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Mathematical modelling of the decomposition of explosives

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Abstract. Studies on mathematical modelling of the molecular and supramolecular structures of explosives and the elementary steps and overall processes of their decomposition are analyzed. Investigations on the modelling of combustion and detonation taking into account the decomposition of explosives are also considered. It is shown that solution of problems related to the decomposition kinetics of explosives requires the use of a complex strategy based on the methods and concepts of chemical physics, solid state physics and theoretical chemistry instead of empirical approach. The bibliography includes 168 references.

I. Introduction

Russian researchers made their pioneering studies on mathematical modelling of the decomposition of explosives in the 1920s – 1930s when N N Semenov, Ya B Zel'dovich and D A Frank-Kamenetskiy had solved the simplest problems in the macrokinetics of thermal explosion and combustion. The invention of first-generation computers made it possible to numerically solve complicated problems in the decomposition macrokinetics of explosives, which are described by a system of nonstationary differential equations, and gave a strong impetus to the development of research in this field. Modern computational facilities allow one to study elementary steps of the decomposition kinetics and mechanisms of explosives by quantum chemical, Monte Carlo and molecular dynamics methods.

Such investigations provide information on relationships between the reactivity of explosives and their molecular and supramolecular structure and aggregation state, on the character and intensity of external physicochemical factors acting on matter and on the mechanisms of combustion and detonation. Studies on the decomposition kinetics and mechanisms of explosives are also of great practical importance.[1, 2] To meet increasing requirements for the operating characteristics of explosives, one should develop a cheap method for fast testing of explosives using theoretical chemistry methods.[2]

The results obtained by domestic researchers in the early stage (from mid-1950s to the early 1990s) of investigations on the decomposition kinetics and mechanisms of explosives were considered in a monograph.[1] Analysis of the studies carried out at that time showed[3] that a number of basic and practically important problems in this field remain unsolved.

The state-of-the-art in theoretical chemistry offers new prospects for solving fundamental and practical problems concerned with investigations of thermal decomposition of explosives using mathematical modelling methods. A key problem to be solved by such methods is to obtain detailed information on the intra- and intermolecular bonds and on the changes in the molecular and supramolecular structures of explosives in the course of chemical reactions and phase transitions. Modelling of elementary steps of decomposition and the molecular structure of explosives usually involves quantum chemical calculations. The totality of elementary steps of decomposition reactions including processes occurring in the course of combustion and detonation is described by a nonstationary system of differential equations which is solved numerically.

In this review we will analyze the studies on mathematical modelling of the electronic, molecular and supramolecular structures of explosives, the mechanisms of elementary steps of the decomposition of explosives, the kinetics of multistep decomposition of explosives depending on their aggregation state and supramolecular structure, as well as on modelling of the combustion decomposition and detonation decomposition of explosives. The aim of the review is to outline prospects for the use of mathematical modelling in solving fundamental and applied problems in the design and applications of explosives. Publications which accumu-

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late the results of studies on mathematical modelling of the structure and decomposition of conventional and promising explosives with allowance for corresponding structure–reactivity relationships are scarce. Mention may only be made of a review [4] on the advances in modelling of combustion of solid fuels and a review [2] that outlines the results of application of theoretical chemistry methods in studies of the effect of compression on the initiation mechanism of reactions that lead to detonation.

II. Mathematical modelling of the structure and properties of explosives

1. The molecular structure

Theoretical chemistry methods allow one to determine the electron density distribution in the molecule of an explosive; this distribution governs the action of intra- and intermolecular forces, the molecular geometry, electrostatic potential and chemical bonding.[5] Establishment of correlations between the electronic structure and reactivity of reacting species is a fundamental problem in chemical physics. Methods of modelling of the electronic structure of reacting species include:

— classical molecular modelling by the Monte Carlo and molecular dynamics methods and

— first-principle quantum chemical calculations.

The state-of-the-art in theory makes it possible to carry out quantum chemical calculations of molecules of explosives and model compounds.[6–10] For instance, the ground-state and transition-state geometries, the Mulliken atomic charge distributions and the electric dipole moments of the simplest nitramine molecules were calculated.[6] Knowledge of these parameters and their variations due to intramolecular motions are significant when considering the chemical properties of compounds. Quantum chemical calculations of molecular force fields were reported [7] and the vibrational spectra of a number of nitro derivatives and simplest nitramines were analyzed. The structure of the potential energy surfaces (PES) of nitroso compounds in the ground and lowest excited electronic states, as well as the corresponding equilibrium geometric parameters, vibration frequencies and potential functions of internal rotation were calculated.[8] The bond lengths and bond angles in ammonium dinitramide $NH_4N(NO_2)_2$ in the gas phase were determined from *ab initio* molecular orbital (MO) calculations.[9,10]

Data on molecular conformations provide much better insight into possible channels of thermal decomposition of explosives. The molecular structures of hexogen and octogen in the gas phase were studied within the framework of the density functional theory (DFT).[11,12] The study of the molecular structure of hexogen in the gas phase revealed a number of conformers separated by rather low energy barriers from 6 to 20.5 kJ mol^{-1}. Therefore, the results of experimental determination of the molecular structure of hexogen in the gas phase correspond to the dynamically averaged structure owing to fast interconversion of conformers. According to calculations, in the gas phase dinitramide $HN(NO_2)_2$ can exist in two forms,[13] the secondary amine $HN(NO_2)_2$ being the most stable. The less stable form, $HON(O)NNO_2$, has four conformers.

Among seven possible tautomers of 5-aminotetrazole (5-ATZ), two isomers whose enthalpies of formation in the gas phase differ insignificantly (by 11.7 kJ mol^{-1}) are the most stable.[14] However, the activation barrier to monomolecular interconversion of these isomers is high ($\sim$210 kJ mol^{-1}) both in the gas phase and in melt. However, interconversion can occur owing to concerted double H-transfer in their dimers.

The conformational structures of methyl nitrate, methyl nitrite and ethyl nitrate were studied.[15,16] The most stable are the *cis*-form of methyl nitrite and the staggered conformation of methyl nitrate. Ethyl nitrate has three stable conformers, the *trans*-conformer being the most stable.

DFT calculations are used to determine the molecular structure of radicals and radical ions.[17] The calculated activation barrier to the formation of the *aci*-form of dinitromethane radical cation is 140.1 kJ mol^{-1}.

