various energy-rich groups in monofunctional compounds are established. Data on decomposition of compounds with mixed functional groups are described. The sites of primary breakdown are determined and the mutual influence of functional groups on the stability is considered.

Key words: high-energy compounds, thermal decomposition, kinetics, interaction of functional groups.

The extensive experimental data on the stability of explosives accumulated in the literature over the last decades make it possible to consider the stability of high-energy compounds, determined by the kinetics of their thermal decomposition. This review deals primarily with the stability of monofunctional compounds of various classes. Intramolecular interaction of groups and stability of polyfunctional compounds, including compounds with different functional groups, are discussed. Finally, autocatalytic decomposition of compounds with different functional groups and interaction of groups *via* decomposition products are considered.

Stability of monofunctional compounds of various classes

Table 1 presents characteristic parameters for decomposition of monofunctional aliphatic compounds of the RX or RXR type (R = Alk) containing 15 energy-rich X groups. The structure of the alkyl group has only a slight effect on the decomposition rate and, therefore, it could hardly influence the stability of these compounds.

The compounds listed in Table 1 are arranged in the order of decreasing stability at 60 °C. In addition, Table 1 contains data on three heterocycles especially enriched in energy. The data refer to the liquid state of substances. The stabilities of compounds with melting points (m.p.) ≤100 °C can increase 10-fold on passing to the solid phase, and those of compounds with m.p. >150 °C can increase more than 100-fold.

The most stable groups in the aliphatic series are $-C(NO_2)_2-$, $-C(NF_2)_2-$, and $-C(NO_2)_2F$. They decompose upon cleavage of the C—N bonds, which have similar strengths in these fragments.

Secondary nitramine groups, which are considered to be the most efficient for the design of high-density and high-energy compounds, can be divided into two types according to their stability. Compounds with a planar nitramine group are highly stable, whereas those containing a pyramidal nitramine group (hexogen, pentogen[3]) are considered to be stable only in the solid state. The more distorted the planar structure of the nitramine group, the longer and, correspondingly, the weaker the $N-NO_2$ bond.[13]

Among difluoroamines with isolated NF_2 groups, two types of substances with different stabilities can also be distinguished. These compounds decompose apparently *via* ionic dissociation of the N—F bond and the decomposition rate depends substantially on the efficiency of solvation of the intermediate ion pair. Shielding of the reaction site by the branched β-substituent prevents solvation and decreases the rate of decomposition. Therefore, substances with an unshielded NF_2 group are nearly 100 times less stable than structures with a shielded NF_2 group.[6]

The $-N(NO_2)F$ and $-N(NO_2)_2$ groups are relatively unstable. Other functional groups can be relatively stable under particular conditions, especially in solid compounds. Nitrogenous heterocycles, furazan, furoxan, and tetrazole, are fairly stable. According to the orbital symmetry rules, a concerted mechanism for the opening of these rings is allowed; however, most often, concerted reaction is precluded by steric repulsion between substituents. Therefore, a stepwise mechanism of decomposition predominates. If the substituents in a furoxan are H or F atoms or linear (N_3) or planar (NO_2, Ph) groups, which create no steric hindrance, the compound inevitably becomes less stable.[11,12]

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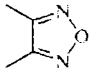
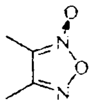
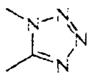
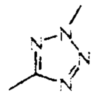
Table 1. Characteristic values of the kinetic parameters of decomposition of groups X in the compounds R—X or R—X—R, where R = Et

