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Chain and monomolecular decomposition of hexogen in solutions

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The decomposition of hexogen dissolved in alkylaromatic hydrocarbons, alcohols, ketones, ethers, chloroform, and some other solvents occurs *via* the chain mechanism. This mechanism is supported by slowing down of the reaction when inhibitors are added, the solvent deuterium kinetic isotope effect, and the dependence of the rate on the reactivity of the C—H bond in solvents. The chain reaction propagates through the transfer of a free valence from the primary N-radicals formed by N—NO_2 bond dissociation to the C-centered radicals of the solvent. The solvents are inert when the C—H bond dissociation energy is >380 or <200 kJ mol^{-1}, and hexogen decomposition in such solvents is monomolecular.

Key words: hexogen, decomposition in solutions, chain mechanism.

Thermal decomposition of secondary nitramines, which form a basis of powerful explosives (Tetryl, RDX (hexogen), octogen, CL-20),[1] is being studied intensely for many decades. The most complicated task is to reveal the mechanism of these reactions. More than ten different mechanisms, including oxygen atom elimination, nitro-nitrite rearrangement, reactions of cycle expansion and reduction, HNO_2 elimination, and heterolytic and homolytic N—NO_2 bond dissociation, were proposed only for the first stage of hexogen decomposition. The decomposition of hexogen simultaneously *via* several channels was also considered. The problems concerning the mechanism of decomposition of nitramines are discussed in detail in the previously published reviews.[2—6] All variants of the first stage, except N—NO_2 bond dissociation, were rejected to the present time. Analysis of the mechanisms proposed[2,3,7,8] showed that they ignored energy effects of the reactions, incorrectly treated the deuterium kinetic isotope effect (DKIE), or used unreliable experimental data. It turned out that all data on the composition of the decomposition products and reaction rates in the gas phase, melt, and solid state can be explained assuming that the first stage of thermal decomposition is the N—NO_2 bond dissociation.

Some doubts upon uniqueness of this mechanism have been cast rather recently because of unusual results obtained for the decomposition of nitramines in solutions. It has been established[9] that hexogen decomposes in benzene more rapidly than in melt, exhibiting a considerable solvent DKIE and a high yield of the intermediate products, *viz.*, nitroso derivatives of hexogen. In order to explain these facts, the direct interaction of hexogen with the hydrocarbon solvent RH at the C—H bond to form free radicals $^{\bullet}OH$ and $R^{\bullet}$ was suggested[9]

$$>NNO_2 + RH \longrightarrow >NNO + {}^{\bullet}OH + R^{\bullet}. \qquad (1)$$

However, the thermochemical studies[2] showed that this reaction is strongly endothermic and cannot occur with a measurable rate because its thermal effect (335 kJ mol^{-1} for benzene) exceeds considerably the apparent[3] activation energy (≤170 kJ mol^{-1}) in solutions.

The decomposition of hexogen in THF was established[10] to have a negative activation volume. This fact is attributed to HNO_2 elimination from the nitramine molecule through the cyclic transition state

$$(RCH_2)(R')NNO_2 \longrightarrow RCH{=}NR' + HNO_2 \qquad (2)$$

$R' = RCH_2$.

This reaction was believed[11] to be responsible for the DKIE in the decomposition of deuterated dimethylnitramine in a solution. However, the theoretical study[8] showed that the DKIE found in the work[11] and the isotope effects in octogen decomposition in the solid phase[12] correspond to the secondary isotope effect accompanying N—N bond dissociation rather than the primary isotope effect, *i.e.*, NO_2 detachment rather than HNO_2 elimination occurs.

Studies of hexogen decomposition in a variety of solvents[13,14] with different chemical and physical properties showed that in many of them, including low-polarity hydrocarbons such as toluene, the reaction occurs more rapidly than in melt. All solvents accelerating decompo-

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sition have mobile hydrogen atoms and exhibit a considerable DKIE. These results suggested that hexogen can decompose *via* the chain mechanism in some solvents.

In this work we continued to study hexogen by the methodology described elsewhere[13] using a wider set of solvents, obtained additional data on DKIE, examined some decomposition products, tested inhibitors of chain reactions, and proposed schemes for hexogen decomposition *via* different mechanisms.