2. The supramolecular structure of explosives in the gas and liquid phases

Many explosives are polar substances. Molecules containing centres of intermolecular interactions can form hydrogen, dipole–dipole and other bonds whose energies vary from 10 to 60 kJ mol^{-1}.

Experiments [18] showed that molten 2,4,6-trinitrotoluene (TNT) contains both free TNT molecules and trimolecular associates. The formation of associates was also detected for dimethylnitramine and nitroglycerol.[19,20] At room temperature, the concentrations of nitroglycerol monomers, dimers, trimers and tetramers are in a 1 : 1 : 4 : 5.5 ratio.

According to quantum chemical calculations, molecular association leads to changes in the internuclear distances in the molecules of explosives. It was established [21] that a transition of dimethylnitramine from the gas phase to the crystal causes the N–N bond in the NNO_2 fragment to shorten from 1.38 to 1.26 Å and the N–O bond to lengthen from 1.22 to 1.25 Å.

Molecular association can influence the reactivities of the molecules owing to changes in the structure of the outer electron shells, to generation of a mutual arrangement of the molecules that favours (or precludes) a chemical reaction, and also owing to reduction of the molecular mobility.[22] The higher the concentration of intermolecular bonds the lower the molecular mobility of the system on the time scale commensurable with the lifetime of the labile bonds. Molecular association can affect not only the reactivity of components, but also the reaction mechanism. A number of high-melting, thermally stable explosives (nitropyrroles, nitro derivatives of pyridine, pyrazole and triazole, furazans, benzo- and pyridofuroxans) show an abrupt decrease in the activation energy of decomposition on going from the vapour to liquid state. This decrease, which can amount to 125 kJ mol^{-1}, is explained by the formation of associates, which creates prerequisites for changes from the radical to molecular mechanism of decomposition.[23]

Thus, association of the molecules of explosives can significantly affect their reactivity; however, the role of association is still to be clarified. In particular, it is believed [1] that association of the molecules of explosives under the decomposition conditions can be ignored. The assumptions of the effect of association of reactant molecules on the reaction kinetics are treated as hypotheses, although fruitful.[24]

In some cases, intermolecular interaction can be rather strong; according to quantum chemical calculations, associates of the molecules of explosives are formed even in the gas phase. For instance, in the gas phase ammonium dinitramide forms molecular complexes, the complex $[NH_3]\cdot[HN(NO_2)_2]$ being the most stable.[10] Gas-phase DFT calculations [25] predict the formation of 1,1-diamino-

2,2-dinitroethylene (FOX-7) dimers; the structure of the most stable dimer almost exactly matches its structure in the crystal.

The structures of 1,3,5-triamino-2,4,6-trinitrobenzene dimers, trimers and tetramers was studied theoretically.[26] It was shown that molecules of this compound can form charge-transfer clusters through intramolecular hydrogen bonds.

3. The supramolecular structure of solid explosives

Prediction of the crystal structure based on the molecular geometry offers prospects for calculations of the properties of explosives in the solid state, *i.e.*, makes it possible to choose an appropriate substance for particular applications prior to synthesis. Gas-phase quantum chemical calculations of isolated molecules were carried out for many explosives that form molecular crystals.[27–30] However, there are only a few studies on solid explosives. This is due to high computational cost. Indeed, the unit cell of a typical molecular crystal contains a large number of atoms and the computing time in electronic structure calculations is at least a cubic function of the size of the system. As a consequence, conventional DFT techniques are of very limited use.[31–33]

DFT calculations were used to determine the lattice parameters of the molecular crystals of octogen, hexogen, nitromethane and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowürtzitane (HNIW); however, the error of determination was large (from 0.2 to 1 Å) due to the fact that the functionals used ignore the van der Waals forces.[34] This severe drawback can be avoided by using new density functionals and/or relatively more complex computational schemes or semiempirical approximations for correlation of instantaneous dipole fluctuations.[35]

Quantum chemical calculations[36] of HNIW molecular crystals revealed a nonplanar environment of the amino nitrogen atom due to the presence of the lone electron pair. Therefore, the nitramine groups can adopt various conformations, while the lone electron pairs of different amine nitrogen atoms have different spatial arrangement and interaction potentials. The electron density distributions in the $\alpha(H_2O)$- and ε-conformers of HNIW (Fig. 1) and the effective atomic charges in different conformers were calculated. From the data in Fig. 1 it follows that the molecular structure of the $\alpha(H_2O)$-conformer of HNIW leads to excess electron density mainly on nitro groups, whereas in the ε-conformer, the charge is localized near the centre of the molecule. The dispersion and electrostatic components of the energy of intermolecular interactions for the HNIW polymorphs $\alpha(H_2O)$, γ and ε were determined; the energy of dispersion interactions was calculated using the '6-exp' potential. It was shown that in different polymorphs the contribution of dipole–dipole interactions is large and comparable with that of van der Waals interactions. This violates the principle of close packing of molecular crystals and the existence of loose HNIW polymorphs becomes possible. It was also shown that different polymorphs have considerably different energies of the van der Waals and dipole–dipole interactions; however, changes in the total energies upon phase transitions are close to zero. The experimental values of the $\alpha(H_2O) \rightarrow \gamma$ and $\varepsilon \rightarrow \gamma$ transition energies agree with the results of calculations.

A quantum chemical study of the energy characteristics of weak inter- and intramolecular interactions in crystals of 3-(2-hydroxyphenyl)-1,2,4-triazoles was reported.[37] The