Group X	E /kJ mol^{-1}	logA [s^{-1}]	60 °C		150 °C		Ref.
			k/s^{-1}	ω^a	k/s^{-1}	ω^a	
$-C(NF_2)_2-$	199	16.0	$6.9 \cdot 10^{-16}$	1.0	$2.9 \cdot 10^{-9}$	1.0	1
$-C(NO_2)_2F$	199	17.0	$6.9 \cdot 10^{-15}$	10	$2.9 \cdot 10^{-8}$	10	2
$-C(NO_2)_2-$	199	17.1	$8.7 \cdot 10^{-15}$	13	$3.7 \cdot 10^{-8}$	13	2
$-N(NO_2)-$ (planar)	172	14.5	$4.0 \cdot 10^{-13}$	580	$2.1 \cdot 10^{-7}$	72	3
$-ONO_2$	168	14.7	$2.9 \cdot 10^{-12}$	$4.0 \cdot 10^{3}$	$1.0 \cdot 10^{-6}$	$2.4 \cdot 10^{3}$	4
$-CH_2N_3$	163	14.4	$6.4 \cdot 10^{-12}$	$9.0 \cdot 10^{3}$	$1.8 \cdot 10^{-6}$	630	5
$-C(NO_2)_3$	180	17.2	$1.0 \cdot 10^{-11}$	$1.5 \cdot 10^{4}$	$1.0 \cdot 10^{-5}$	$3.4 \cdot 10^{3}$	2
$-NF_2$[b] (shielded)	126	9.0	$2.1 \cdot 10^{-11}$	$3.0 \cdot 10^{4}$	$3.2 \cdot 10^{-7}$	110	6
$-N(NO_2)-$[c] (pyramidal)	159	14.5	$3.7 \cdot 10^{-11}$	$5.0 \cdot 10^{4}$	$7.4 \cdot 10^{-6}$	$2.5 \cdot 10^{3}$	3
$-C(NO_2)_2NF_2$	168	16.0	$5.7 \cdot 10^{-11}$	$8.0 \cdot 10^{4}$	$2.2 \cdot 10^{-5}$	$7.5 \cdot 10^{3}$	7
$-C(NO_2)_2N_3$	163	15.5	$8.0 \cdot 10^{-11}$	$1.0 \cdot 10^{5}$	$2.2 \cdot 10^{-5}$	$8.0 \cdot 10^{3}$	—[e]
$-NF_2$[d] (open)	111	8.3	$1.3 \cdot 10^{-9}$	$2.0 \cdot 10^{6}$	$4.1 \cdot 10^{-6}$	$1.4 \cdot 10^{3}$	6
$-NHNO_2$	111	10.1	$1.3 \cdot 10^{-7}$	$2.0 \cdot 10^{7}$	$2.6 \cdot 10^{-4}$	$1 \cdot 10^{5}$	8
$-N(NO_2)F$	126	15.0	$2.1 \cdot 10^{-5}$	$3.0 \cdot 10^{10}$	0.3	$1 \cdot 10^{9}$	9
$-N(NO_2)_2$	121	15.0	$9.0 \cdot 10^{-5}$	$1.0 \cdot 10^{11}$	1.0	$3 \cdot 10^{8}$	10
	193	14.5	$2.3 \cdot 10^{-16}$	3.0	$6.0 \cdot 10^{-11}$	0.01	11
	188	14.8	$1.7 \cdot 10^{-15}$	2.5	$3.2 \cdot 10^{-9}$	1.1	11
	197	14.9	$1.2 \cdot 10^{-16}$	0.17	$4.2 \cdot 10^{-9}$	1.4	12
	176	15.0	$2.0 \cdot 10^{-13}$	400	$2.6 \cdot 10^{-7}$	70	12

[a] Relative rate. [b] In $F_2NMe_2CCMe_2NF_2$. [c] In 1,3-dinitro-1,3-diazacyclopropane. [d] In $F_2NCH_2(CH_2)_2CH_2NF_2$. [e] Unpublished results of the authors.

Intramolecular interaction of functional groups and stability of compounds with mixed functions

The decomposition of polyfunctional compounds is always accelerated by inductive, mesomeric, or steric interactions between functional groups. Table 2 presents known kinetic data on the decomposition of polyfunctional compounds; these data allow several conclusions to be drawn concerning the interaction of active groups.

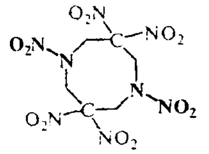
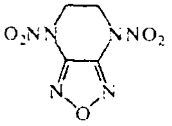
Combination of $-C(NO_2)_3$, $-C(NO_2)_2-$, and $-NO_2$. Molecules of ethane and propane can carry ≤4 nitro groups without losing a level of stability sufficient for practical purposes. For compounds with larger numbers of nitro groups, the energies for bond cleavage D(C—NO$_2$) are less than 155 kJ mol^{-1}. The relatively low values of activation energy together with high values of the preexponential factor ($>10^{17}$ s^{-1}) account for the low stability of these substances. Low stability is also typical of pentane derivatives saturated with nitro groups such as compounds **4** and **5**, in which the γ-NO$_2$ group interacts[2] with the terminal C atom.

A β-nitramine group produces a 6 kJ mol^{-1} decrease in the D(C—NO$_2$) value, while giving a fivefold increase in the rate of decomposition of $C(NO_2)_3$. The presence of a dinitromethyl group has, in its turn, a similar effect on the stability of a nitramine group (compounds **11**—**13**, **16** in Table 2).

Combination of $-N(NO_2)-$ with $-N_3$. A nitramine group in the β-position increases the rate of decomposition of an azide group 40-fold. The activation energy of elimination of N$_2$ from compound **15** is lower than that for monofunctional azides.