Experimental

Hexogen recrystallized from acetone, solid additives (trinitrotoluene, naphthalene, triphenylmethane) reprecipitated from acetone, ethanol, or chloroform, and solvents (reagent grade) additionally dried above Na_2SO_4 and distilled were used. Kinetic measurements were carried out by the manometric method. Reactions were carried out in a glass reactor placed in a metallic shell, which was designed for a pressure of 100 atm. The pressure was measured by the compensation method. This procedure makes it possible to use almost any solvents. In all experiments the reaction was brought to the end. The rate constants were obtained by the treatment of the overall kinetic curves using the first order or autocatalysis first order equation. The maximum error in determination of the rate was ~20% for volatile solvents. The main source of the error, namely, oscillations of the solvent vapor pressure, was related to the accuracy of temperature control (±0.5 °C). The correctness of the manometric procedure was verified by HPLC analysis of hexogen (column 60×2 mm packed with silica gel (5 μm), eluent AcOEt—$CHCl_3$ (3 : 1), flow rate 0.2 mL min^{-1}, UV detection at $\lambda = 270$ nm, retention volume 200 μL). The plot of the surface area of the peak *vs.* concentration was linear in the 0.2—5 mg mL^{-1} concentration interval. Hexogen is poorly soluble in most solvents at ~20 °C and, hence, the concentrations >1% are achieved only at elevated temperatures. After experiments, the solution was concentrated before analysis, and the whole condensed residue was dissolved in the GLC eluent.

Standard GLC procedures were also applied for analysis of light gases (N_2, NO, N_2O, CO, CO_2) and the products formed from solvents. In the first case, two columns packed with Porapac Q were used (diameter 4 mm, lengths 1 and 1.5 m). The sum of diatomic gases (one peak), CO_2, and N_2O were separated on the first column at 20 °C. Triatomic gases were frozen at −90 °C and N_2, CO, and NO were separated on the second column. A column packed with Separon-BD (1.5 m × 4 mm, temperature of the column 180 °C) was used to analyze the liquid products.

The main experiments were carried out at $m/V = 0.5$ with respect to solvent (m is the weighted sample, V is the volume of the vessel) at the concentration of hexogen (C_h) equal to 1%. In special experiments, to reveal the influence of conditions on the rate and composition of the decomposition products, m/V was changed twofold and C_h was changed 100-fold. In most cases the volume of the vessel was 2 mL.

Results and Discussion

Kinetic data. Cage and isotope effects. Comparison of the rate constants of the initial stage (k_1) in different solvents at a constant temperature gives the overall pattern of the influence of solvents on hexogen decomposition. Examples of the kinetic curves have earlier been obtained.[14] The absolute and relative rate constants for 1% solutions at 180 °C are presented in Table 1. In calculations of relative k_1 we took as unity the rate constant in an inert solvent, *viz.*, isooctane,[17] instead of that in melt, as it has been done by the authors of Ref. 13, because the data for the melt are not accurate.[15] The published data on solutions for the 0.01—5% range of hexogen concentrations are also presented in Table 1. Note that neither our data nor those of Ref. 17 confirm the high reaction rate and DKIE of decomposition in benzene found in Ref. 9.

The solvents in the first 13 entries (see Table 1) are inert toward hexogen, and they at least do not noticeably accelerate decomposition compared to the melt. This group of substances is presented by quite different compounds: aliphatic and aromatic hydrocarbons, fluoro, chloro, and nitro benzene derivatives. In benzene, naphthalene, isooctane, and acetonitrile the decomposition rates are the same within the measurement error and insignificantly exceed the rate of the process in the melt. A similar decrease in the decomposition rate in dilute solutions has first been found for dimethylnitramine.[11] A correlation between the decomposition rate and solvent viscosity was observed in four solvents with the known viscosity at ~20 °C (cP), namely, cyclopentane (0.47), cyclohexane (1.0), butanol (4.0), and triacetin (28). The phenomenon was explained by the cage effect in the limiting stage of decomposition, N—NO_2 bond dissociation in the case of dimethylnitramine. Probably, this reason also holds for hexogen. Data on the viscosity of the solvents at 180 °C are lacking. It is known, however, that in the series of related compounds the viscosity changes proportionally to the molecular weight. Taking into account this fact, we can conclude from Table 1 that all compounds decreasing the decomposition rate are more viscous than benzene and the k_1 value and molecular weight demonstrate the opposite change in the series of compounds of the same type (benzene derivatives). There are no reasons to assume that in inert solvents the mechanism of the first stage differs from that accepted for the melt. The Arrhenius parameters found[14] for decomposition in benzene ($E = 163$ kJ mol^{-1}, $\log A = 14.5$) are typical of the N—NO_2 bond dissociation as the limiting stage of the process.