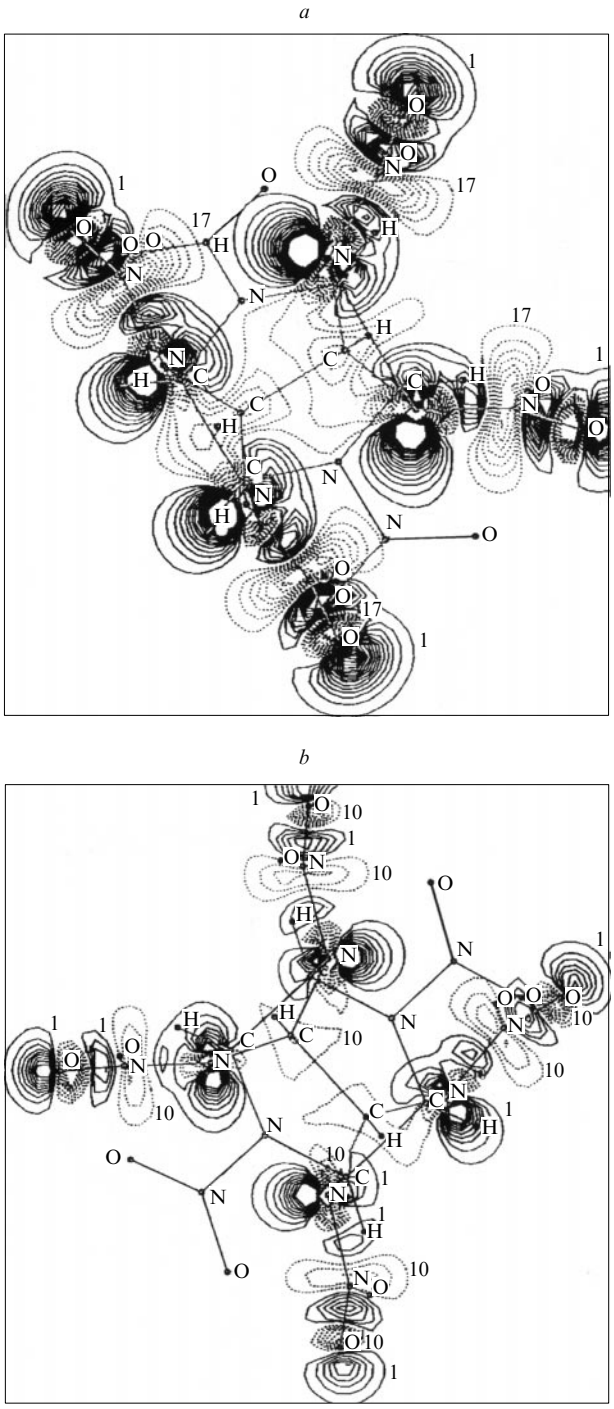


Figure 1. Electron density distribution in molecules of the ε- (*a*) and $\alpha(H_2O)$- (*b*) HNIW modifications.[36]

energies of hydrogen bonds in these compounds are strongly affected by the crystal packing effect, which leads to weakening of the intramolecular hydrogen bond owing to the competitive intermolecular interactions.

It was shown[38] that hydrogen bonds in 4-amino-1,2,4-triazol-5-one play a significant role in dimerization of the molecules and in the crystal packing. The average energy of the hydrogen bond in the dimer of this compound is twice as high as that of water dimer, *i.e.*, the amino group in 4-amino-1,2,4-triazol-5-one is a strong proton donor, while the oxygen atom of carbonyl group is a strong proton

acceptor. The $N-NH_2$ bond is labile and dissociates first on heating or under shock.

The energies of intermolecular interactions in the crystals of trimeric and dimeric molecules of 2-methyl-4-nitroaniline bonded by hydrogen or $\pi-\pi$-bonds were calculated [39] by the TDB3LYP/3-21G+ method. Owing to the size effect, intermolecular interactions in 2-methyl-4-nitroaniline dimers are weak compared to intermolecular interactions in the trimer.

The structures of the crystals containing functional groups with C, H, N and O atoms were calculated based on the potential of intermolecular interaction.[40] In 148 out of 174 systems considered, the predicted crystal structures of nitramines, nitro esters, nitroaliphatic and nitroaromatic compounds matched the experimentally detected configurations. A hybrid DFT technique providing a highly accurate geometry optimization and calculations of the energy of atom–atom interactions in the molecular crystals built of H, C, O, N, F and Cl atoms was developed.[41] On the average, the results of calculations deviate from corresponding experimental values by about 1%. A semiempirical model for the determination of the properties of crystals of organic salts based on their structural formulas was proposed.[42] The electronic energies of solid phases and clusters are calculated in an approximation which uses an approximate functional ignoring the electron orbitals instead of the exact kinetic energy functional used in conventional orbital-based DFT calculations.[43]

A high-precision quantum chemical procedure for calculating the thermodynamic and kinetic parameters of compounds containing C, H, N and O atoms was proposed.[44]

Nitrogen-rich energetic compounds (triazine, heptazine, triazole, tetrazine, tetrazole) have attracted the attention of many researchers due to high density, positive enthalpy of formation and high thermal stability.[45,46] These compounds are thought to be efficient precursors in fabrication of carbon nanospheres and carbonitride nanomaterials, gas generators, smokeless pyrotechnic fuels and fuels for microcombustion systems.

Successful application of quantum chemical calculations in screening of high-power explosives was demonstrated in studies on the determination of optimum molecular structure of the cage compounds N_x, N_xO_y and $N_8C_8H_8$.[47–49] Taking the N_{14} molecule whose cage consists of two pairs of tetragons sharing an edge as an example, it was shown that the introduction of oxygen atoms leads to transformation of the common N–N bond to the group N–O–N, strain relief and subsequent stabilization of the molecule (Fig. 2). A study on the design of high-density, high-power explosives based on binary azides aimed at the synthesis of $C(N_3)_4$ and the synthesis of $Si(N_3)_4$ was reported.[50]

Great potential of quantum chemical methods is used in calculations of the properties of particular molecules. Much less attention has been paid to the explanation for the results obtained using such fundamental notions in chemistry, as the chemical bond, molecular structure and mutual influence of structural fragments. Among a few studies in this field, noteworthy is a study [51] whose authors proposed a quantum chemical procedure for analysis of the electronic structure and physicochemical properties of complex molecules in terms of orbital interactions between molecular fragments. This approach as such was proposed earlier,[52] but was not systematically used in analysis of intramolecular interactions to distinguish between the key mechanisms

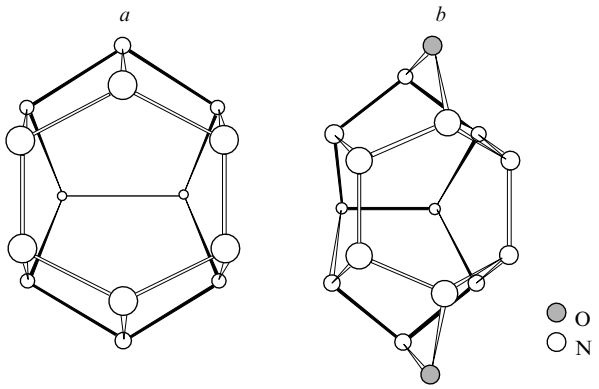


Figure 2. Molecular structures of N_{14} (*a*) and $N_{14}O_2$ (*b*).[48]

of the mutual influence of structural fragments in complex organic molecules (inductive effect, conjugation, *etc.*) and in studies of their correlations with physicochemical properties.