The stability of an azide group is apparently highly sensitive to the presence of N atoms in the α-position.

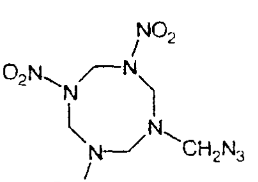
Table 2. Kinetic parameters of decomposition of polyfunctional compounds

Compound[a]	Medium	T/°C	E /kJ mol^{-1}	log(A) [s^{-1}]	k/s^{-1} (150 °C)	ω[b]	Ref.
$\mathrm{FC(NO_2)_2}\mathbf{C(NO_2)_3}$ (**1**)	Melt	88—140	155	17.08	$1.7 \cdot 10^{-2}$	1700	2
$\mathrm{FC(NO_2)_2}\mathbf{C(NO_2)_2F}$ (**2**)	Melt	107—180	177	18.00	$1.6 \cdot 10^{-4}$	7000	2
$\mathrm{FC(NO_2)_2CH_2CH_2C(NO_2)_2F}$ (3)	Melt	150—200	193	16.44	$4.8 \cdot 10^{-8}$	2	14
$[\mathbf{(NO_2)_3C}\mathrm{CH_2]_2CH(NO_2)}$ (**4**)	Melt	120—140	148	15.86	$3.8 \cdot 10^{-3}$	380	14
$[\mathbf{FC(NO_2)_2}\mathrm{CH_2]_2C(NO_2)_2}$ (5)	Melt	130—160	152	16.00	$1.8 \cdot 10^{-3}$	$8 \cdot 10^4$	14
$\mathbf{(NO_2)_3C}\mathrm{CH_2CH_2COOCH_2C(NO_2)_2F}$ (**6**)	Melt	130—193	174	16.75	$2.0 \cdot 10^{-5}$	2	15
$\mathrm{F(NO_2)_2CCH_2CH_2COOCH_2}\mathbf{C(NO_2)_3}$ (7)	Melt	130—193	174	16.47	$1.1 \cdot 10^{-5}$	1	15
$\mathrm{CH_3N(NO_2)CH_2}\mathbf{C(NO_2)_3}$ (**8**)	Melt	130—180	169	16.74	$7.4 \cdot 10^{-5}$	7	16
$[\mathbf{(NO_2)_3C}\mathrm{CH_2]_2N(NO_2)}$ (**9**)	Melt	110—150	154	15.60	$3.8 \cdot 10^{-4}$	38	16
$[\mathbf{(NO_2)_3C}\mathrm{CH_2N(NO_2)CH_2]_2}$ (**10**)	Solution[c]	130—180	170	16.80	$5.9 \cdot 10^{-5}$	6	16
$\mathrm{CH_3}\mathbf{N(NO_2)}\mathrm{CH_2C(NO_2)_2F}$ (**11**)	Solution[c]	175—210	170	14.90	$1.0 \cdot 10^{-6}$	5	16
$\mathrm{[FC(NO_2)_2CH_2]_2}\mathbf{N(NO_2)}$ (**12**)	Solution[c]	160—210	167	14.92	$2.3 \cdot 10^{-6}$	11	16
$\mathrm{[FC(NO_2)_2CH_2}\mathbf{N(NO_2)}\mathrm{CH_2]_2}$ (**13**)	Solution[c]	160—210	168	15.29	$3.3 \cdot 10^{-6}$	16	16
$\mathrm{O_2NN(CH_2CH_2}\mathbf{ONO_2}\mathrm{)_2}$ (**14**)	Melt	150—170	188	18.58	$2.1 \cdot 10^{-5}$	3	17
$\mathbf{N_3}\mathrm{CH_2[N(NO_2)CH_2]_4}\mathbf{N_3}$ (**15**)	Melt	120—180	152	14.59	$7.2 \cdot 10^{-5}$	40	18
 (**16**)	Melt	170—210	162	14.50	$1.5 \cdot 10^{-6}$	7	—[d]
$\mathbf{FC(NO_2)_2}\mathrm{CH_2CH_2C(NF_2)_2Me}$ (**17**)	Melt	150—200	196	16.60	$3.0 \cdot 10^{-8}$	1.3	—[d]
$\mathbf{(NO_2)_3C}\mathrm{CH_2CH_2C(NF_2)_2Me}$ (**18**)	Melt	110—140	181	17.80	$3.0 \cdot 10^{-5}$	3	—[d]
$\mathbf{(NO_2)_3C}\mathrm{CH_2CH_2OOCCH_2CHNF_2CCH_2NF_2}$ (**19**)	Melt	110—140	181	17.90	$3.9 \cdot 10^{-5}$	4	—[d]
 (**20**)	Solid phase	115—130	136	17.30	3.3	10^5	19
$\mathbf{O_2NNHCH_2NHNO_2}$ (**21**)	Melt	110—130	125	12.26	$6.6 \cdot 10^{-4}$	1.8	20
$\mathbf{O_2NNHCH_2CH_2NHNO_2}$ (**22**)	Melt	184—254	127	12.8	$1.2 \cdot 10^{-3}$	3.3	21