The series of inert solvents ends with acetonitrile. The latter, along with nitromethane, is characterized by

Table 1. Experimental rate constants of decomposition (k_1) of 1% solutions of hexogen in different solvents at 180 °C

Entry	Solvent[a]	$k_1 \cdot 10^4/\mathrm{s}^{-1}$	k_1/k_1^{iso} [b]
1	Melt[15]	0.43	0.86
2	1,2,4-Trichlorobenzene	0.13	0.26
3	*m*-Dinitrobenzene	0.17	0.34
4	$C_{12}F_{26}$	0.21	0.42
5	Nitrobenzene	0.23	0.46
6	Dicyclohexyl phthalate[16]	0.25	0.50
7	Ph_3CH	0.26	0.52
8	Triacetin	0.32	0.64
9	Diphenyl	0.38	0.76
10	Naphthalene	0.48	0.96
11	Isooctane	0.50	1.00
12.1	PhH	0.55	1.10
12.2	PhH [17]	0.39	0.78
12.3	PhH (C_h = 0.8 wt.%)	0.54	1.08
12.4	PhH (C_h = 0.44 wt.%)	0.53	1.06
12.5	PhH + I_2 (4.4 wt.%)	0.54	1.08
12.6	PhH + *p*-dinitrosobenzene (1.3 wt.%)	0.55	1.10
12.7	PhH-d_6	0.58	1.16
12.8	PhH + $(CH_2O)_3$ (1 wt.%)	0.65	1.30
12.9	PhH + NO (500 Torr)	0.69	1.38
12.10	PhH + $PhCH_2OH$ (2.48 wt.%)	0.80	1.60
12.11	PhH-d_6 [9] (C_h = 0.1 wt.%)	1.40	2.80
12.12	PhH [9] (C_h = 0.1 wt.%)	1.93	3.86
12.13	PhH + Ph_2NH (0.93 wt.%)	2.84	5.68
12.14	PhH + piperidine (5.2 wt.%)	21.0	4.20
13.1	MeCN	0.63	1.26
13.2	MeCN-d_3	0.73	1.46
14.1	Me_2CO	0.72	1.44
14.2	Me_2CO-d_6	0.28	0.56
14.3	Me_2CO [17] (C_h = 0.05—0.1 wt.%)	0.93	1.86
14.4	Me_2CO + THF (1 : 1)	2.46	4.92
15	Trinitrobenzene	0.74	1.48
16	Diphenylmethane	0.79	1.58
17	*o*-Dinitrobenzene	0.82	1.64
18.1	Trinitrotoluene	0.86	1.72
18.2	Trinitrotoluene[15] (C_h = 0.5—5 wt.%)	0.59	1.18
18.3	Trinitrotoluene[18] (C_h = 5 wt.%)	1.33	2.66
19	*tert*-Butylbenzene	0.95	1.90
20	$PhCH_2OH$	0.96	1.92
21	Isopropylbenzene	1.18	2.36
22.1	Toluene	1.25	2.50
22.2	Toluene + NO (500 Torr)	0.19	0.38
22.3	Toluene-d_3	0.33	0.66
22.4	Toluene + NO_2	0.45	0.90
22.5	Toluene + *p*-dinitrobenzene (1.54 wt.%)	0.76	1.52
22.6	Toluene + $(CH_2O)_3$ (0.6 wt.%)	1.31	2.62
22.7	Toluene + I_2 (1.44 wt.%)	2.55	5.10
23	Ionol	1.27	2.54
24	Cyclohexanol	1.95	3.90
25	AcOEt	2.03	4.06
26.1	PhOH	2.03	4.06
26.2	PhOH-d_6	1.60	3.20
27.1	$CHCl_3$	2.04	4.08
27.2	$CDCl_3$	1.41	2.82
28.1	*m*-Xylene	2.67	5.34
28.2	*m*-Xylene + NO_2 (500 Torr)	0.27	0.54
28.3	*m*-Xylene-d_{10}	0.48	0.96
29	THF	2.93	5.86
30.1	*p*-Xylene	2.96	6.92
30.2	*p*-Xylene + NO (500 Torr)	1.52	3.04
30.3	*p*-Xylene + *p*-dinitrosobenzene (0.78 wt.%)	1.96	3.92
30.4	*p*-Xylene + I_2 (1.5 wt.%)	2.57	5.14
31.1	1,4-Butanediol	3.59	7.18
31.2	1,4-Butanediol (C_h = 3 wt.%)	3.40	6.80
31.3	1,4-Butanediol (C_h = 0.3 wt.%)	3.48	6.96
32.1	MeCH(OH)Me	4.32	8.64
32.2	$CD_3CD(OD)CD_3$	1.18	2.36
33	Triethylene glycol	4.81	9.62
34	PhCHO	5.07	10.14
35.1	Glycerol	5.55	11.10
35.2	Glycerol + NO_2	1.20	2.40
35.3	Glycerol + NO	3.61	7.22
35.4	Glycerol + $(CH_2O)_3$ (0.6 wt.%)	5.67	11.34