III. Mathematical modelling of elementary steps of decomposition

1. Gas-phase reactions of model compounds

To establish a relationship between the reactivity of explosives and their structure, aggregation state and supramolecular structure, one should know the rate constant, activation energy and pre-exponent in the Arrhenius equation for the primary elementary step of decomposition. Knowledge of these parameters is also needed for prediction of the stability of explosives on storage and for the determination of safe conditions for their synthesis and processing.

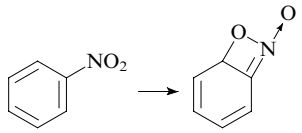
Usually, molecules of explosives contain a number of active (often, different-type) reaction centres. It is believed that, due to complexity of the molecular structure of real explosives, it is convenient to begin investigations of relationships between their reactivity and the molecular and electronic structure with studies of simple molecules having a single reaction centre. However, one should keep in mind that the results obtained should be transferred to actual explosives with a great care because the interaction of atomic groups in the molecule of a real explosive causes redistribution of the electron density between them.

Khrapkovskii *et al.*[15–17,53–66] carried out DFT studies of the primary steps of gas-phase decomposition reactions of some model C-, O- and N-nitro compounds including nitroalkanes, nitroalkenes, aromatic and heteroaromatic nitro derivatives, nitramines and nitroesters. They determined the molecular structures of the compounds under study, the atomic charge distributions, the enthalpies of formation, the activation energies and the enthlapies of reactions of monomolecular thermal decomposition.

A review [66] includes systematized data on the mechanisms of gas-phase monomolecular decomposition of model C-nitro compounds (nitroalkanes, nitroalkenes and nitroarenes) obtained from quantum chemical calculations. The authors of that review considered specific features of competition between different mechanisms and the effect of the molecular structure on the changes in the Arrhenius parameters of the primary step of the reaction. It was established that, generally, the primary step of decomposition of aliphatic C-nitro compounds can be a homolytic dissocia-

tion of the $C-NO_2$ bond, elimination of nitrous acid, a nitro–nitrite rearrangement and decomposition *via* the *aci*-form of the nitro compound.[57,58,66] The decomposition of nitroalkenes can begin with homolytic dissociation of the $C-NO_2$ bond, elimination of nitrous acid, nitro–nitrite rearrangement and decomposition *via* the *aci*-form and *via* the 1,2-oxazete-2-oxide ring.[63,66] As the temperature of thermal decomposition of nitroalkenes increases to 400–500°C, homolytic dissociation of the $C-NO_2$ bond becomes the main route due to positive entropy of activation of this reaction.[57,61,63,66] Studies on the mechanism of gas-phase decomposition of the simplest aminonitroethylenes (models for the explosive FOX-7) showed [53,66] that the most probable reaction channel involves the formation of substituted oxazetes in the limiting stage.

Thermal decomposition of aromatic nitro derivatives can begin with homolytic dissociation of the $C-NO_2$ bond, nitro–nitrite rearrangement and formation of a bicyclic intermediate.[60,66]



Owing to high activation entropy the decomposition by the radical mechanism proceeds faster. On lowering the temperature, the contribution of nitro–nitrite rearrangement increases.

The results of studies of the simplest alkyl nitrates and alkyl nitrites were reported.[15,16] It was established that differences between the dissociation energies of the $O-NO_2$ and $O-NO$ bonds and the barriers to elimination of HNO (for methyl nitrite) and HNO_2 (for methyl nitrate) are low. Decomposition of ethyl nitrate by the radical mechanism can be accompanied by elimination of HNO_2 or HNO_3 followed by a conformational transition from the *trans*- to *gauche*-conformation.

The effect of the molecular structure on the changes in the pre-exponent (A) in the Arrhenius equation was studied taking gas-phase monomolecular radical decomposition of aliphatic alcohol *O*-nitrates with abstraction of NO_2 group and non-radical decomposition with elimination of HNO_2 and HNO_3 as examples. According to calculations,[54] elimination of HNO_2 cannot compete with the homolytic dissociation of the $O-NO_2$ bond first of all because of lower A values because the activation enthalpy of elimination is only 4–6 kJ mol^{-1} higher than the energy of this bond.

The activation barriers to bimolecular decomposition of nitroalkenes as the most probable channel of thermal decomposition of these compounds in the liquid phase and in the gas phase at high pressures was evaluated by quantum chemical methods.[57,60,62] According to calculations, bimolecular and monomolecular decomposition of nitroalkenes can compete with each other. For instance, the activation barriers to the rate-limiting steps of bimolecular decomposition of nitroethylene are nearly 50% of the activation barrier to isomerization to the 1,2-oxazete-2-oxide ring.

In most studies on mathematical modelling of thermal decomposition of model gaseous *N*-nitramines it is assumed that the primary step of the reaction is homolytic dissociation of the $N-NO_2$ bond. Theoretical investigations [55,56] of alternative mechanisms of gas-phase decomposition of primary *N*-nitramines revealed that energetically the most favourable reaction channel involves isomerization with the formation of the *aci*-form by intramolecular hydrogen transfer from the amino nitrogen atom to the nitro group with subsequent cyclization of the *aci*-form followed by elimination of water and formation of nitrogen and aldehyde.

A DFT and *ab initio* MO study [67] of possible mechanisms of gas-phase decomposition of $HN(NO_2)_2$ showed that the isomer $O_2NNN(O)OH$ formed upon proton transfer and its conformers can undergo interconversions owing to inter- or (more slowly) intramolecular proton transfer. It was established that the decomposition begins with abstraction of NO_2 from the $HN(NO_2)_2$ molecule or its isomer.

Pivina and co-workers studied how the mechanism of gas-phase thermal decomposition of C- and N-nitro compounds is related to the functional environment of the NO_2 group.[68–77] The most probable mechanism of thermal decomposition was chosen based on the results of DFT calculations of activation energies (E_a) ignoring the value of the pre-exponent A. Analysis of the results obtained in theoretical studies of the decomposition mechanism of C- and N-nitro compounds revealed a significant role of isomerization of the starting nitro compound in the primary step of thermal decomposition.[69] It was established that not only the radical mechanism, but also the nitro–nitrite rearrangement, prototropic rearrangement with the formation of the *aci*-form and isomerization to 1,2-oxazet-2-oxide ring are possible. When discussing the decomposition mechanism, it was assumed that the radical mechanism of the primary act of decomposition corresponding to a large activation volume becomes unfavorable for the gas-phase decomposition at high and ultrahigh pressures. Classification [68–77] of nitro compounds depending on the features of the functional environment of the nitro group made it possible to determine both possible and preferred mechanisms of the primary step of decomposition for all structural types in question. However, the conclusions drawn [68–77] are qualitative and no quantitative relationships between the kinetic characteristics of reaction and the functional environment of the NO_2 group were reported.

