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The mechanism of thermal decomposition of secondary nitramines

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Abstract. A critical review of the published data on the mechanism of decomposition of secondary nitramines is presented. Based on the data available, it is concluded that the first step of decomposition always includes cleavage of the $N-NO_2$ bond, which is followed by various secondary reactions and sometimes by chain processes. The effects of structures of nitramines on their stabilities are considered. The bibliography includes 113 references.

I. Introduction

Thermal decomposition of secondary nitramines including potent explosives, such as tetryl (*N*-methyl-*N*,2,4,6-tetranitroaniline), hexogen (1,3,5-trinitro-1,3,5-triazacyclohexane), octogen (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane), cyclotetramethylenetetranitramine, hexanitrohexaazaisowurtzitan (CL-20), *etc*.,[1] has been the subject of intensive studies over many decades. In addition to numerous original papers, this topic has been considered in several reviews.[2–8]. Elucidation of the mechanism of decomposition of secondary nitramines is one of the most complicated problems. The diversity of the decomposition products which depends on the reaction conditions suggests the existence of several competing channels of decomposition of secondary nitramines. More than 10 putative mechanisms for the first step of decomposition of hexogen and octogen have been proposed. These include abstraction of the oxygen atom from the nitro group, nitro – nitrite rearrangement, ring expansion and contraction, elimination of HNO_2 and heterolytic and homolytic dissociation of the $N-NO_2$ bond. All these mechanisms, with the exception of the latter, were rejected as being inconsistent with the thermochemical values of the thermal effects of the reactions or contradictory to the theoretical interpretation of the deuterium kinetic isotope effect (DKIE) or based on unreliable experimental data. The use of high-precision methods for kinetic measurements and analysis of the primary reaction products and calculation of the dissociation energy of the $N-NO_2$ bond have made it possible to establish a reliable reaction mechanism. By the late 1980's a definite conclusion could be drawn that the homolytic cleavage of the $N-NO_2$ bond is the only reaction characteristic of the first step of decomposition of secondary nitramines in both the melt and the solid state. This assumption was repetitively put forward in previous studies (see, *e.g.,* Refs 4 and 5). However, some of the results obtained in the study of secondary nitramines in solutions were at variance with a simple homolysis of the $N-NO_2$ bond. Thus the decomposition of hexogen in benzene is characterised by a DKIE of the solvent and in tetrahydrofuran this reaction has a negative activation volume, *i.e*., its rate does not decrease with an increase in the external pressure, which is typical of the bond cleavage, but shows a tendency to increase. It was not until the late 1990's that the decomposition of hexogen in certain solvents was shown to follow the chain mechanism; however, the first step of decomposition always includes the cleavage of the $N-NO_2$ bond.

The main attention in the study of the decomposition mechanism of secondary nitramines is given to three compounds, *viz*., *N*-nitrodimethylamine (dimethylnitramine, DMNA), the first member in the series of aliphatic nitramines and its typical representative, which is especially suitable for the study of the decomposition products; hexogen, a cyclic nitramine with pyramidal nitramine groups; and octogen, a hexogen analogue with planar nitramine groups. The nature of the decomposition products and the isotope effects have been established for these compounds and theoretical calculations of the rates of individual decomposition steps have been carried out. The kinetic parameters (the activation energies and preexponential factors) of decomposition reactions for several dozens of nitramines have been determined.

Analysis of the mechanism of thermal decomposition of nitramines (in the examples of the three aforementioned key compounds) is mainly based on the studies which contain information relevant to elucidation of the mechanism. The kinetic characteristics of initial decomposition steps of all nitramines studied are discussed and the correlation between the reaction rates, the structure of the starting compound and the specific decomposition mechanism is analysed.

We started our consideration of decomposition mechanism with the description of non-catalytic processes reflecting the thermal stabilities of concrete compounds. Other aspects of the decomposition of secondary nitramines, *e.g*., reactions on their combustion, are considered in detail in the review.[8]

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II. The mechanism of thermal decomposition of dimethylnitramine

The first study devoted to the decomposition of DMNA was carried out by Flournoy[9] in 1962. It was found that the decomposition of this compound in vapour at pressures of 0.25–1.0 atm is first order, the reaction rate being independent of the addition of NO. The decomposition products include Me_2NNO (80%), $MeNO_2$, CO_2, CO, H_2O, N_2O, NO and N_2, the extent of decomposition at 165 °C being 1.6%. A comparison of the experimental value of the activation energy E_a (222 ± 21 kJ mol^{-1}) with the energy of the N–N bond cleavage [D(N–N)] calculated on the basis of approximate thermochemical data (230 kJ mol^{-1}) (see Ref. 10) prompted a conclusion that the decomposition of DMNA begins with the cleavage of the N–N bond and proceeds in accordance with the reactions (1)–(3).

$$Me_2NNO_2 \longrightarrow Me_2N^{\bullet} + NO_2, \quad (1)$$

$$NO_2 + Me_2NNO_2 \longrightarrow NO + \text{oxidation products}, \quad (2)$$

$$Me_2N^{\bullet} + NO \longrightarrow Me_2NNO. \quad (3)$$

It is noteworthy that the cited paper[9] does not provide any evidence for a direct reaction of NO_2 with DMNA. In all probability, the reaction (2) is an overall process of formation of light gases upon decomposition of DMNA. A more detailed description of the reaction (2) can be found in Refs 11 and 12. Using a manometric method, Korsounskii *et al.*[11,12] have demonstrated that at initial vapour pressures $p_0 = 0.08-0.5$ atm the reaction proceeds with acceleration by a two-step consecutive pathway. The rate constant for the initial step k_1 does not depend on p_0, while the rate constant for the second step k_2 increases with the increase in p_0. The Arrhenius parameters for k_1 [$E_a = 170.8$ kJ mol^{-1} and $\log A = 14.1$ (s^{-1})] were ascribed to the reaction (1). It was found that the decomposition rate of DMNA increases upon addition of NO_2, however, an increase in the decomposition rate was also observed after addition of formaldehyde which binds NO_2. In the presence of an excess of CH_2O, the decomposition of DMNA is described by a first-order equation; further addition of NO_2 does not influence the reaction rate. Thus, the increase in the reaction rate is limited by a factor of three.

To account for these facts, it was suggested that NO_2 plays a dual role in the decomposition of DMNA, namely, it reacts with nitramine by the reaction (2) and recombines with the radical $Me_2N^{\bullet}$ with regeneration of DMNA, *i.e.,* the reaction (–1) occurs, which is the reverse of the reaction (1).

$$Me_2N^{\bullet} + NO_2 \longrightarrow Me_2NNO_2. \quad (-1)$$

At NO_2 concentrations existing during decomposition of DMNA, the reaction (–1) prevails over the reaction (2). In the presence of CH_2O, the activation energy E_a is equal to 162.8 kJ mol^{-1} and $\log A = 13.7$ (s^{-1}). Probably, in this case the activation energy was determined not very accurately. Thus, the increase in the decomposition rate of DMNA in the presence of CH_2O should be due to an increase in the preexponential factor rather than to a decrease of the activation energy. In addition, it should be kept in mind that the values of $A < 10^{14}$ s^{-1} are not typical of the cleavage of the N–NO_2 bond. A more reliable value of E_a was obtained for pure DMNA, and this was identified with D(N–N).[11]

The decomposition rates and activation energies of other aliphatic and cyclic nitramines (*e.g.*, diethylnitramine, di-n-propylnitramine, nitromorpholine) and dinitropiperazine are similar to those for DMNA. Thermochemical calculations[2] give D(N–N) equal to 193.4 kJ mol^{-1}, which is inconsistent with that determined by a kinetic method; nevertheless, this is used in subsequent studies (see, *e.g.*, Ref. 13). Shaw and Walker[2] estimated D(N–N) in DMNA using the enthalpy of formation of the radical $Me_2N^{\bullet}$ (159 kJ mol^{-1}) calculated for the reaction:

$$Me_2NH \longrightarrow Me_2N^{\bullet} + H^{\bullet}$$

taking D(N–H) equal to 393.5 kJ mol^{-1}.

The last value was obtained in the study of high-vacuum pyrolysis (VLPP) of dimethylamine[14] and appeared to be erroneous. The use of a more precise value of D(N–H) (360 kJ mol^{-1}) and of $\Delta H_f^{\circ}(Me_2N)$ (123.4 kJ mol^{-1}) taken from the reference book[15] yields the magnitude of D(N–NO_2) in DMNA close to 167.5 kJ mol^{-1}.

In more recent studies,[16] the decomposition of DMNA was studied under static conditions at 193–251 °C and in a shock tube at 527–727 °C, the concentration of DMNA being determined by a spectral method. Over the whole temperature range, E_a was equal to 92 kJ mol^{-1}, which can most probably be explained by imperfection in the experimental procedure. Presumably,[16] the formation of Me_2NNO occurred in the reaction (3), whereas NO was formed in the reactions (4) and (5).

$$Me_2N^{\bullet} + NO_2 \longrightarrow 2\,MeNO, \quad (4)$$

$$MeNO \longrightarrow Me^{\bullet} + NO. \quad (5)$$

In 1989, Golden *et al.*,[17,18] who studied the pyrolysis of DMNA by the VLPP method, found the iminoxyl radical Me_2NO and NO among the reaction products. Assuming that these radicals are generated in the primary reaction, the authors proposed a decomposition mechanism for DMNA which involved the nitro–nitrite rearrangement, *i.e.*, an elementary reaction which proceeds *via* the formation of transition state **A**.

$$Me_2NNO_2 \longrightarrow \underset{\mathbf{A}}{(Me_2NONO)^{\neq}} \longrightarrow Me_2NO + NO.$$