[a] Specific features of some processes (concentration of hexogen (C_h), concentration of inhibitors, pressure) are also indicated.
[b] k_1^{iso} is the decomposition rate constant in isooctane.

the highest dielectric constant among all solvents tested, and naphthalene is the strongest π-donor among them. These compounds belong to the group of inert solvents. Therefore, the medium polarity and the solvent ability to form charge-transfer complexes have no effect on the decomposition of hexogen.

The second group of solvents comprises compounds in which decomposition occurs more rapidly than in melt. These are alkylaromatic hydrocarbons, alcohols, ketones, aldehydes, chloroform, and some others. Their common property is the presence of mobile hydrogen atoms,[13] *i.e.*, fairly weak C—H bonds in nonpolar compounds like toluene or rather stable but polar and reactive[19] C—H bonds in such compounds as chloroform and alcohols. These solvents have no other common properties. Noninert solvents always manifest the solvent DKIE, indicating the reaction with C—H bond dissociation.

The plot of k_1 *vs.* dissociation energy of the C—H bond of the solvent (D(C—H)) has a minimum. Since data on D(C—H) are scarce, we can trace only roughly the dependence using aliphatic hydrocarbons

(D/kJ mol^{-1} > 380), toluene (356), *m*-xylene (325), *p*-xylene (322), diphenylmethane (262), and triphenylmethane (~255) as reference points.[20] In aliphatic hydrocarbons, including isooctane, the rate constant is almost the same as that in the melt. The rate constant is already threefold higher in toluene and 5—7-fold higher in *m*- and *p*-cresols. In diphenylmethane k_1 is yet higher than that in benzene but lower than those in cresols and even in toluene. Triphenylmethane inhibits decomposition. In solvents with the polarized C—H bonds (in chloroform and alcohols) the influence of the solvent is noticeable at D(C—H) > 360 kJ mol^{-1}.

At 180 °C the maximum acceleration (by 11 times) is in glycerol. Such an increase in k_1 is observed against the background of the expected triple (as in the most viscous inert solvents) decrease in the rate due to the cage effect. When the temperature decreases, the difference in the rate constants of hexogen decomposition in the melt and solution increases due to the lower activation energy in solutions. In toluene $E_a = 158$ kJ mol^{-1}, and in 1,4-butanediol it is 135 kJ mol^{-1}.[12]

Analysis of products. After hexogen was completely decomposed, N_2, N_2O, CO, CO_2, traces of NO, and minor amounts of CH_2O and H_2O were found in the gas phase. The peculiarity of decomposition in solutions is the dependence of the molar yield (φ, mol mol^{-1} of hexogen) of the gaseous products on the concentration of hexogen C_h (wt.%) (Table 2). For decomposition in melt the overall yield of the gaseous products is ~5 moles per mole of hexogen.[3] The main results of these experiments is that the yield of the gaseous products decreases sharply for the decomposition in solutions with $C_h < 5\%$.

It was found by HPLC that the decomposition of a 1% solution of hexogen in toluene produce benzaldehyde, benzonitrile, and benzyl alcohol in yields of 0.43, 0.32, and 0.43 mol mol^{-1} of hexogen, respectively. Phenylnitromethane and benzoic acid were also found in minor amounts. Thus, the results of analysis confirm the involvement of solvents in the reaction.

Table 2. Molar yield (φ) of the gaseous products as a function of the hexogen concentration (C_h) in different solvents

Solvent	C_h (wt.%)	φ/mol mol^{-1} of hexogen				
		Σ*	N_2	N_2O	CO	CO_2
Benzene	0.5	0.5	—	—	—	—
	2	4.2	2.37	0.20	0.85	0.50
	8	5.5	—	—	—	—
Toluene	0.5	1.3	—	—	—	—
	1.5	3.0	1.11	1.11	0.07	0.28

* Overall yield of the gaseous products, including water vapor and CH_2O.