Note that in discussing the accuracy of calculations the calculated activation energy is often compared with the E_a value determined by the methods of formal kinetics.[66,69] However, there are no grounds for *a priori* treatment of the theoretically determined rate constant for the primary elementary step (*i.e.*, activation energy) as equal to the rate constant k_{exp} (activation energy) for the overall process, which is determined by the methods of formal kinetics.[3] Experimentally, the E_a values are usually determined with a large spread which amount to, *e.g.*, 43.5 for hexogen (gas phase) and even 108.8 kJ mol^{-1} for tetril (melt).[78] Therefore, there is no problem to choose an experimental activation energy value equal to the value obtained from theoretical calculations; however, this equality does not characterize the accuracy of calculations. It should also be noted that often the decomposition of explosives initially follows a number of competitive channels at comparable rates.[3]

2. Model reactions

Kinetic studies of those elementary steps of a complex mechanism of thermal decomposition that follow the primary step of decomposition of explosives are necessary for mathematical modelling of the kinetics of the overall

process. This problem has attracted relatively little attention so far.

Isomerization of nitrogen tetroxide

$$O_2N-NO_2 \rightleftharpoons ONO-NO_2$$

in the gas phase was studied, the energy barrier and the Gibbs free energy were determined and the effect of water on the activation parameters of the reaction was considered.[79] It was established[80] that nitrosyl nitrate $ONO-NO_2$ exhibits oxidative properties owing to the appearance of nitrosonium cations NO^+ in the reaction

$$ONO-NO_2 \rightleftharpoons NO^+ + NO_3^-.$$

The isomerization

$$HNO \rightleftharpoons HON$$

was studied and it was shown[81] that water molecules favour the occurrence of the process and that the preferred channel involves three water molecules.

Clearly, reactions involving the major intermediates of decomposition reactions have been poorly studied so far. A theoretical study of the interaction of CH_2OH radical with NO_2 revealed a total of 14 components and 28 transition states.[82] The process begins with barrierless formation of adduct $HOCH_2NO_2$, which then decomposes by the mechanism of concerted reactions involving dissociation of the C–N bond and H-shift to give CH_2O and HONO; this agrees with experimental data. Less probable is the formation of adduct $HOCH_2ONO$ followed by dissociation of the C–N bond and then C–O bond.

A ground-state PES study[83] of the system $NH_2 + NO_2$ showed that barrierless association of these two radicals results in NH_2NO_2 and NH_2ONO. Subsequent decomposition of these intermediates gives H_2O, N_2O, H_2NO and NO. The PES of the low-lying singlet and triplet states of the simplest nitramine NH_2NO_2 (an intermediate of the decomposition of hexogen, octogen and other explosives) were studied.[84] The PES of the reaction of NN–H radicals with atomic oxygen was studied in detail.[85] Three adducts with the formula N_2OH were located on this PES, *viz*., ONHN, *cis*-ONNH and *trans*-ONNH. The channels of the reaction resulting in NO + NH, $N_2O + H$, $N_2 + OH$ and HNO + N were characterized. The rate constants for each channel were calculated using the Rice–Ramsperger–Kassel–Marcus theory. The enthalpy of formation of NN–H radical was determined and it was shown that the reaction of NN–H with an oxygen atom does not contribute largely to the formation of NO in combustion of any system containing these radicals.

According to quantum chemical calculations,[86] the decomposition of nitramines involves bimolecular reactions between the starting compound and final products. It was established[87] that NO_2 can be oxidized by hexogen or primary products of its decomposition to NO_3 both thermodynamically and kinetically.

3. Decomposition of explosives in the gas phase

The primary steps of decomposition of urea nitrate, $HN(NO_2)_2$, $NH_4N(NO_2)_2$, HNIW, hexogen, octogen, organic azides and some other conventional and promising explosives in the gas phase were studied by the DFT and *ab initio* methods.[88–98]

Electronic structure calculations of urea and urea nitrate in the gas phase were reported.[91,92] It was established that in the gas phase urea nitrate has two isomers and each of them is an eight-membered acid–base complex stabilized by two hydrogen bonds formed by the nitric acid proton and the urea nitrogen or oxygen atoms. The calculated hydrogen bond energies are 57.3 and 34.3 kJ mol^{-1} and the standard enthalpies of formation of the isomers are −429 and −155 kJ mol^{-1}, respectively. In both isomers, double proton transfer within the hydrogen bonded cyclic structure can occur with ease. In such case, HNO_3 plays the role of a catalyst. The nitric acid-catalyzed decomposition of urea to HNCO and NH_3 is the most probable decomposition channel of urea nitrate while NH_3, HNCO, HNO_3 and ammonium nitrate are the major primary products of decomposition. Mathematical modelling allowed one to determine[91] the order of the elementary steps of the urea nitrate decomposition involving one intermediate and two transition states (TS1 and TS2) with successive elimination of NH_3, HNCO and HNO_3. The primary step of decomposition is intramolecular transfer of a proton from one amino group to the other resulting in NH_3. The TS1 state is a four-membered ring. The intermediate formed after proton transfer undergoes a transition to TS2. No four-membered ring N–H–N–C is formed in the case of $(NH_2)_2COH^+$, which is the ground state of crystalline urea nitrate; therefore, it is assumed that the decomposition of a crystal of this compound should be initiated by some external factor (heating or shock) to break down the 2D network of strong hydrogen bonds in the crystal structure.

The PES profile of the primary steps of ammonium dinitramide decomposition in the gas phase is shown in Fig. 3. Cleavage of the hydrogen bond in $NH_3 \cdot HON(O)NNO_2$ and elimination of NO_2 result in an intermediate, HON(O)N, which can undergo transformation to $HNNO_2$ *via* H-shift (activation barrier is 143.2 kJ mol^{-1}). Decomposition of HON(O)N and $HNNO_2$ can produce $HN + NO_2$, $OH + N_2O$, HNO + NO. Decomposition of $NH_3 \cdot HN(NO_2)_2$ begins with cleavage of the hydrogen bond and leads to $HNNO_2$.