However, the next year this conclusion was refuted. The decomposition of DMNA was studied by the multiphoton laser excitation method[13] at 1.3×10^{-7} atm using a CO_2-laser with $\nu = 971.9$ cm^{-1} close to the internal rotation frequency of the CH_3 group in DMNA (987 cm^{-1}). Mass spectrometric studies revealed Me_2NNO, $CH_2{=}NMe$, $CH_2{=}NOH$, NO, NO_2 and Me_2NNMe_2 to be the pyrolysis products. The effect of free radical scavengers, such as Cl_2, NOCl, NO and NO_2, on the composition of the reaction products was studied and the concentration ratios $Me_2NNO : Me_2NNO_2$, $Me_2NCl : Me_2NNO_2$, $CH_2{=}NOH : Me_2NNO_2$ and $NO_2 : Me_2NNO_2$ were determined quantitatively. The addition of Cl_2 and NOCl resulted in the formation of Me_2NCl; the yield of NO_2 increased and the yield of tetramethylhydrazine decreased. The yields of Me_2NNO, $CH_2{=}NOH$, Me_2NNMe_2 and NO_2 increased in the presence of NO. The addition of NO_2 had no effect on the yield of Me_2NNO, but increased the yield of $CH_2{=}NOH$. The addition of DMNA-d_6, which does not absorb the energy of the laser irradiation due to the lack of the resonance frequency and, correspondingly, does not dissociate, resulted in the formation of $(CD_3)_2NNO$ but not $(CD_3)_2NN(CD_3)_2$ or $Me_2NN(CD_3)_2$. The results obtained were rationalised[13] on the basis of occurrence of the following reactions:

$$Me_2NNO_2 \longrightarrow Me_2N^{\bullet} + NO_2, \quad (1)$$

$$Me_2N^{\bullet} + Cl_2 \longrightarrow Me_2NCl + Cl^{\bullet},$$

$$Me_2N^{\bullet} + Me_2NNO_2 \longrightarrow Me_2NO + Me_2NNO, \quad (6)$$

$$Me_2N^{\bullet} + Me_2N^{\bullet} \longrightarrow Me_2NNMe_2, \quad (7)$$

$$Me_2NO \longrightarrow MeNO + Me^{\bullet},$$

$$MeNO \longrightarrow CH_2{=}NOH,$$

$$Me_2N^{\bullet} + NO \longrightarrow Me_2NNO, \quad (3)$$

$$Me_2N^{\bullet} + NO_2 \longrightarrow Me_2NO + NO, \quad (8)$$

$$Me_2N^{\bullet} + NO_2 \longrightarrow Me_2NNO_2. \quad (-1)$$

Thus, it was concluded that the cleavage of the N–N bond is the primary step in the decomposition of DMNA. The reaction of

Table 1. Vibration frequencies of models of transition states for the reactions (1), (9) and (10).[13]

Bond or group	ν (ground state) /cm^{-1}	ν (transition state) /cm^{-1}		
		cleavage of N–N bond	elimination of HONO	rearrangement
C–H	2940(6)		2000	
N–O	1560			
H–C–H	1430(4)		1000	
N–O	1300		1200	1500
N–N	1250	see [a]	690	690
C–N–C	1200	840		
H–C–N	1150(6)	800(6)	800	
C–N	1100(2)		1430	
C–N–N	800(2)	560(2)		600
N–N–O	640(3)	450(3)	830	450
C–N	230(2)	160(2)	460	
N–N	150	50	see [a]	see [a]

[a] Free rotation.

the radical $Me_2N^{\bullet}$ with the starting DMNA (6) was introduced into the scheme of secondary reactions.

The Reiss–Ramsperger–Kassel–Marcus (RRKM) theory was used [13] to calculate the rate constants for the reactions (1), (9) and (10) depending on the internal excitation energy (E^*) of the DMNA molecule in the range of 188–335 kJ mol^{-1}. The vibration frequencies of the models of transition states of these reactions are given in Table 1, the energy characteristics are listed in Table 2.

$$Me_2NNO_2 \xrightarrow{k_{N-N}} Me_2N^{\bullet} + NO_2, \quad (1)$$

$$Me_2NNO_2 \xrightarrow{k_{iso}} Me_2NONO, \quad (9)$$

$$Me_2NNO_2 \xrightarrow{k_{elim}} CH_2{=}NMe + HONO. \quad (10)$$

It was found that $k_{N-N}/k_{iso} = 10^{2.2}\exp(-6.5/RT)$. Hence, at 877 °C where the nitro–nitrite rearrangement was supposed to take place,[18] the contribution of this route does not exceed 10%, which is below the threshold sensitivity of the experiment. The rate constant for the elimination of HONO at $E^* = 188.4$ kJ mol^{-1} was nearly 100 times lower than k_{N-N}.

It was also found [13] that Me_2NH, which is formed in the disproportionation reaction of the radical $Me_2N^{\bullet}$

$$Me_2N^{\bullet} + Me_2N^{\bullet} \longrightarrow Me_2NH + MeN{=}CH_2,$$

undergoes decay on the wall upon interaction with NO_2.

Table 2. Energy characteristics of transition states and kinetic parameters of the reactions (1), (9) and (10).[13]

Parameter	Ground state	Reactions		
		(1)	(9)	(10)
E_z /kJ mol^{-1}	249	220.6	241	245.3
E_0 /kJ mol^{-1}	–	194.6	178	167.4
I^*/I	1	6	1	1.5
ΔH_0 /kJ mol^{-1}	–	194.6	11.7	119.3
log$A$ (s^{-1})	–	15.5	12.7	13.3

Note. E_z is the zero energy of a molecule; E_0 is the critical energy of the reaction; I^*/I is the ratio of the moments of inertia of a molecule in the transition and ground states.

The energy profiles for the cleavage of the N–N bond and other reactions were calculated using the MNDO and MNDO/3 methods. [19] It was shown that the radical $Me_2N^{\bullet}$ readily reacts with NO_2. A mechanism of decomposition of DMNA including the reactions (3)–(5) and (8) *inter alia* has been substantiated.

$$Me_2NNO_2 \longrightarrow Me_2N^{\bullet} + NO_2, \quad (1)$$

$$Me_2N^{\bullet} + NO_2 \longrightarrow Me_2NO + NO, \quad (8)$$

$$Me_2N^{\bullet} + NO_2 \longrightarrow (MeNO)_2 \longrightarrow 2\,MeNO, \quad (4)$$

$$MeNO \longrightarrow Me^{\bullet} + NO, \quad (5)$$

$$Me_2N^{\bullet} + NO \longrightarrow Me_2NNO, \quad (3)$$

$$Me^{\bullet} + NO_2 \longrightarrow MeO^{\bullet} + NO,$$

$$Me^{\bullet} + NO_2 \longrightarrow MeNO_2.$$

Summation of the reactions that have been proved in the experimental and theoretical studies cited above together with well-established oxidation reactions of the radical $Me^{\bullet}$ and methyl nitrite by nitrogen dioxide [20] yields a detailed scheme of decomposition of DMNA in vapour (Scheme 1).

Scheme 1

$$Me_2NNO_2 \longrightarrow Me_2N^{\bullet} + NO_2, \quad (1)$$

$$Me_2N^{\bullet} + NO_2 \longrightarrow Me_2NNO_2, \quad (-1)$$

$$Me_2N^{\bullet} \longrightarrow CH_2{=}NMe + H^{\bullet}, \quad (11)$$

$$Me_2N^{\bullet} + NO_2 \longrightarrow Me_2NO + NO, \quad (8)$$

$$Me_2N^{\bullet} + NO \longrightarrow Me_2NNO, \quad (3)$$

$$Me_2N^{\bullet} + Me_2NNO_2 \longrightarrow Me_2NO + Me_2NNO, \quad (6)$$

$$2\,Me_2N^{\bullet} \longrightarrow Me_2NNMe_2, \quad (7)$$

$$Me_2NO \longrightarrow MeNO + Me^{\bullet},$$

$$MeNO + NO_2 \longrightarrow MeNO_2 + NO,$$

$$MeNO \longrightarrow Me^{\bullet} + NO,$$

$$MeNO \longrightarrow CH_2{=}NOH,$$

$$MeNO + 2\,NO \longrightarrow MeO^{\bullet} + N_2 + NO_2,$$

$$Me^{\bullet} + NO_2 \longrightarrow CH_2O + HNO_2,$$

$$2\,HNO_2 \longrightarrow H_2O + NO + NO_2,$$

$$MeO^{\bullet} + NO_2 \longrightarrow CH_2O + NO,$$

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

In Scheme 1, the reaction (11) is characterised by a relatively high activation energy and may compete with the reactions (3) and (8) at very low pressures. Under normal conditions, the reaction (6) does not occur (otherwise, the inhibiting effect of NO would be apparent); the recombination reaction (7) is also related to secondary processes. Undoubtedly, the oxidation of DMNA by nitrogen dioxide occurs at high pressures of NO_2, the relative ease of oxidation seems to be due to the presence of a trivalent nitrogen atom in the DMNA molecule.

The kinetics of decomposition of DMNA at 240 °C in various solvents was studied at DMNA concentrations ranging from 0.01 mass % to 0.5 mass %. The first-order rate constants $10^4 k$ s^{-1} were determined using a chromatographic method [21] and were found to be equal to 11 (in cyclopentane), 9.3 (in cyclohexane), 9 (in isooctane), 3.2 (in n-butanol), 1.73 (in benzene) and 0.71 [in glycerol triacetate (triacetin)].

The effect of the solvent on the decomposition of DMNA was interpreted [21] in terms of the cage effect, which should have been manifested due to the reversibility of the initial step of dissociation of the N–N bond. Presumably, cleavage of the N–N bond is accompanied by an alternative decomposition route, *viz*., elimination of HONO.

The DKIE value equal to 1.56 observed in the decomposition of DMNA-d_6 in benzene at 240 °C is an argument in favour of a mechanism which involves elimination of HNO_2. However, as follows from the general theory of the kinetic isotope effect,[22] this value is too small for the primary isotope effect, but is rather consistent with the secondary isotope effect due to a decrease in the rocking vibration frequencies of the CH_3 groups in the radical $Me_2N^{\bullet}$ formed upon cleavage of the N–N bond. This conclusion was totally confirmed by calculations of the isotope effects carried out in 1997.[23]

There is additional evidence in favour of the above-mentioned mechanism.[21] The volume of activation ($\Delta V^{\neq}$) of DMNA decomposition in isooctane (227 °C, 2% solution, 10^3-10^4 atm) was equal to 30 $cm^3\ mol^{-1}$. Should elimination of $HONO^{\bullet}$ occurred, the value of $\Delta V^{\neq}$ would be negative. The decomposition of a 1 : 1 $Me_2{}^{14}N{}^{14}NO_2 - Me_2{}^{15}N{}^{15}NO_2$ mixture resulted in total redistribution of the label in the reaction products, such as Me_2NNO, NO and N_2. The decomposition of $Me_2N^{15}NO_2$ in the presence of $^{14}NO_2$ resulted in total redistribution of the label in Me_2NNO as well. It was also found[21] that the $^{15}NO_2$ group in $Me_2N^{15}NO_2$ is partly exchanged for free nitrogen dioxide $^{14}NO_2$. These data altogether clearly demonstrate that Scheme 1 involves the reactions (−1) and (3).