Influence of inhibitors. The deuterium kinetic isotope effect found in this work and in Ref. 13 for solvents, which enhance the decomposition rate, and the composition of products prove the involvement of the solvents in the decomposition process. However, these facts cannot be a rigorous proof for the chain mechanism proposed previously.[13] The inhibitor method provides more reliable data. The problem of inhibition of chain reactions during the decomposition of explosives was not considered earlier because in the most cases these reactions do not develop due to suppression by the decomposition products such as NO, NO_2, nitroso compounds, and nitroxyl radicals. The difference between activation energies of the reactions of free radicals with NO or NO_2 and with saturated molecules is at least 40 kJ mol^{-1}. Therefore, chain reactions are completely suppressed already at concentrations of these inhibitors of 0.1—0.01 mol.%.

Among the listed chemical acceptors of free radicals, only NO is formed in great amounts during hexogen decomposition.[3] This gas is poorly soluble in organic liquids (<1% at ~20 °C) and, hence, the capture of free radicals by it is improbable. An advantage of NO is its entire inertness toward hexogen and solvents. Therefore, NO was used first of all as an inhibitor at a pressure of 500 Torr, which exceeds the NO pressure at the end of the reaction by ~3 times. In addition, the influence of other known inhibitors of chain reactions, *viz.*, *p*-dinitrosobenzene, I_2, NO_2 (500 Torr), phenol, and diphenylamine (see Table 1), was studied.

In the presence of NO, NO_2, and *p*-dinitrosobenzene, the hexogen decomposition rate in toluene decreases to that in benzene (Fig. 1). In addition, NO and *p*-dinitrosobenzene slow down the decomposition of hexogen in *p*-xylene and glycerol to the same extent as NO_2 does

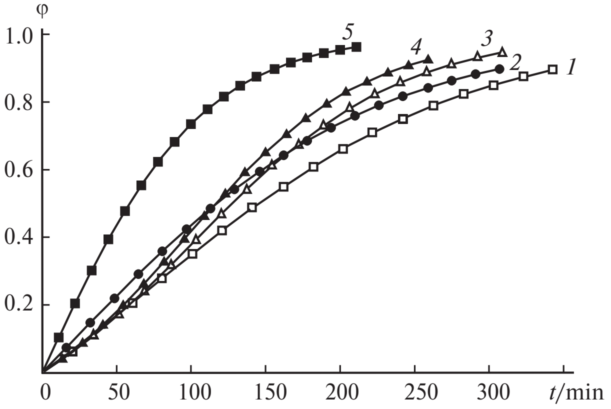


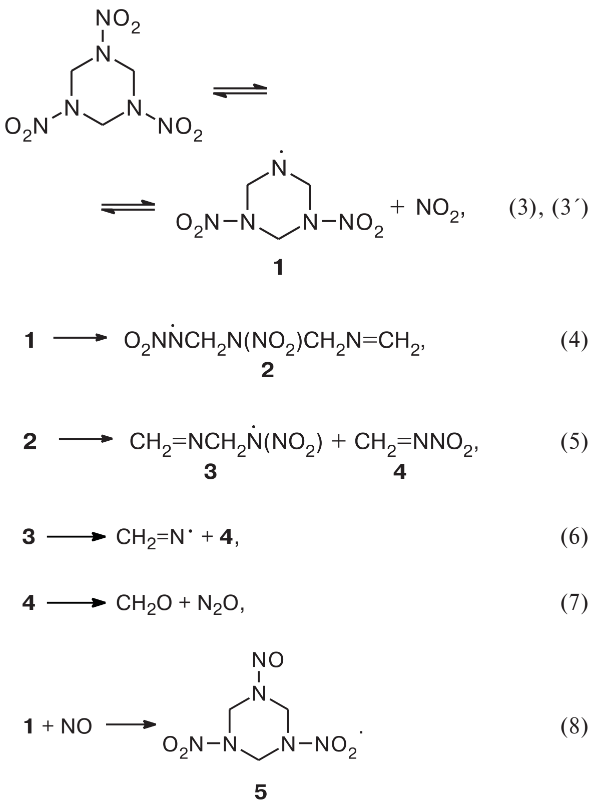
Fig. 1. Hexogen decomposition at 180 °C in benzene (*1*), in toluene with an additive of NO_2 (500 Torr) (*2*), in toluene with an additive of NO (500 Torr) (*3*), in toluene with an additive of *p*-dinitrosobenzene (*4*), and in toluene (*5*) (φ/mol mol^{-1} of hexogen is the molar yield of gaseous reaction products).