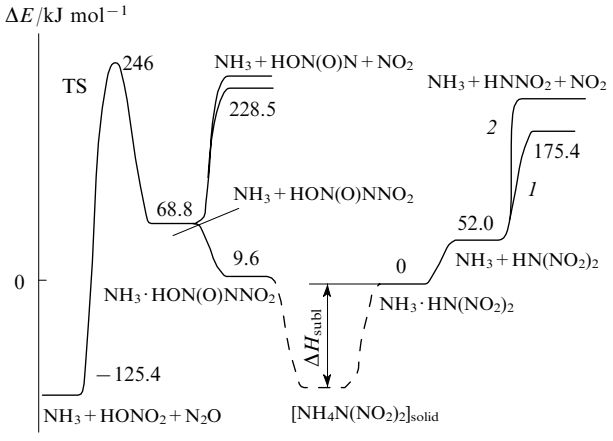


Figure 3. Ammonium dinitramide PES profile calculated at the MP4(SDQ)/6-31 + G(d,p)//MP2/6-31G(d) (*1*) and -G1 (*2*) levels of theory.[9]

Based on the results of theoretical calculations, two main decomposition mechanisms of organic azides were proposed:[93–95]

1) release of N_2 with the formation of imine

$$RCH_2N_3 \longrightarrow RCH{=}NH + N_2;$$

2) formation of a cyclic transition state in which a proton or alkyl group are transferred to the electron-deficient nitrogen atom. In addition, the sequence of elementary steps, the number and type of intermediates and transition states and the activation energies of different steps were determined. However, in most cases the pre-exponent A was not calculated.

The energies of bond dissociation in hexanitrostilbene and a number of its derivatives were determined by the DFT/B3LYP-31G* method.[96] It was shown that the $C-NO_2$ bond is the weakest in the nitro and amino derivatives of this compound, whereas decomposition of the hydroxy derivatives begins with isomerization involving transfer of hydrogen atom from the $H-O$ bond.

The stability of *ortho*- and *para*-substituted phenylpentazoles was studied by the DFT method.[97] It was established that the decomposition of phenylpentazoles with the formation of N_2 and a corresponding azide is a first-order reaction. The stability increases with an increase in the electron-donating character of substituents and decreases upon introduction of electron-donating groups into *para*-position.

Mathematical modelling of the primary steps of thermal decomposition of 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one dimer by the DFT method showed that the energy barrier to elimination of CO_2 is 369 kJ mol^{-1} and the sequence of elementary steps involves the formation of four intermediates and five transition states.[98]

According to quantum chemical calculations,[14] exact description of the primary step of thermal decomposition of 5-aminotetrazole can be obtained only if the formation of H-bonded dimers and their subsequent transformations are taken into account. The energy barriers to reactions involving dimers are lower than the barriers to monomolecular reactions of decomposition of 5-aminotetrazole.

Using quantum chemical methods,[99] one can calculate the rate constant for an elementary reaction; however, the problem of quantitative correlation between the reactivity, structure and physical properties of reactants remains unsolved.

An example of successful application of mathematical modelling to investigations of the gas-phase decomposition kinetics and mechanism of explosives is provided by complex (theoretical and experimental) investigations of the decomposition of ammonium dinitramide. An almost complete description of the mechanism and kinetics of the process (including parameters of the Arrhenius equation) was reported in a review.[100] Note that out of 218 elementary steps of the decomposition of this compound only 37 (17%) involve an increase in the number of species, 14 steps (6.5%) lead to a decrease in the number of species and the remaining 167 steps have no effect on this parameter. However, each elementary step contributes to the kinetics of the process, which is determined by the rate constant for this step and its role in the reaction mechanism irrespective of the character of changes in the number of species. Thus, the data on the decomposition mechanism of ammonium dinitramide (see above) provide a convincing proof that the kinetic results obtained manometrically, by monitoring the course of the decomposition from the change in pressure (*i.e.*, the number of species) in the closed volume, are only approximate characteristics of the reactivity of explosives.

4. Decomposition of explosives in the condensed phase

Main approaches developed in theory of liquid-phase reactions (numerical modelling by the Monte Carlo and molecular dynamics methods, studies of Langevin stochastic equations, Fokker–Planck equation, Bohm–Gross kinetic equation) have been considered in detail in a review.[101] The publication provides an overview of the advances in theory and demonstrates the potential and limitations of mathematical modelling of elementary steps of liquid-phase reactions taking calculations of the rate constants for particular reactions, including reactions with electron transfer, as examples. However, some features of liquid-phase processes (formation of dissipative structures, effect of the supramolecular structure on the reaction dynamics) were not considered.

Compared to the data on gas-phase decomposition of explosives, data on the elementary steps of the decomposition of explosives in the condensed phase are scarce and less reliable.[1,3,102] For instance, no substantiated chemical schemes of liquid-phase decomposition of some classes of explosives are available; also, opinions are different as to true reasons for different decomposition rates of compounds from some classes of nitro compounds in the gas and liquid phases.[103] One should keep in mind that the reaction mechanism can change on going from the gas phase to the liquid state,[102] but even if the elementary reactions remain unchanged, the physics of the reactions in the condensed phase is significantly different from that of gas-phase reactions. Namely, the ratios of the rates of competing reactions, the rate-limiting steps and the physical meaning of the kinetic constants are often changed. Investigations of decomposition in the condensed phase by the methods of formal kinetics are complicated if gaseous products are formed in the course of the process. Differences between the mechanisms of decomposition in different phases ignoring the distribution of reaction products (and sometimes, reactants) between the phases lead to dependence of the reaction kinetics on the ratio of the mass of the sample (m) to the volume of the reaction vessel (V). The problem of the influence of experimental conditions (in particular, the m/V ratio) on the results of formal kinetic studies has been discussed in the literature, but with no much effect.