The formation of N_2 upon decomposition of DMNA was rationalised[21] by insertion of oxygen of the nitro group into the C–H bond

$$\begin{array}{l} MeN(CH_2OH)-N=O \longrightarrow MeN(CH_2OH)-N=O \longrightarrow MeN=NOH + CH_2O, \\ MeN=NOH \longrightarrow N_2 + MeOH, \end{array} \qquad (12)$$

or by elimination of HNO_2 with subsequent nitrosation of $MeN=CH_2$.

$$Me_2NNO_2 \longrightarrow MeN=CH_2 + HNO_2 \longrightarrow MeN=NOH + CH_2O.$$

Since neither CH_2O nor MeOH was detected among DMNA decomposition products, the formation of N_2 can be explained by occurrence of the reaction (13), which proceeds with extremely high efficiency despite its trimolecular character.[24]

$$MeNO + 2\,NO \longrightarrow Me^{\bullet} + N_2 + NO_3. \qquad (13)$$

It was assumed[21] that the formation of N_2 and acetone upon decomposition of diisopropylnitramine results from insertion or elimination reactions:

$$2\,(Me_2CH)_2NNO_2 \longrightarrow (Me_2CH)_2NNO + 2\,Me_2CO + N_2 + H_2O.$$

However, in this case, too, these products can be formed in ordinary reactions, since it is known that radicals $Me_2\dot{C}H$ and $Me_2CHO^{\bullet}$ yield acetone in oxidising media.[25]

$$(Me_2CH)_2NNO_2 \longrightarrow (Me_2CH)_2N^{\bullet} + NO_2,$$

$$(Me_2CH)_2N^{\bullet} + NO_2 \longrightarrow Me_2CHNO + Me_2\dot{C}H + NO,$$

$$(Me_2CH)_2N^{\bullet} + NO \longrightarrow (Me_2CH)_2NNO,$$

$$Me_2CHNO + 2\,NO \longrightarrow Me_2\dot{C}H + N_2 + NO_3,$$

$$Me_2\dot{C}H + NO_2 \longrightarrow Me_2CHO^{\bullet} + NO,$$

$$Me_2CHO^{\bullet} + NO_2 \longrightarrow Me_2C=O + HNO_2.$$

Thus, the data available on the secondary decomposition products do not contradict the cleavage of the N–N bond in the first step. It may thus be expected that the decomposition of other aliphatic secondary nitramines will also proceed in a similar fashion ($E_a \approx 170$ kJ mol^{-1}, $A \approx 10^{14.5}\ s^{-1}$) and will yield *N*-nitroso compounds, aldehydes, N_2 and H_2O as the main products.

III. The mechanism of decomposition of hexogen and octogen

Decomposition of hexogen and octogen follows the same regularities; therefore, these reactions are often studied simultaneously. The differences in the spatial structures of the nitramine groups[26] of these compounds affect only the initial rates, but not the reaction mechanism.

The first study of thermolysis of hexogen melts was carried out in 1944 (for a review, see Ref. 8). The presence of nitrogen dioxide in the decomposition products suggested that the initial step involved the cleavage of the $N-NO_2$ bond.

More detailed studies on the decomposition kinetics of hexogen and octogen were carried out in 1948–1949.[27,28] The decomposition rates of hexogen were measured in the gas phase, melts and solutions in dicyclohexyl phthalate and 2,4,6-trinitrotoluene. The decomposition of octogen was studied both in vapour and in the solid state. The decomposition products contained large amounts of CH_2O and H_2O as well as N_2, N_2O, NO, CO and H_2. Tables 3 and 4 illustrate quantitative data on the

Table 3. Yields of hexogen decomposition products (mol).[4]

Products	Product yields at different temperatures (°C)										
	195 (5)[a]	195 (9)[a]	195 (92)[a]	206	212 (19)[a]	212 (93)[a]	225	267	300	600	800
N_2	0.83	0.65	1.26	1.00	1.08	0.99	1.16	1.03	0.72	0.66	0.60
N_2O	1.4	0.92	1.08	0.95	1.22	1.36	0.98	0.76	0.66	0.60	0.57
NO	0.86	1.30	0.509	0.98	0.23	0.45	0.54	0.75	2.27	2.70	–
H_2CO	1.1	1.2	1.04	traces	traces	0.97	traces	traces	0.33	–	–
CO	0.20	0.16	0.359	0.76	0.41	0.52	0.40	0.29	0.18	0.93	0.90
CO_2	0.50	0.30	0.698	0.89	0.54	0.61	0.48	0.44	0.12	0.18	0.15
HCN	traces	traces	traces	–	0.23	0.03	–	–	0.18	1.32	1.38
NO_2	–	–	–	–	traces	traces	–	–	–	–	–
NH_3	0.83	0.69	0.342	–	–	–	–	–	–	–	–
HCO_2H	0.93	0.60	0.367	–	–	–	–	–	–	–	–
NO_3^-	traces	0.29	0.095	–	–	–	–	–	–	–	–
NO_2^-	traces	traces	0.023	–	–	–	–	–	–	–	–
H_2O	traces	traces	traces	traces	traces	0.97	traces	traces	–	–	–
H_2	–	–	–	–	–	–	0.09	0.06	–	–	–
$HOCH_2NHCHO$	traces	traces	traces	–	–	–	–	–	–	–	–

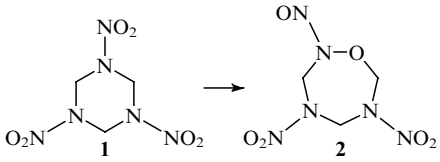
[a] The extent of decomposition of hexogen is given in parentheses (%).

decomposition products of hexogen and octogen [27–32] which are summarised in the review.[4] Later, minor decomposition products (H_2NCHO, $MeNHCHO$, Me_2NCHO, Me_2NNO, Me_2NNO_2) were identified.[33] The reliability of the results obtained [33] is doubtful due to ambiguity of the interpretation of mass-spectrometric data. Therefore, it is the products formed in high molar yields (CH_2O, N_2O, N_2, NO, CO, CO_2, HCN and H_2O) that can serve as the basis for an analysis of the decomposition mechanism. The non-volatile residue † of the polyamide type was also taken into consideration; its yield depended on the experimental conditions and could reach 10%.[33]

Table 4. Yields of octogen decomposition products (mol).[4]

Products	Yields at different temperatures (°C)							
	226	226	258	280	285	300	600	800
N_2	0.19	0.47	0.47	1.16	0.93	0.80	1.00	0.88
N_2O	1.56	2.52	2.57	1.51	1.60	1.72	1.00	0.68
NO	0.24	0.42	0.55	0.95	1.20	2.40	2.80	–
CH_2O	2.71	1.26	0.47	traces	0.86	1.44	0.16	–
CO	0.19	0.40	0.47	0.57	0.42	0.24	1.44	1.28
CO_2	0.30	0.56	0.54	0.64	0.30	0.16	0.24	0.20
HCN	0.02	0.02	0.07	–	0.52	0.48	1.60	1.84
NO_2	–	–	–	–	–	–	–	–
NH_3	–	–	–	–	–	–	0.12	–
H_2O	–	–	–	traces	–	–	–	–
H_2	traces	traces	traces	–	–	–	–	–
$(CN)_2$	traces	traces	traces	–	–	–	–	–

According to Robertson,[28] the major reaction products, *viz*., CH_2O and N_2O, are formed due to transfer of an oxygen atom from the nitro group of hexogen (**1**) to the neighbouring CH_2 group. The ring expansion product, *viz*., compound **2**, undergoes decomposition to give CH_2O and N_2O.

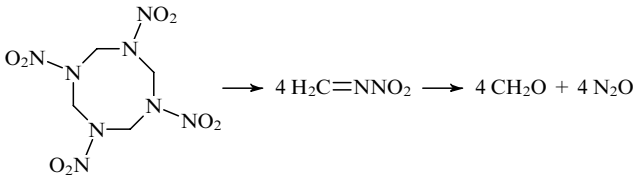


A typical methodological error has been made in the study [28] where the products of secondary reactions were ascribed to the first reaction step.[29]

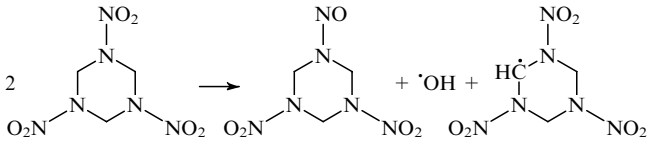
Studies of the solid-phase and solution (*m*-dinitrobenzene) decomposition of hexogen and octogen revealed a weak concentration dependence of the reaction rate.[34] The experimental values of activation energies coincided with those obtained by Robertson.[28] Cleavage of the N–NO_2 bond was postulated as the initial step of the reaction on the basis of approximate thermochemical estimates of D(N–N) in hydrazine derivatives.[35]

Valuable information for the interpretation of the mechanism was obtained using a tracer method.[30] Studies of the decomposition of octogen with a ^{15}N-labelled nitro group and a ^{14}N-labelled amino group revealed formation of $^{14}N^{15}NO$, $^{14}N^{15}N$, ^{15}NO and $HC^{14}N$ exclusively. The formation of products with such distribution of the label may occur by various routes, but cleavage of the C–N bond (rather than of the N–N bond) was thought to be predominant and a fragmentation mechanism with simultaneous cleavage of four C–N bonds was postulated.[30]

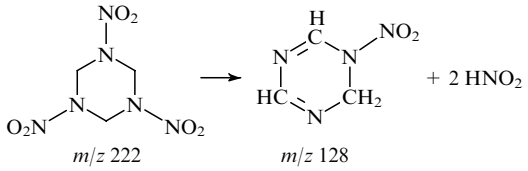
† The term 'non-volatile residue' was introduced [33] for the description of condensation products of the polyamide type which are always formed in small amounts upon decomposition of hexogen and octogen.