in *m*-xylene and glycerol (see Table 1). The inhibition of the reaction in active solvents is not so pronounced because *p*-dinitrosobenzene is a weak inhibitor of the molecular type and the concentration of gaseous NO and NO_2 in a solution at an external pressure of 500 Torr is insufficient to capture all free radicals. Phenol, diphenylamine, and I_2 do not inhibit the decomposition of hexogen. Phenol reacts with hexogen, diphenylamine perhaps accelerates decomposition *via* the donor-acceptor interaction mechanism, and I_2 in benzene is inert but increases the reaction rate in toluene acting, most likely, as an initiator. The dual behavior of diiodine in chain reactions is well known.[21] Depending on conditions, I_2 can act as an inhibitor or an initiator of chain processes.

The results obtained by the inhibitor method confirm the hypothesis[13] about the chain mechanism of hexogen decomposition in solvents with weak C—H bonds and the monomolecular mechanism of decomposition in inert media. In this connection, it seems reasonable to consider the kinetic schemes of the reactions[13] in detail and check their accordance with the experimental data.

Scheme of nonchain decomposition. The commonly accepted scheme of the monomolecular decomposition of hexogen in solutions, which is in accordance with the kinetic parameters and explains the formation of great amounts of CH_2O and N_2O, has first been proposed in Ref. 3 (Scheme 1, reactions (3)—(8)).

Scheme 1



(3), (3′)

1

$$\mathbf{1} \longrightarrow O_2N\dot{N}CH_2N(NO_2)CH_2N{=}CH_2, \quad \mathbf{2} \qquad (4)$$

$$\mathbf{2} \longrightarrow CH_2{=}NCH_2\dot{N}(NO_2) + CH_2{=}NNO_2, \quad \mathbf{3}, \mathbf{4} \qquad (5)$$

$$\mathbf{3} \longrightarrow CH_2{=}N^{\bullet} + \mathbf{4}, \qquad (6)$$

$$\mathbf{4} \longrightarrow CH_2O + N_2O, \qquad (7)$$

$\mathbf{1}$ + NO ⟶ (8)

5

Scheme 1 does not contain secondary processes, in particular, the interaction of NO and NO_2 with free radicals of the C- and N-types, polymerization and oxidation of unsaturated compounds, isomerization of nitroso compounds, and some others. The following stages are most probable:

$$\mathbf{1} + NO_2 \longrightarrow$$
$$\longrightarrow O{=}NCH_2N(NO_2)CH_2N(NO_2)CH_2N{=}O, \quad \mathbf{6} \qquad (9)$$

$$\mathbf{6} \longrightarrow HON{=}CHN(NO_2)CH_2N(NO_2)CH{=}NOH, \quad \mathbf{7} \qquad (10)$$

$$\mathbf{7} \xrightarrow{\text{Polymerization}} \text{Nonvolatile residue}, \qquad (11)$$

$$\mathbf{4} \xrightarrow{\text{Polymerization}} \text{Nonvolatile residue}, \qquad (12)$$

$$\mathbf{7} + NO_2 \xrightarrow{\text{Oxidation}} \text{Gaseous products}, \qquad (13)$$

$$\mathbf{4} + NO_2 \xrightarrow{\text{Oxidation}} \text{Gaseous products}, \qquad (14)$$

$$\mathbf{3} + NO \longrightarrow CH_2{=}N{-}\dot{C}H_2 + N_2O + NO_2, \quad \mathbf{8} \qquad (15)$$

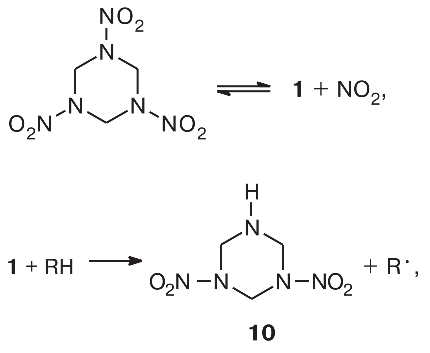
$$\mathbf{3} + NO_2 \dashrightarrow \mathbf{8} + 2\,NO + NO_2. \qquad (16)$$