Mathematical modelling of the decomposition of explosives in the condensed phase by quantum chemical methods has attracted little attention so far, being too labour-consuming. Nevertheless, it should be noted that the quantum chemical approach can be used in studies of the supramolecular structure of explosives. For instance, mathematical modelling allows one to calculate the thermal stability of associates of the molecules of explosives in the liquid phase and to take into account the effect of molecular association on the kinetics of the primary steps of decomposition.[91,98]

The effect of the molten state on the thermochemistry, rate constants for and energy barriers to different steps of the decomposition of 5-aminotetrazole was taken into account [14] by calculating the free energy of solvation determined by the B3LYP/6-311G(d,p) method within the framework of the PCM model.[104]

Investigations of the decomposition of explosives are closely related to such a fundamental problem in chemical kinetics, as the development of a physical model for solid-phase reactions with allowance for phase formation and phase transitions. Solid-phase decomposition of explosives is accompanied by the formation of gaseous products

followed by their separation into an individual phase. The kinetics of solid-phase decomposition of explosives depend on the free volume of the crystal, on the type of free volume elements (vacancies, vacancy clusters, micropores, *etc.*) and their evolution in the course of decomposition. In the literature, mathematical description of the formation of a new phase has attracted considerable attention.[105,106] Mathematical description of nucleation and growth of vacancy pores in crystals [106] is based on the kinetic equation for the formation of a new phase (see Ref. 107). The size of vacancy aggregates that form a specific kind of clusters, *viz.*, vacancy pores (negative crystal) is tens and hundreds of lattice constants. The vacancy distribution near each vacancy pore is inhomogeneous (a vacancy 'gas' cloud). The diffusion supply of vacancies and their deposition on pores cause the pores to move and grow. The main processes leading to changes in the pore distribution in supersaturated vacancy 'gas' are condensation, evaporation and surface diffusion of vacancies, as well as coagulation of pores. A closed kinetic equation for the description of the evolution of vacancy pores in the size space and in the coordinate space under γ-irradiation was derived.[106]

Detailed description of the primary step of thermal decomposition of explosives in the solid phase by mathematical modelling methods that would into account modern solid-state physics concepts of the actual crystal structure, is still unavailable. Decomposition of explosives accompanied by the formation of solid and gaseous products at high conversions, when separation of solid products into individual phase determines the steady-state development of the process, was considered.[108] Expressions for the interface velocities, characteristic width of the reaction zone and the concentration distribution were derived for the simplest case of a reversible first-order reaction ignoring defectiveness of the crystal structure and the effect of mechanical strain and deformations within the crystal on the reaction rate.

A dislocation-chain mechanism of decomposition of crystalline explosive was proposed [1,109] and a mathematical model for propagation of the reaction front was formulated in the steady-state approximation. According to this model, decomposition of an explosive occurs on dislocations, which are multiplied under the action of mechanical strain. The model ignores diffusion of reaction products, provides no substantiation for the form of the dependence of the dislocation multiplication rate on strain and concentration of dislocations, leaves the mechanical problem out of consideration and has an arbitrary specification of stress distribution. Also, the model ignores relationships between the stress-strain state of the crystal, the fracture micromechanics and the pressure of gaseous products, as well as some steps of plastic deformation of a crystalline material [110,111] such as annihilation of dislocations, mutual trapping of dislocations in intercrossing slip planes, absorption of dislocations by grain boundaries and multiplication of dislocations due to double cross slip. The model assumes that the decomposition rate is proportional to the concentration of dislocations; however, this contradicts experimental data.

At present, quantum chemical approaches for modelling the kinetics of primary steps of solid-phase decomposition of explosives are being developed.[26,43,91,112,113] In particular, it was proposed to carry out DFT calculations using an approximate kinetic energy functional without detailed consideration of electron orbitals instead of exact orbital-based kinetic energy functional.[43] A nonempirical approximate density functional for exchange energy was reported.[113] The main idea of the Coarse-Grained Chemical Reaction Model (CGCRM) approach elaborated for better understanding of complex multiscale phenomena occurring on different time and length scales consists in neglect of insignificant fragments of the system or replacement of an atomic group by a functional group on the longer scale of the computational model.[114] This approximation allows one to overcome the temporal and spatial limitations of computer modelling on the atomic level without losing information on the microlevel. It was used in studies of a system consisting of 130 000 molecules that could participate in 12 different reactions; a total of about 118 000 chemical acts were modelled.

Carrying out mathematical modelling of spatially distributed physicochemical processes, one should take into account various fluctuations. The collective behaviour of a system is determined by the local behaviour of its components. If the system becomes inhomogeneous due to fluctuations, all averaged variables, which can correctly characterize the state of the entire system, are difficult to determine. An efficient tool for solving such problems is the use of probabilistic cellular automata, in particular, the Direct Simulation Monte Carlo (DSMC) technique.[115]

IV. Mathematical modelling of multistep decomposition of explosives

Studies of the kinetics and mechanisms of decomposition of model and real explosives, transformations of intermediates to final products, and specific features of combustion and detonation of explosives require construction of mathematical models of multistep chemical reactions. Decomposition of explosives is described by a complex kinetic scheme including from a few hundreds (ammonium dimitramide) to a thousand (ammonium perchlorate) of steps.[100,116] Various mathematical modelling methods can play a significant role in determining still unknown reasons for specific features of the kinetics of multistep thermal decomposition of explosives.[3]

A methodology for computer modelling of multistep thermal decomposition mechanisms of various classes of nitro compounds was developed.[68–77] In the framework of this approach, decomposition of starting compounds and interactions of intermediates in the reaction medium are described in the form of expert rules (reaction generators) which are used for sorting various combinations of the starting compounds and the structures of intermediates formed in the thermal decomposition of explosives. This methodology and corresponding software allow one to model complete reaction mechanisms of thermal decomposition of various types of nitro compounds. The most probable channels of thermal decomposition are determined based on the results of E_a calculations for the corresponding elementary reactions ignoring the A value. In essence, this principle is based on the admission of equal values of the pre-exponents A for the channels under consideration. Meanwhile, it was empirically established that usually the higher E_a the higher A and *vice versa* (so-called compensation effect), *i.e.*, the most probable channel can be determined only if both E_a and A are known. Experiments also showed that decomposition of explosives can simultaneously proceed by several concurrent channels at similar rates even in the initial step.[3] If the competing elementary

steps of the overall process have different activation energies, changes in temperature cause the contributions of these steps to the overall process to change.