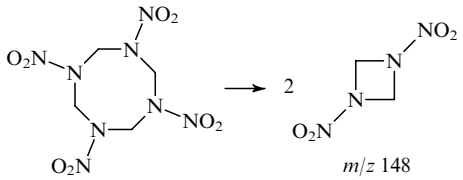
An X-ray diffraction analysis carried out in 1971 revealed [36] the existence of a very tight contact (smaller than the sum of the van der Waals radii of O and H atoms) between a nitro group of one hexogen molecule and a hydrogen atom of the other molecule. Based on these data, a bimolecular reaction was proposed which included direct interaction of two hexogen molecules. However, this hypothesis is untenable due to high endothermicity of this process.



The decomposition of hexogen and octogen was studied using mass spectrometric methods. Thus the decomposition of hexogen vapour in a flow reactor at 240–290 °C resulted in the appearance of species with m/z 128. This has made it possible to propose a mechanism for fast cleavage of two HONO molecules (for a review, see Ref. 8).



The decomposition of hexogen and octogen in vacuum (10^{-3}–10^{-5} atm) afforded species with m/z 148.[37,38] It was thus assumed that the decomposition of octogen involves opening and contraction of the ring and elimination of HNO_2.[38]



However, in these studies the vapours of the starting compounds and their decomposition products were not separated and their inlet into the chamber of the mass spectrometer occurred simultaneously. As a result, the ions generated upon fragmentation of the hexogen or octogen molecules under the electron impact might be mistaken for thermolysis products.

A significant contribution to the study of decomposition mechanisms of octogen was made in 1977 [2] when all the mechanisms postulated so far (with the exception of the cleavage of NO_2 and elimination of HNO_2 *via* a five-membered transition state) were abandoned based on the results of thermochemical estimates of thermal effects for different reactions. The equation for the calculation of the cleavage rate of the N–N bond appears as:

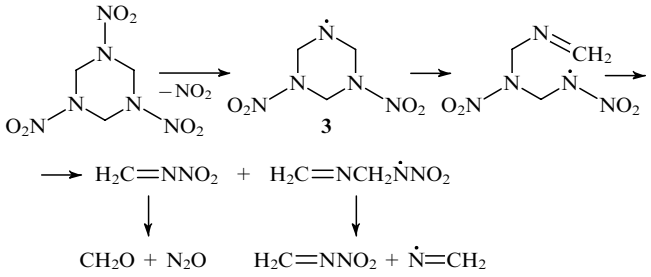
$$\log k_{N-N} = 16.4 - \frac{46\,200}{2.3\,RT}\ s^{-1},$$

and that for the elimination of HNO_2 as:

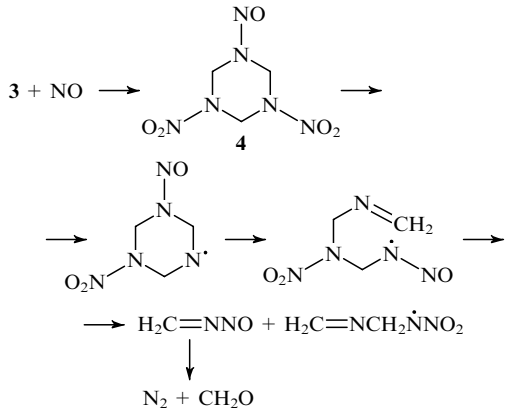
$$\log k_{elim} = 10.8 - \frac{38\,000}{2.3\,RT}\ s^{-1}.$$

It was found that a change in the decomposition mechanism occurred at 333 K.

A remarkably detailed analysis of the decomposition mechanism of hexogen and octogen was made by Schroeder [3,4] who has explained the formation of the major products by secondary reactions following cleavage of the $N-NO_2$ bond.[4]



This scheme was supplemented by an entrapment of the radical **3** by nitrogen oxide and dissociation of the $N-NO_2$ bond in nitroso derivative of RDX **4** formed.



EPR studies have shown [39] that pyrolysis products of hexogen at 260 °C contain large amounts of NO_2 and $H_2C=N^{\bullet}$ radicals, which is a direct proof of the Schroeder scheme.[4]

However, Schroeder noted that it is the elimination of HNO_2, rather than the abstraction of NO_2 that prevails in the gas phase at low temperatures. This statement was made on the basis of the rather low activation energy obtained for the decomposition of hexogen vapour ($\sim$ 125 kJ mol^{-1}). In our opinion, the data available are contradictory and the use of the activation energy measured with a large error is unreliable for an adequate explanation of the mechanism.

The kinetic isotope effect in the decomposition of HMX-d_8 in the solid phase was measured.[40] It was found that the ratio of the rate constants for normal and labelled HMX (k_H/k_d) was equal to 2 in the induction period and to 0.8 and 1.0 in the acceleration and deceleration steps, respectively. These measurements were performed using differential thermal analysis; therefore, it was correctly noted that the data obtained were more relevant to the overall process rather than to its first elementary step, particularly to heat liberation reactions.[23] For example, the products of oxidation of formaldehyde by nitrogen dioxide were often found in early decomposition steps of octogen.[5,7,8]

The formal kinetic regularities of decomposition of hexogen and octogen in the solid phase and the effects of gaseous decomposition products on the reaction rates have been studied.[36,41–44] It was found that the solid-phase reaction is complicated by several factors, *e.g.*, evaporation of the sample and fast reaction occurring in the gas phase, melting of the sample on the decomposition products, autocatalysis and a cage effect. Thus, the decomposition rate depends on the degree of filling of the reaction vessel with the substance, pressure of extraneous gases, mass and even the shape of the sample. Some products, *e.g.*, N_2, CO and CO_2, inhibit the decomposition by preventing the evaporation of the substance and, as a consequence, the course of the gas-phase process. The addition of NO_2 and O_2 produces an even stronger effect, most probably due to reversibility of the first step of decomposition.

The rate and activation energy measured in the decomposition of solid samples do not fit into the mechanism of monomolecular radical cleavage of the N–N bond, since this reaction is superimposed by numerous secondary processes. All these side factors were taken into consideration and the lowest values of the rate constant were obtained in the solid phase (k_{solid}).[26]

Significant progress has been made in the past decade in the development of highly sensitive dynamic methods for monitoring the decomposition of hexogen and octogen. One of them, *viz.*, FT-IR spectroscopy, was used for monitoring the decomposition of solid hexogen and octogen in a nitrogen atmosphere at heating rates up to 200 K s^{-1} (see Refs 45 and 46). The main reaction products are NO_2, N_2O, CH_2O and HCN. The concentrations of NO_2 and CH_2O decrease with time, while that of NO increases, which suggests that formaldehyde is oxidised by nitrogen dioxide. These results fit well into the Schroeder scheme.[4]

A procedure for studying the primary step in the decomposition of hexogen in the solid phase has been developed.[47,48] A thin film of the sample is placed onto a massive support and irradiated *in vacuo* by short (35 μs) pulses of a CO_2 laser at 77 K. This leads to instantaneous heating of the support to 1200 K and cooling to 400 K within 3×10^{-3} s. The decomposition products were analysed by IR spectroscopy directly in the solid phase which remained after partial evaporation of the sample. The dimer N_2O_4 was identified as the only primary decomposition product. Further analysis based on the use of the tracer method revealed that NO_2 molecules forming the dimer originate from different hexogen molecules, *i.e.*, one hexogen molecule always yields only one NO_2 species. This can be regarded as a direct proof that the cleavage of the $N-NO_2$ bond is the only initial step in the decomposition of solid hexogen.

A more complicated situation was observed when the decomposition of hexogen was studied in solutions. An analysis of hexogen and its decomposition products in benzene and benzene-d_6 by liquid chromatography quite unexpectedly revealed [49] that the rate of this reaction is higher in solutions than in the melts. A kinetic isotope effect of the solvent was observed at 180 °C (k_H/k_d = 1.6). This was accounted for by a direct reaction of hexogen with a solvent:

$$>NNO_2 + RH \longrightarrow ROH + >NNO.$$

Actually, this reaction is hardly possible, since its endothermic thermal effect is no less than 250 kJ mol^{-1}, while the activation energy of hexogen decomposition does not exceed 170 kJ mol^{-1}. Besides, these data were not confirmed experimentally in further studies.[50] However, the possibility of the interaction of hexogen with solvents first postulated in 1985 [49] was corroborated by an analysis of their effects on the decomposition rate constant. The results of early studies suggest that such solvents as dicyclohexyl phthalate and *m*-dinitrobenzene are inert in the decomposition of hexogen.[28,34] However, subsequent studies have shown that the reaction rates strongly depend on the nature of the solvent in dilute solutions (Table 5).

It was found [52] that the decomposition of hexogen in THF has a negative activation volume ($\Delta V^{\neq} = -11$ cm^3 mol^{-1}). Thus, it was suggested that it is the elimination of HNO_2, rather than the homolytic cleavage of the N–N bond that is predominant in polar solvents. In this case, the transition state is polar and stabilised by the solvent. No additional evidence was given in favour of this pathway that was rejected earlier in the studies of DMNA decomposition in polar solvents and decomposition of hexogen in the melts and the solid state. As for elimination of HNO_2, it does not provide any adequate explanation for the fact that some hexogen analogues including octogen are characterised

Table 5. Effect of the solvent on the decomposition rate of hexogen at 180 °C.

Solvent	$10^4 k$ /s^{-1}	Ref.
Melt	0.43	28
Benzene	0.40	50
m-Dinitrobenzene	0.17	34
Dicyclohexyl phthalate	0.25	28
Trotyl	0.56	28
	1.32	51
Acetone	0.92	50
Benzophenone	1.95	51

by positive values of activation volumes in the decomposition in more polar solvents, *e.g.,* acetonitrile.[52]

The decomposition of 0.05% solutions of hexogen in benzene, acetone and isooctane was studied using a chromatographic method.[50] In this study, mononitrosohexogen, the yield of which in solution exceeded severalfold that in the melt, was identified as an intermediate product. This fact did not receive any adequate interpretation either, although it is evident that the solvent does influence the yields of nitroso derivative of RDX in one way or another. Unfortunately, the range of solvents used for the study of hexogen decomposition by chromatographic methods could not be expanded.