Decomposition starts from the dissociation of the N—N bond. This reaction, as any decomposition of a molecule to radicals, is reversible, due to which the cage effect should be manifested in viscous media. Radical **1** isomerizes to **2** followed by decomposition and the final formation of the inactive radical $CH_2{=}N^{\bullet}$. In addition, radical **1** reacts with NO and NO_2. Mononitrosohexogen (**5**) is reversibly formed in reaction (8) as an intermediate, whose decomposition is tenfold faster than the decomposition of hexogen.[10] The interaction of radical **1** with NO_2 in reaction (9), according to the theoretically substantiated mechanism of the interaction of aminyl radicals with NO_2,[22] should result in cycle opening and formation of highly reactive nitroso compound **6** and then oxime **7**. The conversion of NO to N_2 can involve compound **6**. The polymerization producing a nonvolatile residue is the most probable channel of transformation of oxime **7**. The authors of Ref. 23 used the term "nonvolatile residue" to designate condensed products of the type of polyamides, which are always formed in minor amounts upon the decomposition of hexogen and octogen. The second source of the nonvolatile residue is the polymerization of **4** (reaction (12)) competing with decomposition in reaction (7). Similarly to nitroethylene, compound **4** is stable but prone to polymerization. In the presence of NO_2, unsaturated compounds **4** and **7** are readily oxidized to form gaseous products. Note that reactions (4) and (5) occur only because radicals **1** and **2** contain the unstable $H_2CN{-}NO_2$ bond (75 kJ mol^{-1})[7] in the β-position to the free valence. This bond is already absent from radical **3**. In addition, the yield of N_2O upon hexogen decomposition is not 2 moles, as it follows from Scheme 1, but only 1—1.5 moles.[3] Therefore, it can turn out that reaction (6) does not occur at all. The authors of Ref. 23 were first to cast doubt upon its occurrence in the gas phase. Instead of participation in reaction (6), nitraminyl radical **3** in the presence of nitrogen oxides can undergo transformations in reactions (15) and (16) to form radical **8**,[24] which is readily oxidized and can produce $HOCH_2NHCHO$, *viz.*, one of the products of hexogen decomposition,[3] and gaseous substances.

The concentration of nitrogen dioxide in a solution depends on the partial pressure in the gas phase to a much greater extent than does the concentration of NO due to the formation of the N_2O_4 dimers. Therefore, the ratio of rates of reactions (9) and (8) under other equal conditions decreases with a decrease in the hexogen concentration in a solution. Correspondingly, the yield of nitrosohexogen as intermediate product increases, which has previously been observed.[9,11] For the same reason, polymerization reactions (11) and (12) should occur more rapidly than oxidation reactions (13) and (14) because of a sharp decrease in the NO_2 concentration in strongly dilute solutions. This can explain a considerable decrease in the yield of the gaseous products and an increase in the yield of the nonvolatile residue at C_h <5 wt.%.

Scheme of chain reaction. Based on the assumption that the first stage of decomposition is unchanged and the initial reaction rate increases only in the RH solvents reacting with the decomposition products, we can propose the following *a priori* scheme of the chain reaction:

Scheme 2

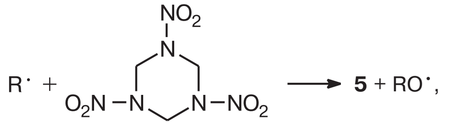


(3), (3′)

(17)

10

$$NO_2 + RH \longrightarrow HONO + R^{\bullet}, \qquad (18)$$



(19)

$$RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet}, \qquad (20)$$

$$\mathbf{5} \longrightarrow \mathbf{1} + NO, \qquad (8')$$

$$R^{\bullet} + NO_2 \longrightarrow RO^{\bullet} + NO, \qquad (21)$$

$$R'CH_2O^{\bullet} + NO_2 \longrightarrow R'CHO + HNO_2 \qquad (22)$$

R = R′CH$_2$,

$$R^{\bullet} + NO_2 \longrightarrow RNO_2, \qquad (23)$$

$$R'CH_2 + NO \longrightarrow R'CH_2NO \longrightarrow R'CH{=}NOH \longrightarrow R'CN + H_2O \qquad (24)$$

R = R′CH$_2$,

$$RNO + 2\,NO \longrightarrow RO^{\bullet} + N_2 + NO_2. \qquad (25)$$

The chain reaction starts with the transfer of the free valence in reactions (17) and (18) to the solvent from NO_2 and radical **1** formed at the first stage of decomposition. Reaction (17) has a substantial advantage over reaction (18) being more exothermic by ~40 kJ mol^{-1}. As shown below, additives of NO_2 do not accelerate but slow down the process and, hence, reaction (18) can be neglected as a source of free radicals.