[a] The sites of primary decomposition of the molecule are marked by the boldface font. [b] ω is the ratio of the observed rate constant to that predicted using Table 1. [c] Solution in TNT (trinitrotoluene). [d] Unpublished results of the authors.

Upon α-substitution, the heteroatom probably initiates the heterolysis of the C—N_3 bond, which explains the very low stability[2] of compound **23**.

Combination of identical —$\mathbf{ONO_2}$, —$\mathbf{NF_2}$, —$\mathbf{N(NO_2)}$—, or —$\mathbf{NHNO_2}$ groups. When two nitro groups occupy vicinal positions, the stability of each of them diminishes approximately 5 times.[23] The parameters characterizing decomposition of substances with difluoroamine groups in the same arrangement do not change.[6] The same occurs with nitramine groups: when separated by one methylene bridge, they virtually do not influence decomposition of each other. Only in some cyclic structures (hexogen, pentogen[3]), can the nitramine group assume a pyramidal shape due to steric strain and the D(N—NO_2) value decreases.


23

The reactivity of primary nitramine groups separated by one or two methylene bridges (compounds **21** and **22**) remains virtually equal to that found for monofunctional compounds. The stability of primary nitramines in the liquid phase is relatively low. However, polyfunctional compounds, which usually have high melting points,[24] can be fairly stable in the solid state owing to the crystal lattice effect retarding the decomposition.

Combination of —$\mathbf{ONO_2}$ and —$\mathbf{N(NO_2)}$—. A β-nitramine group increases the rate of decomposition of a nitrate group 3—4-fold, *i.e.*, it acts similarly to a neighboring nitro group.

Heterocycles. Furazanyl, furoxanyl, and tetrazolyl fragments are characterized by high degrees of aromaticity. Like phenyl radicals, these groups account for resonance interaction in the molecule. This increases the energy of binding with α-substituents and decreases that for β-substituents. A furazan ring strongly influences the stability of a nitramine group (see Table 2, compound **20**). The combination of steric and electronic effects decreases the D(N—NO_2) value to 134 kJ mol^{-1}.

Interaction of groups *via* decomposition products. Many explosives decompose by an autocatalytic mechanism. Decomposition products act most often as acid or base catalysts. Thus cleavage of nitro esters is catalyzed by nitric acid[25] and picric acid serves as the catalyst in thermal decomposition of tetryl.[26] Hydrogen fluoride catalyzes decomposition of difluoroamines.[6] Polynitroalkanes are highly sensitive to bases. Nitramines and nitro esters are also sensitive to bases, although to a lesser degree. Acids accelerate decomposition of azides.

In the case of compounds with different groups, the products resulting from decomposition of one functional group can influence destruction of the other one. If the system contains an active catalyst, an autocatalytic process can be observed even at an early stage and thus affect the stability of the compound.

In the case of combination of $-ONO_2$ and $-CH_2NF_2$ groups or $-C(NO_2)_3$ and $-ONO_2$ groups, acid and redox autocatalysis of decomposition of the nitro ester fragment is enhanced by the products of decomposition of neighboring groups; this can accelerate destruction of high-energy compounds. Stabilization by weak bases, typical of nitro esters, is impossible due to the high sensitivity of the $-C(NO_2)_3$ and $-CH_2NF_2$ groups to bases. In other cases, it can be suggested that catalysis by decomposition products would not have noticeable influence on the initial steps of decomposition, which determine the substance stability.

The regularities considered here allow rough evaluation of the stability of new compounds based on their structural formula. A discrepancy between the real and predicted stability would point most likely to a new mechanism of decomposition of high-energy compounds.