Clues to the problems related to decomposition of hexogen in solutions were obtained through the use of a highly efficient manometric technique which permits one to measure pressures up to 100 atm directly in glass reaction vessels.[53–55] The rate constants for the decomposition of hexogen at 180 °C were measured systematically in various solvents differing in their structures and properties. These studies included the measurements of DKIE of the solvents and an analysis of the effects of chain reaction inhibitors on the decomposition rate. The main results of these studies are summarised in Table 6.

The solvents from 1,2,4-trichlorobenzene to acetonitrile (Table 6) are inert with respect to hexogen, at least they do not cause any appreciable increase in the decomposition rate in comparison with the melt. This group includes structurally diverse compounds, *e.g.*, aliphatic and aromatic hydrocarbons, fluorinated alkanes, chloro- and nitro-derivatives of benzene. In benzene, naphthalene, isooctane and acetonitrile, the decomposition rates are similar within the limits of the experimental error and exceed only slightly that in the melt. However, in other solvents of this group they are lower than in the melt, which can be attributed to the cage effect characteristic of viscous media. A similar effect was observed for DMNA,[21] the first decomposition step for which, *viz*., the cleavage of the N—N bond, is reversible.

Acetonitrile and nitrobenzene manifest the highest values of dielectric permeability in comparison with other solvents, naphthalene being the most potent π-donor. However, all these compounds are inert with respect to hexogen. As a consequence, such

Table 6. Decomposition rate constants (k_1) of 1% solutions of hexogen in different solvents at 180 °C.[55]

Solvent	$10^4 k$ /s^{-1}	$k_1/k_{\text{isooctane}}$	Solvent	$10^4 k$ /s^{-1}	$k_1/k_{\text{isooctane}}$
Melt	0.43	0.86	Toluene	1.25	2.50
1,2,4-Trichlorobenzene	0.13	0.26	Toluene + NO (∼4 atm)	0.19	0.38
m-Dinitrobenzene	0.17	0.34	Toluene-d_3	0.33	0.66
$C_{12}F_{26}$	0.21	0.42	Toluene + NO_2	0.45	0.90
Nitrobenzene	0.23	0.46	Toluene + 1.54% DNB	0.76	1.52
Dicyclohexyl phthalate	0.25	0.50	Toluene + 0.6% $(CH_2O)_3$	1.31	2.62
Ph_3CH	0.26	0.52	Toluene + 1.44% I_2	2.55	5.10
Triacetin	0.32	0.64	Ionol	1.27	2.54
Biphenyl	0.38	0.76	Cyclohexanol	1.95	3.90
Naphthalene	0.48	0.96	Ethyl acetate	2.03	4.06
Isooctane	0.50	1.00	Phenol	2.03	4.06
Benzene	0.55	1.10	Phenol-d_6	1.60	3.20
	0.39	0.78	$CHCl_3$	2.04	4.08
	0.54 [a]	1.08	$CDCl_3$	1.41	2.82
	0.53 [b]	1.06	*m*-Xylene	2.67	5.34
Benzene + 4.4% I_2	0.54	1.08	*m*-Xylene + NO_2 (∼ 4 atm)	0.27	0.54
Benzene + 1.3% DNB [c]	0.55	1.10	*m*-Xylene-d_{10}	0.48	0.96
Benzene-d_6	0.58	1.16	THF	2.93	5.86
Benzene + 1% $(CH_2O)_3$	0.65	1.30	*p*-Xylene	2.96	6.92
Benzene + NO (4 atm)	0.69	1.38	*p*-Xylene + NO (∼ 4 atm)	1.52	3.04
Acetonitrile	0.63	1.26	*p*-Xylene + 0.78% DNB	1.96	3.92
Acetonitrile-d_3	0.73	1.46	*p*-Xylene + 1.5% I_2	2.57	5.14
Acetone	0.72	1.44	Butane-1,4-diol	3.59	7.18
	0.93	1.86		3.40 [d]	6.80
Acetone-d_6	0.28	0.56		3.48 [e]	6.96
Acetone + THF (1 : 1)	2.46	4.92	MeCH(OH)Me	4.32	8.64
Trinitrobenzene	0.74	1.48	$CD_3CD(OD)CD_3$	1.18	2.36
Diphenylmethane	0.79	1.58	Triethylene glycol	4.81	9.62
o-Dinitrobenzene	0.82	1.64	PhCHO	5.07	10.14
Trinitrotoluene	0.86	1.72	Glycerol	5.55	11.10
tert-Butylbenzene	0.95	1.90	Glycerol + NO_2	1.20	2.40
$PhCH_2OH$	0.96	1.92	Glycerol + NO	3.61	7.22
Cumene	1.18	2.36	Glycerol + 0.6% $(CH_2O)_3$	5.67	11.34

[a] Concentration of hexogen, 0.8 mass %. [b] Concentration of hexogen, 0.44 mass %. [c] DNB, 1,4-dinitrosobenzene. [d] Concentration of hexogen, 3 mass %. [e] Concentration of hexogen, 0.3 mass %.

factors as polarity or tendency of a solvent to form charge-transfer complexes do not influence the decomposition rate of hexogen.

The second group includes solvents where decomposition occurs at higher rates in comparison with the melt. This group includes alkylaromatic hydrocarbons, alcohols, ketones, aldehydes, chloroform and some other compounds. Their common property is the presence of labile hydrogen atoms, *i.e.*, unstable C–H bonds (in the case of non-polar compounds, *e.g.*, toluene) or relatively stable, but polarised and therefore highly reactive C–H bonds as, *e.g.*, chloroform and alcohols. These solvents always manifest DKIE, which suggests involvement of the cleavage of the C–H bond.

The curve for the dependence of the decomposition rate constant of hexogen (k_1) on the bond dissociation energy D(C–H) of the solvent has a maximum. The data on D(C–H) are scarce; therefore, a regularity can be established only approximately using the D(C–H) values (in kJ mol^{-1}) as reference points for the following solvents: aliphatic hydrocarbons, toluene (356), *m*-xylene (325), *p*-xylene (322), diphenylmethane (262) and triphenylmethane ($\sim$ 255).[15] The rate constants measured in aliphatic hydrocarbons, *e.g.*, isooctane, are nearly the same as in the melt. In toluene, this increases threefold, whereas in *m*- and *p*-xylene the difference between k_1 values in the melt and in solution is as high as five- to sevenfold. For diphenylmethane, the k_1 value is higher than for benzene, but lower than for xylenes and even for toluene. Triphenylmethane inhibits the decomposition. The solvents containing polar C–H bonds ($CHCl_3$, alcohols) strongly affect reaction rates at D(C–H) > 360 kJ mol^{-1}.

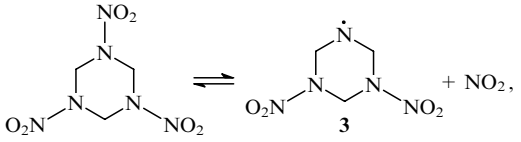
At 180 °C, the maximum increment in k_1 (11-fold when compared with the melt) is observed for glycerol. With a decrease in temperature, the difference between k_1 values in the melt and in solution is expected to increase due to lower activation energy in solutions. The activation energy E_a in inert benzene is equal to 169 and in toluene and butane-1,4-diol it is equal to 158 and 135 kJ mol^{-1}, respectively.

The decomposition products of hexogen in the gas phase contain N_2, N_2O, CO, CO_2, trace amounts of NO and small amounts of formaldehyde and water. Lower molar yields of gaseous products with a decrease in the concentration of hexogen is characteristic of decomposition in solutions. In the melt, the total yield of gaseous products is about 5 mol per mol of hexogen, whereas in 0.5% solution in benzene it is as low as 0.5 mol. It was found that the decomposition of 1% hexogen in toluene affords benzaldehyde, benzonitrile and benzyl alcohol in 0.43, 0.32 and 0.43 mol yields per mol of hexogen, respectively. Phenylnitromethane and benzoic acid are also present in small amounts. These findings provide supporting evidence for the involvement of the solvent in the reaction.

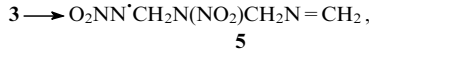
The DKIE was observed in all solvents that accelerate the decomposition, and typical inhibitors of chain reactions (*e.g.*, NO, NO_2, *p*-dinitrosobenzene) bring the rate constant down to a level characteristic of inert solvents. These data altogether led to a hypothesis [53] on a chain decomposition mechanism of hexogen in solvents containing reactive C–H bonds and a monomolecular mechanism for this decomposition in inert media. Detailed kinetic schemes for both mechanisms were developed and rationalised; it was shown that they are consistent with the experimental data.[53, 55]

An example of a non-chain decomposition mechanism of hexogen in solutions is given in Scheme 2.

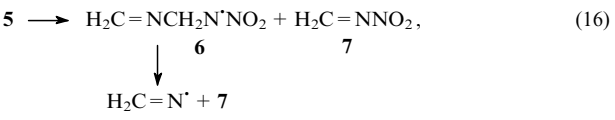
Scheme 2



(14)



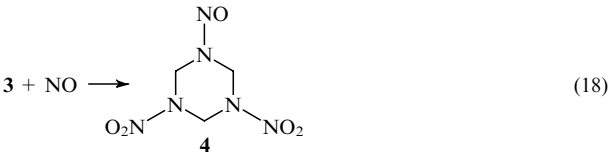
(15)



(16)

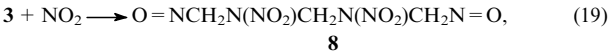


(17)

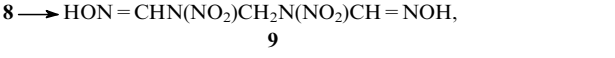


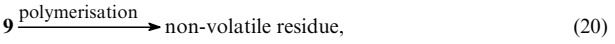
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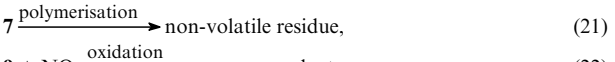


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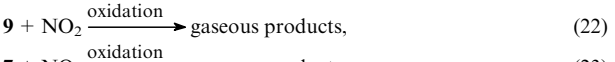




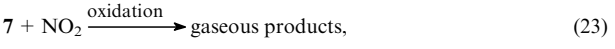
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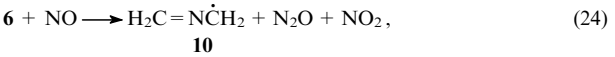
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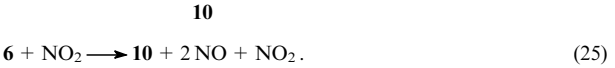
(22)



(23)



(24)



(25)

The reactions (14)–(18) reproduce the basic decomposition mechanism proposed by Schroeder.[4] Other reactions are common to the reactions of NO and NO_2 with free radicals of the C- and N-types as well as for polymerisation and oxidation of unsaturated compounds, isomerisation of nitroso compounds and some other reactions.