Reaction (17) prevents the decay of the free valence due to the intramolecular isomerization and decomposition of radical **1** when the N-radicals (inactive in the reaction with the nitro group) are replaced by the reactive (in this respect) C-centered radicals of the solvent. The solvent isotope effect appears at this stage. Finally, its rate is confined above by the D(C—H) values at which reaction (17) can compete with reaction (4). For nonpolar compounds the upper D(C—H) limit is 360 kJ mol^{-1}. In the presence of polar C—H bonds adjacent to the heteroatoms (chloroform, alcohols), reaction (17) occurs also rather rapidly at D(C—H) > 360 kJ mol^{-1}.

The $R^{\bullet}$ radicals decay in the reactions with NO_2 and NO and can react with hexogen. This reaction can occur when the concentration of the inhibitor is at most four orders of magnitude lower than that of hexogen. This condition is fulfilled, most likely, only due to the very low solubility of NO in organic solvents. Besides, the products of nitramine decomposition should not contain nonvolatile and soluble chemical acceptors of free radicals, for example, C-nitroso compounds. This condition is most likely fulfilled because the formation of condensed products from the methylene groups of hexogen is barely expected and the concentration of intermediate products like **6** is low. Note that reaction (19) confines below the range of the D(R—H) values at which the reactivity of the $R^{\bullet}$ radical is retained and the chain propagation reactions continue. The combination of reactions (17) and (19) provide the extreme plot of k_1 *vs.* D(C—H), which is observed experimentally.

According to Scheme 2, the *N*-nitroso compounds formed in the intermediate stage are unstable and can decompose to recover the N-radicals. This condition is also fulfilled for hexogen: it is known that its nitroso analogs are much less stable than hexogen.[25] In most noninert solvents the reaction obeys the first or close to the first order, indicating that mononitrosohexogen (**5**), which is the most stable of the nitroso derivatives of hexogen, is not accumulated as intermediate product or at least is accumulated to a less extent than in inert solvents.[12] This is reasoned by the decomposition of compound **5** by free radicals similarly to hexogen. Amino derivative **10** can catalyze hexogen decomposition similarly to other amines (see Table 1, entries *12.13* and *12.4*). However, this product is not retained to the end of reaction: it is readily oxidized and decays by the interaction with nitrogen dioxide.[3]

The rates of bimolecular reactions of chain initiation and propagation, *i.e.*, stages (17) and (19), increase with an increase in the pressure. Therefore, in noninert solvents the stability of hexogen at high pressures, which are used in determination of the activation volume, should decrease. This fact explains naturally the negative activation volume found for hexogen decomposition in THF,[10] which is one of the most active solvents. Note that, according to the published data,[10] several compounds close to hexogen in structure, for example, 1,3,3,5,5-pentanitropiperazine, also have negative activation volumes in THF. Other hexogen analogs, including octogen, studied in solutions of MeCN (which is an inert solvent, according to our data) are characterized by positive activation volumes.

The schemes of monomolecular and chain decomposition explain, as shown above, the main experimental facts, including the dependence of the yield of gaseous products on the hexogen concentration, the high yield of mononitrosohexogen (**5**) in strongly dilute solutions, the presence of the cage effect, and, which is most important, the accelerating effect of some solvents and the negative activation volume during hexogen decomposition in a THF solution.

Thus, we established that the decomposition of hexogen, although under specific conditions, is the chain process, which is rarely met in the decomposition of explosives. Chain propagation is effected by the transfer of the free valence to a solvent, which is favored by the low concentration of gaseous product, inhibitors NO and NO_2, in the solution and the absence of nonvolatile acceptors of free radicals in the products of hexogen decomposition. The latter fact related to the structure of hexogen seems to play the main role, and it distinguishes hexogen from the most of other secondary nitramines. In the case of dimethylnitramine, whose final decomposition product is stable dimethylnitrosamine and intermediate products are nitrosomethane and methylenoxime (all of them are good acceptors of free radicals), no chain reactions are observed.[11] All solvents, including alcohols, are inert toward dimethylnitramine.

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