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References

1. A. V. Fokin, V. N. Grebennikov, G. B. Manelis, and G. M. Nazin, *Dokl. Akad. Nauk*, 1993, **332**, 735 [*Dokl. Chem.*, 1993 (Engl. Transl.)].
2. G. M. Nazin and G. B. Manelis, *Usp. Khim.*, 1994, **63**, 327 [*Russ. Chem. Rev.*, 1994, **63**, 313 (Engl. Transl.)].
3. Yu. M. Burov and G. M. Nazin, *Kinet. Katal.*, 1982, **23**, 12 [*Kinet. Catal.*, 1982, **23** (Engl. Transl.)].
4. B. A. Lur'e and B. S. Svetlov, *Teoriya vzryvchatykh veshchestv* [*Theory of Explosives*], Vysshaya Shkola, Moscow, 1967, 41 (in Russian).
5. G. Geiseler and W. Konig, *Z. Phys. Chem.*, 1964, **227**, 81.
6. V. N. Grebennikov, G. M. Nazin, G. B. Manelis, and A. V. Fokin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 336 [*Russ. Chem. Bull.*, 1994, **43**, 315 (Engl. Transl.)].
7. V. N. Grebennikov, G. M. Nazin, and G. B. Manelis, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 649 [*Russ. Chem. Bull.*, 1995, **44**, 628 (Engl. Transl.)].
8. R. S. Stepanov, A. M. Astakhov, Yu. V. Kekin, and L. A. Kruglyakova, *Izv. Vuzov. Khimiya Khim. Tekhnol.*, 1998, 41, No. 2, p. 35 (in Russian).
9. M. Graff, C. Gotzmer, and J. W. E. McQuiton, *J. Org. Chem.*, 1967, **32**, 3827.
10. B. L. Korsunskii, G. V. Sitonina, B. S. Fedorov, F. I. Dubovitskii, and L. T. Eremenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 790 [*Bull. USSR Acad. Sci., Div. Chem. Sci.*, 1989, **38**, 710 (Engl. Transl.)].
11. V. G. Prokudin, G. M. Nazin, and G. B. Manelis, *Dokl. Akad. Nauk SSSR*, 1980, **255**, 917 [*Dokl. Chem.*, 1980 (Engl. Transl.)].
12. V. G. Prokudin, V. S. Poplavskii, and V. A. Ostrovskii, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2209 [*Russ. Chem. Bull.*, 1996, 45, 2094 (Engl. Transl.)].
13. T. B. Brill and Y. Oyumi, *J. Phys. Chem.*, 1986, **90**, 2679.
14. V. N. Grebennikov, V. G. Prokudin, and G. M. Nazin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2822 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 2596 (Engl. Transl.)].
15. V. G. Matveev, D. A. Nesterenko, and L. T. Eremenko, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2455 [*Russ. Chem. Bull.*, 1998, **47**, 2375 (Engl. Transl.)].
16. B. L. Korsunskii, V. G. Matveev, L. D. Nazina, and G. M. Nazin, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 253 [*Russ. Chem. Bull.*, 1998, **47**, 247 (Engl. Transl.)].
17. F. I. Dubovitskii, Yu. I. Rubtsov, V. V. Barzykin, and G. B. Manelis, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1960, 1126 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1960, No 6, 1049 (Engl. Transl.)].
18. Y. M. Burov and G. M. Nazin, *Proc. 29th Int. Ann. Conf. of ICT*, Karlsruhe, Germany, 1998, 60.
19. D. G. Patil and T. B. Brill, *Thermochim. Acta*, 1994, **235**, 225.
20. R. S. Stepanov, A. M. Astakhov, L. A. Kruglyakova, and Yu. V. Kekin, *Zh. Obshch. Khim.*, 1998, **68**, 810 [*Russ. J. Gen. Chem.*, 1998, **68** (Engl. Transl.)].
21. A. J. B. Robertson, *Trans. Faraday Soc.*, 1948, **44**, 677.
22. T. B. Brill, R. J. Karpowicz, T. M. Haller, and A. L. Rheingold, *J. Phys. Chem.*, 1984, **88**, 4134.
23. A. G. Afanas'ev, B. A. Lur'e, and B. S. Svetlov, *Teoriya vzryvchatykh veshchestv* [*Theory of Explosives*], Vysshaya Shkola, Moscow, 1967, 63 (in Russian).
24. V. P. Ivshin, M. S. Komelin, and V. A. Tartakovskii, *Uspekhi khimii organicheskikh soedinenii azota* [*Advances in the Chemistry of Organic Nitrogen Compounds*], Nauka, St. Petersburg, 1997, p. 29 (in Russian).
25. K. K. Andreev and B. S. Samsonov, *Teoriya vzryvchatykh veshchestv* [*Theory of Explosives*], Vysshaya Shkola, Moscow, 1987, 22 (in Russian).
26. R. C. Farmer, *J. Chem. Soc.*, 1920, **117**, 1603.

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