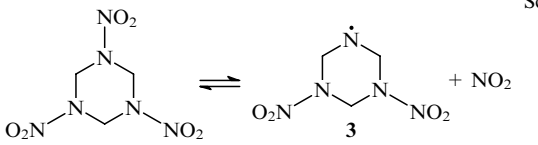
The decomposition begins with the dissociation of the N–N bond [reaction (14)]. Like any other dissociation of a molecule into radicals, this reaction is reversible and a cage effect can be observed in viscous media. The radical **3** undergoes isomerisation into the radical **5** which is then decomposed by the reaction (16) to yield an inactive radical $CH_2=N^{\cdot}$. The radical **3** reacts also with NO and NO_2. The reversible formation of mononitroso derivative of RDX **4** proceeds *via* the reaction (18). In contrast to unsubstituted aliphatic *N*-nitroso compounds, which are more stable than the corresponding secondary nitramines,[56, 57] nitroso compounds containing electronegative substituents (including diazacyclohexane derivatives) are less stable [58, 59] than their nitramine analogues. Compound **4** is formed as an intermediate product; its decomposition occurs 10 times faster than that of hexogen.[52] According to a theoretically rationalised mechanism of the reaction of aminyl radicals with NO_2 (see Ref. 60), the reaction (19) of the radical **3** with NO_2 should result in ring opening and the formation of a highly reactive dinitroso compound **8** and then of dioxime **9**. Polymerisation with the formation of a non-volatile residue [reaction (20)] is the most probable route to the conversion of the oxime **9**. Polymerisation of the unsaturated compound **7** [reaction (21)], which competes with its decomposition [reaction (17)], is yet another source of a non-volatile residue. Like nitroethylene, compound **7** is stable but prone to polymerisation. In the presence of NO_2, the unsaturated compounds **9** and **7** are easily oxidised to form gaseous products. It is noteworthy that the reactions (14) and (15) occur only with the radicals **3** and **5** containing a labile (75 kJ mol^{-1}) H_2C-NNO_2 bond in the β-position relative to the free valence.[61] The radical **6** contains no such bond.

The yield of N_2O is 1–1.5 molecules per molecule of hexogen rather than 2 as should follow from Scheme 2.[3] It is possible that the dissociation of the radical **6** into $CH_2=N^{\cdot}$ and compound **7** does not take place at all (the probability of such reaction in the

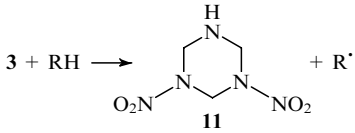
gas phase was first put in doubt [33]). Instead, the nitraminyl radical **6** is converted into the radical **10** in the presence of nitrogen oxides in the reactions (24) and (25).[62] The latter radical is easily oxidised to yield $HOCH_2NHCHO$, one of the decomposition products of hexogen,[3] and gaseous compounds.

The concentration of nitrogen dioxide in a solution depends on the partial pressure in the gas phase much more strongly than the concentration of NO. Therefore, the ratio of the rates of the reactions (19) and (18) will decrease with hexogen concentration, all other conditions being the same. The yield of the intermediate nitroso derivative **4** will increase correspondingly (*cf.* Refs 49 and 50). Similarly, the polymerisation reactions (20) and (21) will occur faster than the oxidation reactions (22) and (23) due to a sharp decrease in NO_2 concentration in very dilute solutions. This accounts for a significant decrease in the yields of gaseous products and an increase in the yield of the non-volatile residue at hexogen concentrations < 5%. Chain decomposition of hexogen in solution (RH is the solvent) is presented in Scheme 3.[55]

Scheme 3



(14)



(26)

$$NO_2 + RH \longrightarrow HNO_2 + R^{\bullet}, \quad (27)$$

$$R^{\bullet} + \mathbf{1} \longrightarrow \mathbf{4} + RO^{\bullet}, \quad (28)$$

$$RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet},$$

$$\mathbf{4} \longrightarrow \mathbf{3} + NO,$$

$$R^{\bullet} + NO_2 \longrightarrow RO^{\bullet} + NO,$$

$$RO^{\bullet} + NO_2 \longrightarrow R'CHO + HNO_2,$$

$$R^{\bullet} + NO_2 \longrightarrow RNO_2,$$

$$R^{\bullet} + NO \longrightarrow RNO \longrightarrow R'CH{=}NOH \longrightarrow R'CN + H_2O,$$

$$RNO + 2\,NO \longrightarrow RO^{\bullet} + N_2 + NO_2.$$

R′ is R containing one CH_2 unit less.

The chain reaction begins with the reactions of the free radical **3** and NO_2, which are generated in the first step of decomposition, with the solvent [reactions (26) and (27)]. The reaction (26) is preferable, since it is more exothermic than the reaction (27) by nearly 40 kJ mol^{-1}. As a source of free radicals, the latter reaction can be neglected, since the addition of NO_2 decelerates rather than accelerates the process.

By virtue of the reaction (26) free radicals are not extinguished, and N-centred radicals inactive with respect to the nitro group are converted into C-centred radicals of the solvent. The isotope effect of the solvent is manifested in this step. The maximum rate of the reaction of the radical **3** with the solvent [reaction (26)] is reached at those $D(C-H)$ values which enable the competition of the reaction with the rearrangement of the radical **3** [reaction (15)]. For non-polar solvents, this value is equal to 360 kJ mol^{-1}. In solvents containing polar C–H bonds adjacent to heteroatoms (chloroform, alcohols), the reaction (26) proceeds at a sufficiently high rate even at $D(C-H) >$ 360 kJ mol^{-1}. The reaction (28) occurs only in the solvents in which the radical $R^{\bullet}$ retains its activity and the chain propagates. A combination of the reactions (26) and (28) results in the appearance of an extremum on the experimental curve for the dependence of k_1 on $D(C-H)$.

Extinction of the radicals $R^{\bullet}$ occurs in their reactions with NO_2 and NO, these are consumed in the reaction (28) with hexogen. The reaction of the radical $R^{\bullet}$ with hexogen occurs only where the concentration of the inhibitor (NO, NO_2, *etc.*) is four orders of magnitude lower than that of hexogen. This condition is usually fulfilled, since NO is poorly soluble in the liquid phase where other non-volatile inhibitors are virtually absent.

The rates of bimolecular reactions of the chain generation and propagation [reactions (26) and (28)] increase with pressure; therefore, the stability of hexogen in non-inert solvents will decrease at high pressures used for the determination of the activation volume. Hence, the negative activation volume of decomposition of hexogen in THF, one of the most active solvents,[52] can easily be explained. Many structural analogues of hexogen, *e.g.*, trinitrosohexogen and 1,3,3,5,5-pentanitropiperazine, are also characterised by negative activation volumes in THF.[52] Other hexogen analogues, including octogen, that were studied in acetonitrile (but not in THF), which was inert in this concrete case,[55] have positive activation volumes.

Despite their obvious incompleteness, the schemes of monomolecular (see Scheme 2) and chain decomposition of hexogen (see Scheme 3) in solutions [53, 55] provide an explanation for the principal experimental results, *e.g.*, the dependence of the yields of gaseous products on the concentration of hexogen, high yields of mononitrosohexogen in very dilute solutions of inert solvents, cage effects and, what is even more important, enhancing effects of some solvents and the negative activation volumes in the decomposition of hexogen in THF.

Further chain propagation is provided by the reaction of the radicals **3** with the solvent. This is favoured by low concentrations of gaseous inhibitors (NO and NO_2) in solutions and the absence of non-volatile free radical scavengers which cannot be formed from the methylene groups of hexogen. Apparently, this factor is the most important. Thus the final decomposition products of DMNA contain stable dimethylnitrosamine, while the intermediate products contain nitrosomethane and formaldoxime,[13] both of which are efficient free radical acceptors. Therefore, no chain reactions occur in the case of DMNA. All the solvents including alcohols are inert with respect to DMNA. The solvents listed in Table 6 appeared to be inert with respect to hexanitrohexaazaisowurtzitan (CL-20) as well.[54] Although the nitramine groups of this compound are structurally similar to those of hexogen, CL-20 cannot be regarded as its complete analogue. Owing to the presence in CL-20 of a stable carbon backbone, its decomposition affords numerous reactive products which remain in the condensed phase and prevent the onset of the chain reaction.[63, 64]

In contrast, the chain decomposition of octogen is very well-expressed.[54] As in hexogen, the nitramine groups are separated only by methylene groups, therefore, the formation of condensed products possessing inhibitory properties is prevented.

The chain mechanism described above eliminates all contradictions in the interpretation of decomposition reactions of hexogen and octogen. In solutions as well as in the melt and in the solid state, homolysis of the N–NO_2 bond is the first decomposition step.

IV. Structures and stabilities of secondary nitramines. Kinetic data

Unlike studies on DMNA, hexogen and octogen that have been the subjects of comprehensive examination (both theoretical and experimental), studies on the thermal decomposition of other secondary nitramines were largely confined to measurements of reaction rates and determination of kinetic parameters under various experimental conditions. Since the kinetic parameters of decomposition reflect its mechanism, it is appropriate to consider the correspondence of the kinetic data with the mechanism involving dissociation of the N–NO_2 bond. The known formal

kinetic characteristics of the decomposition of secondary nitramines are given in Table 7.

The maximum difference in the decomposition rates of nitramines is three orders of magnitude, data on decomposition of nitramines in the solid phase being set aside, since the rates here are determined not only by their structures, but also by their physical properties. This difference is only partly due to the errors in the determination of activation energies used for extrapolation of rate constants to reference temperature. In general terms, the differences in the decomposition rates are determined by the dependence of the energy of the N—N bond on the structure of the nitramine. It has been shown for the first time [26] that stability of a nitramine depends critically on the spatial structure of its nitramine groups. The activation energies for the decomposition

Table 7. Kinetic characteristics of decomposition reactions of secondary nitramines.

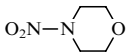
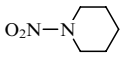
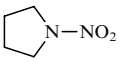
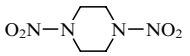
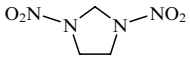
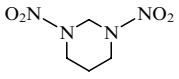
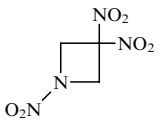
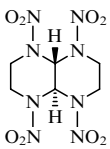
Compound	Formula	Medium	Method [a]	T /°C	E_a /kJ mol^{-1}	log$A$ (s^{-1})	$10^5 k$ /s^{-1} (200 °C)	Ref.
Dimethylnitramine	Me_2NNO_2	gas	GLC	165–200	221.8	20	3.5	9
		"	see [b]	–	193.4	15.8	0.3	2
		"	MM	180–260	170.8	14.1	1.8	11
		gas + CH_2O	MM	180–240	162.8	13.7	0.6	12
		solution in isooctane	LC	200–300	195.5	17.8	17.9	50
		melt	LC	200–280	159.1	13.2	4.8	50
Diethylnitramine	Et_2NNO_2	gas	MM	180–240	174.1	15.1	1.3	65
		solution in isooctane	LC	200–300	188.8	16.6	2.6	50
Dipropylnitramine	$Pr^n_2NNO_2$	gas	MM	200–240	176.2	14.8	2.2	65
		solution in isooctane	LC	220–260	200.9	17.6	2.9	50
Diisopropylnitramine	$Pr^i_2NNO_2$	the same	LC	200–300	178.3	15.9	18.4	50
		solution in acetone	LC	220–250	183.8	161	9.2	50
N-Nitromorpholine		the same	MM	210–245	162.8	13.6	4.2	66
N-Nitropiperidine		gas	MM	210–240	176.2	14.8	2.5	65
		solution in benzene	LC	220–300	201.8	16.6	0.2	50
		solution in acetone	LC	240–290	198.8	16.3	0.3	50
N-Nitropyrrolidine		the same	LC	240–290	215.6	18.4	0.4	50
N,*N*′-Dinitropiperazine		gas	MM	200–240	159.9	13.6	8.9	26
		gas + NO	MM	220–250	151.1	12.0	0.2	26
		solution in nitrobenzene	MM	225–245	155.3	12.0	0.8	66
		solution in trinitrobenzene	MM	230–245	191.7	15.7	0.4	67
		solution in acetone	LC	240–290	220.2	19.1	0.6	50
		melt	MM	216–250	198.4	17.3	2.5	66
N,*N*′-Dinitroimidazolidine		gas	MM	170–200	146.5	13.5	213	26
		gas + NO	MM	170–200	169.1	15.6	87	26
		solution in *m*-dinitrobenzene	MM	170–210	155.7	13.6	26	66
		solution in acetone	LC	200–240	200.1	19.1	132	50
		solution in trinitrobenzene	MM	120–210	158.6	14.0	29	67
		melt	MM	135–200	155.3	13.9	57	66
		"	LC	200–250	197.6	18.7	77	50
1,3-Dinitro-1,3-diazacyclohexane		solution in acetone	LC	200–280	205.5	18.0	2.0	50
		solution in ethanol	LC	200–300	167.4	14.6	13	50
		melt	LC	240–260	175.4	15.4	11	50
1,3,3-Trinitroazetidine		solution in acetone	LC	189–263	182.5	16.4	20	50
		melt	LC	220–250	182.9	16.3	12	50
		"	LC	160–250	195.9	17.5	10	68
		solution in benzene	LC	160–260	168.7	14.7	100	68
		solution in acetone	LC	189–280	182.5	16.5	44	68
		solution in methanol	LC	180–240	128.5	11.4	1600	68
trans-1,4,5,8-Tetranitrodecahydropyrazino[2,3-*b*]pyrazine		solid phase	DSC	204–234	209.7	18.9	6	69

Table 7 (continued).

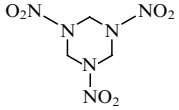
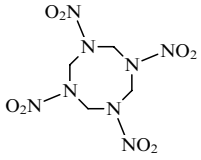
Compound	Formula	Medium	Method [a]	T /°C	E_a /kJ mol^{-1}	log$A$ (s^{-1})	$10^5 k$ /s^{-1} (200 °C)	Ref.
Hexogen		gas	DSC	208–256	145.2	13.5	550	70
		"	MM	170–190	125.6	11.7	688	71
		"	MM	170–200	146.5	13.5	213	26
		"	–	165–247	125.6	11.8	908	3
		"	MM	175–202	169.1	16.0	220	72
		gas + NO	MM	170–200	169.1	15.6	85	26
		solution in trotyl	MM	195–280	171.6	15.5	40	28
		solution in dicyclohexyl phthalate	MM	201–280	173.7	15.4	33	28
		solution in *m*-dinitro-benzene	MM	160–200	166.2	14.3	9	34
		solution in trotyl	MM	166–184	154.5	13.9	71	51
		solution in benzophenone	MM	–	158.2	14.5	110	51
		solution in polyphenyl ether	DSC	–	200.9	–	–	73
		solution in acetone	LC	200–240	190.0	17.9	83.4	50
		solution in benzene	LC	206–256	161.1	14.1	23	5
		melt	LC	200–250	158.2	14.3	68	50
		"	MM	232–247	197.2	18.3	34	70
		"	MM	213–299	198.8	18.5	35.5	28
		"	GLC	–	203.8	19.2	53	29
		"	DSC	210–261	189.2	–	–	74
		"	DSC	–	180.4	16.4	31	75
		"	Ic	204–225	171.6	–	–	76
		"	DSC	204–240	209.7	19.6	28	77
		"	TGA	205–220	200.1	18.7	41	78
		"	DTA	197–267	207.2	20.8	914	79
		solid phase	MM	150–197	213.1	18.6	12	80
		the same	MM	150–197	217.7	19.1	1.2	34
		"	MM	140–190	166.6	11.2	0.01	81
		"	MM	178–200	190.4	17.7	48	82
		"	MM	170–198	180–264	–	–	83
		solid phase + CH_2O	MM	170–197	184.2	–	–	84
		the same	MM	–	173.7	14.5	2.1	3
		"	MM	130–180	165.3	11.7	0.03	71
Octogen		gas	MM	171–215	221.4	20.2	2630	51
		"	MM	230–250	133.9	13.2	6	28
		"	MM	205–280	165.3	14.2	9	26
		"	MM	245–275	159.1	12.5	0.9	72
		"	–	–	193.4	16.4	1.2	2
		solution in *m*-dinitro-benzene	MM	171–215	187.9	16.0	1.5	73
		solution in acetone	LC	189–289	210.1	18.9	5.7	50
		melt	MM	271–314	220.6	19.7	2.3	28
		"	DSC	271–285	214.7	18.8	1.2	82
		solid phase	MM	176–230	158.6	11.2	0.05	34
		the same	MM	150–170	150.7	10.8	0.15	85
		"	MM	180–210	171.6	12.8	0.1	71
		"	DTA	185–280	172.5	14.3	2.0	86
		"	DTA	160–250	113.0	10.0	170	86
		"	DSC	251–263	175.8	–	–	75
		"	MM	261–276	205.1	17.8	0.55	87
		"	MM	130–180	158.6	9.2	10^{-3}	88
		"	LC	230–270	221.4	18.4	9.0	50
		"	DTA	229–269	187.1	15.9	1.9	43
		"	IRS	166–194	204.3	19.8	192	87
		solid phase + N_2 (35 atm)	DTA	229–269	108.4	8.5	35.5	43
		solid phase + N_2 (1 atm)	TGA	229–269	146.9	11.5	2.0	43
		solid phase + air (1 atm)	TGA	229–269	205.1	17.0	0.25	43
		solid phase + O_2 (1 atm)	TGA	229–269	208.0	17.1	0.15	43

Table 7 (continued).

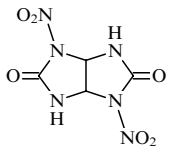
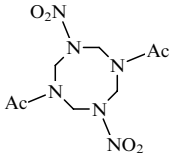
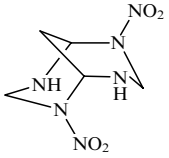
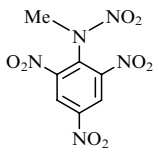
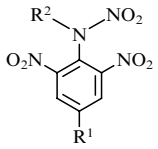
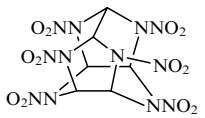
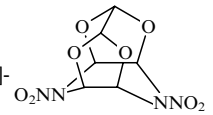
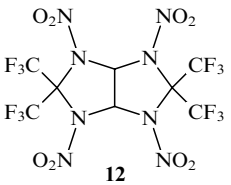
Compound	Formula	Medium	Method [a]	T /°C	E_a /kJ mol^{-1}	log$A$ (s^{-1})	$10^5 k$ /s^{-1} (200 °C)	Ref.
1,4-Dinitrotetrahydroimidazo-[4,5-*d*]imidazolidine-2,5-dione		solid phase	DSC	225 – 245	217.7	20.9	27	59
1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane		solid phase	DSC	250 – 270	175.8	15.3	4.0	59
3,7-Dinitro-1,3,5,7-tetraazabicyclo-[3.3.1]nonane		solid phase	–	–	192.1	16.6	4.0	59
Aliphatic nitramines	$R^1N(NO_2)R^2$							
	R^1 = Me, R^2 = $(CH_2)_2CO_2Me$	solution in di-butyl phthalate	MM	200 – 230	169.1	13.7	1.3	89
	R^1 = Me, R^2 = $(CH_2)_2CN$	the same	MM	190 – 230	175.4	14.4	1.2	90
	R^1 = Me, R^2 = CH_2OMe	"	MM	190 – 230	171.2	13.9	1.0	89
	R^1 = Me, R^2 = $(CH_2)_2CO_2H$	"	MM	200 – 230	170.8	14.0	1.5	89
	R^1 = Me, R^2 = $(CH_2)_2CO_2H$	"	MM	180 – 220	167.8	14.7	16	91
	R^1 = $(CH_2)_2CN$, R^2 = CH_2Fc (see [c])	"	MM	160 – 180	179.6	17.3	2.7	90
	R^1 = $(CH_2)_2$. .$C(NO_2)_2Me$, R^2 = CH_2Fc	"	MM	180 – 200	154.0	12.9	0.01	89
	R^1 = R^2 = $(CH_2)_2CN$	"	MM	210 – 250	172.9	13.9	0.1	89
	R^1 = R^2 = $(CH_2)_2CO_2H$	"	MM	200 – 240	170.8	14.1	1.6	89
	R^1 = R^2 = CH_2Fc	"	MM	190 – 200	161.2	13.5	0.05	90
	R^1 = R^2 = $(CH_2)_2CO_2Me$	"	MM	210 – 250	170.4	13.7	0.8	90
	R^1 = R^2 = $CH_2C(NO_2)_2Me$	solution in *m*-dinitrobenzene	MM	145 – 170	166.2	15.7	230	92
N-Methyl-*N*,2,4,6-tetranitroaniline (tetryl)		melt	MM	211 – 260	160.7	15.4	460	27
		"	TGA	132 – 164	146.1	12.9	59	93
		"	IC	131 – 155	150.7	13.8	148	94
		"	MM	140 – 165	167.4	16.0	330	95
		"	MM	150 – 175	150.3	13.5	166	90
		"	MM	130 – 139	254.9	27.3	10^3	96
		"	MM	140 – 150	232.3	14.5	10^3	97
		"	MM	150 – 175	146.5	–	–	98
		"	DSC	170 – 174	242.8	–	–	99
		solution in poly-phenyl ether	DSC	–	140.2	–	–	73
		solid phase	DSC	–	217.7	12.5	10^3	96
		the same	DSC	–	153.2	12.7	62	96
		"	DSC	–	229.8	–	–	73

Table 7 (continued).

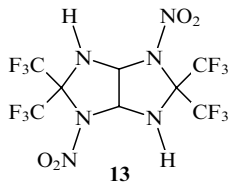
Compound	Formula	Medium	Method [a]	T /°C	E_a /kJ mol^{-1}	log$A$ (s^{-1})	$10^5 k$ /s^{-1} (200 °C)	Ref.
Other aromatic nitramines								
	R^1 = OMe, R^2 = Me	solution in *m*-dinitrobenzene	MM	145–165	134.4	12.4	323	89
	$R^1 = R^2$ = Me	the same	MM	150–170	143.2	13.4	416	89
	R^1 = Cl, R^2 = Me	"	MM	145–165	141.1	13.1	346	89
	R^1 = Br, R^2 = Me	"	MM	155–175	141.5	13.4	638	89
	$R^1 = NO_2$, R^2 = Et	"	MM	144–165	139.4	13.9	3432	89
	$R^1 = NO_2$, $R^2 = Pr^n$	"	MM	135–155	136.9	13.3	1630	89
	$R^1 = NO_2$, $R^2 = Pr^n$	"	MM	130–150	140.2	14.2	5537	89
Hexanitrohexaaza-isowurtzitan (CL-20)		solution in acetone	LC	146–226	177.5	17.6	1088	50
		solution in *m*-dinitrobenzene	MM, TG	150–195	189.6	18.6	450	100
		solid phase	TGA	190–204	151.9	13.6	71	101
		the same	TGA, DSC	160–180	172.0	13.8	0.8	100
		solid phase + air (1 atm)	MM, TG	183–211	223.5	20.5	7.3	102
4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diaza-tetracyclo[5.5.0.0^{5,9}0^{3,11}]-dodecane		gas	MM	240–250	163.3	14.1	1.2	101
		solution in dibutyl phthalate	MM	210–250	167.5	13.5	1.0	101
		solid phase	MM	210–225	196.8	15.4	0.05	101

[a] Designations: GLC, gas-liquid chromatography; MM, manometric method; LC, liquid chromatography; DSC, differential scanning calorimetry; Ic, isothermic calorimetry; TGA, thermogravimetric analysis; DTA, differential thermal analysis; TG, thermogravimetry; IRS, IR spectroscopy. [b] Thermochemical calculation. [c] Fc, ferrocenyl.

of planar nitramine groups are, on average, 172 kJ mol^{-1}, whereas that for the pyramidal group does not exceed 160 kJ mol^{-1}. In the case of hexogen, two of three nitramine groups are pyramidal, and it is 100 times less stable than octogen with all of the four groups planar. Low stability is also characteristic of 1,3-dinitro-1,3-diazacyclopentane (see Table 7) with pyramidal nitramine groups. At the same time, all the nitramines containing planar groups are decomposed at approximately the same rates. The frequencies of anti-symmetrical oscillations of the nitro groups (ν_{as}) are determined by the extent of the deviation of the nitramine groups from the planar structure.[103] The dependence of ν_{as} on the length of the N–N bond is linear. In its turn, the elongation of the bond is accompanied by a decrease in its strength. The maximum values of ν_{as} around 1600 cm^{-1} are observed for the nitramine groups attached to a five-membered ring or to even more strained rings as, *e.g.,* in CL-20 (see Table 7) or in compounds **12** and **13**.[103]



12



13

The frequency of anti-symmetrical oscillations of the nitro group ν_{as} of hexogen is 1570 (see Ref. 103) (*cf.* 1605 cm^{-1} for CL-20) (see Ref. 100). Therefore, CL-20 is 10 times less stable than hexogen.

There is a correlation between ^{13}C and ^{15}N chemical shifts in the NMR spectra and the kinetic parameters of the decomposition reactions.[104, 105] This correlation provides additional support in favour of a decomposition mechanism of secondary nitramines which involves cleavage of the N–NO_2 bond. This can also be used for predicting the stabilities of novel nitramines.

Resonance conjugation of the nitramine group with a phenyl substituent or another system of π-bonds is yet another factor which determines the stabilities of nitramines. For example, the activation energy for the decomposition of tetryl is 21 kJ mol^{-1} lower than that of dimethylnitramine and the reaction rate is 200 times higher. Nevertheless, the effect of conjugation on the D(N–NO_2) is rather weak. Similar structural changes, *i.e.*, passage from MeX to $PhCH_2X$, decrease the energies of the C–X bonds (X = H, NO_2, Hal) by 60 kJ mol^{-1} (see Ref. 15). The induction effects of substituents in the α- or β-positions on D(N–NO_2) and the decomposition rates of nitramines are very small.[90] This explains why virtually all secondary nitramines manifest high thermal stabilities and are widely used as explosives. The reduction of stabilities of secondary nitramines to a level which makes impossible their practical application requires a combination of two adverse factors, *viz*., the presence of two substituents that can manifest resonance conjugation (*e.g*., heterocycles) or a combined effect of the pyramidal structure of the nitramine group and one such substituent.

Thus, the formal kinetic parameters and the dependence of the decomposition rates on nitramine structures can be explained within the framework of an integral mechanism which postulates the cleavage of the N–NO_2 bond. It may be expected that other nitramines will manifest a decomposition mechanism similar to that of DMNA, hexogen or octogen and the decomposition rates will obey the regularities described above. For example, the decomposition rate in the liquid phase of a popular novel high-energy compound CL-20, which contains four pyramidal nitramine groups, is higher than that of hexogen or 1,3-dinitro-1,3-diazacyclopentane each containing two groups of the same structure.[54, 63, 64, 100–102, 106–108] This prognosis is fully corroborated by experimental results (see Table 7). Extrapolation of a detailed scheme of the non-chain decomposition of hexogen to CL-20 prompts an unambiguous conclusion about the formation of low-volatile nitroso compounds, aldehydes, unsaturated com-

pounds, and stable iminoxyl radicals. Determination of the functional groups in condensed products corroborates this conclusion.[63,64] The chain decomposition of CL-20 in solutions is impossible due to the formation of products able to scavenge free radicals. Indeed, all the solvents studied are inert with respect to CL-20.[54] Yet another novel promising explosive reagent, *viz.*, 1,3,3-trinitroazetidine (see Table 7), contains two functional groups that can undergo decomposition, *viz.*, a nitramine group and a dinitromethylene group. A comparison of parameters of decomposition of compounds containing such groups [109] suggests that the cleavage of the $N-NO_2$ bond at temperatures below 200 °C occurs several times faster than that of the $C-NO_2$ bond, whereas at 240 °C the rates of these reactions become similar. A conclusion about the existence of two parallel channels for decomposition of 1,3,3-trinitroazetidine with approximately the same rates was drawn on the basis of direct kinetic measurements and identification of the decomposition products.[68]

V. Conclusion

Significant progress has been achieved in the study of the mechanism of the first step of thermal decomposition of nitramines. Thus it has become possible to predict the rate of this step, which determines the thermal stability of a compound. Contrariwise, secondary reactions including those of the starting compound have been rather poorly studied. Reactions of nitramines with nitrogen dioxide have not been investigated; as yet, little is known about the autocatalysis of decomposition of nitramines in liquid and solid phases and the mechanism of autocatalysis also remains to be elucidated. Studies along these lines will be continued in the near future. A quantitative description of detailed decomposition schemes for the simplest molecules [110,111] can be used for the calculation of combustion rates.

The problem of decomposition of nitramines in the solid phase is closely related to the general problem of chemical kinetics, *viz.*, the development of a physical model of solid-phase monomolecular reactions. Analysis of effects of various factors, such as defects of a crystal lattice and phase transitions,[112] on the decomposition of hexogen and octogen have given a strong impetus to the further progress of these studies.[82,83,88] A search for nitramines that decompose in a non-localised manner, *i.e.*, uniformly over the whole crystal, presents special interest for investigators. Verification of semi-empirical models [113] allowing estimation of decomposition rate constants in the solid phase k_{solid}, requires comprehensive investigations which will include determination of the main characteristics of a crystal and study of a relationship between k_{solid} and melting temperature, structure and specific properties of a crystal, *e.g.*, compressibility, free volume, density and their temperature dependences. The immense diversity of secondary nitramines which differ in both decomposition rates and physical properties, leaves hope that compounds for such investigations will be found.

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