Mechanisms of thermal decomposition of some C- and N-nitro compounds were modelled.[68–77] In particular, the decomposition mechanism of 3(5)-nitro-1,2,4-triazole was studied;[69,72] a number of tautomers are possible for this compound. It was established that the mechanisms of their decomposition are similar. Calculations predict the lowest thermal stability for the *aci*-nitro-tautomer of 3(5)-nitro-1,2,4-triazole. Its decomposition is energetically more preferable compared to other tautomers. Possible decomposition channels include homolytic abstraction of hydroxyl radical (channel I, E_a = 194 kJ mol^{-1}), breakdown of the 1,2,4-triazole ring with elimination of nitrogen (channel II, E_a = 232 kJ mol^{-1}), C—N bond dissociation (channel III, E_a = 381 kJ mol^{-1}) and abstraction of an oxygen atom in the *aci*-nitro fragment (channel IV, E_a = 309 kJ mol^{-1}). As an example, Fig. 4 presents a fragment of the computer-generated thermal decomposition mechanism of the *aci*-nitro-tautomer of 3(5)-nitro-1,2,4-triazole proceeding by channel I. Modelling showed that not only the experimentally detected [N_2, N_2O, NO, CO_2, HCN, HNCO, 3(5)-nitroso-1,2,4-triazole and 1,2,4-triazolone],[117] but also some other products can be formed.

Considerable attention has been paid to the discussion of the mechanisms of multistep decomposition of model C-nitro compounds to elementary, experimentally detectable products.[66]

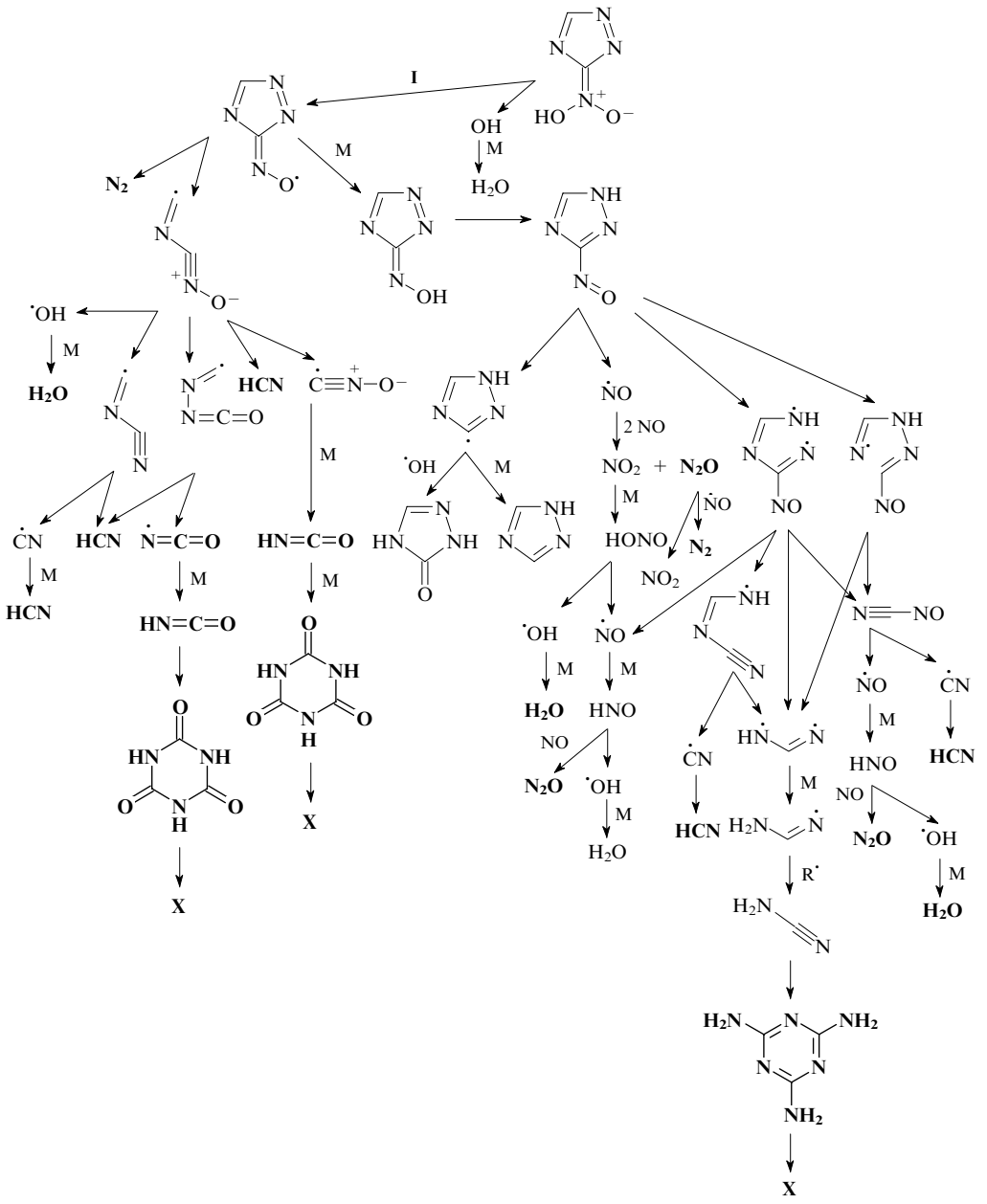


Figure 4. Fragment of computer-generated mechanism of thermal decomposition of *aci*-nitro-tautomer of 3(5)-nitro-1,2,4-triazole.
The primary step is homolytic abstraction of hydroxyl radical (channel I).[72] M is molecule, R is radical and X is the condensed residue. The experimentally detected decomposition products are given in semi-bold.

Multistep character of the reaction mechanism including reversible, concurrent and successive steps as well as catalysis by intermediates or final products leads to formation of spatial and temporal dissipative structures.[118, 119] In the former case, the distribution of reactants, rates of elementary steps and the overall process are spatially inhomogeneous on the microlevel. In the latter case, the concentration of intermediates and the rates of their formation oscillate with time in a regular or random fashion. As applied to explosives, the onset of oscillations was first experimentally detected in the decomposition of moist nitrocellulose,[120] then in the decomposition of some explosives in the presence of water and in decomposition of aqueous HNO_3 solutions.[121, 122] Spatial inhomogeneity of thermal decomposition of crystalline explosives was established experimentally.[1, 123] However, inhomogeneity of liquid-phase thermal decomposition of explosives has been studied neither experimentally nor theoretically.

The decomposition mechanism of explosives may include hundreds of elementary steps.[100] The state-of-the-art in modern theory of dynamic systems is such that it can offer efficient tools for analysis of the behaviour of reaction systems including the determination of their stability. Exact quantitative description of the evolution of a complex reaction system requires the use of numerical methods, knowledge of the reaction mechanism and the rate constants for each elementary step. Qualitative assessment of the behaviour of complex systems is simplified if one can combine groups of similar reactions and use analytical solutions to simple systems of differential equations.

Stability studies of reaction systems are important for both elucidation of reaction mechanisms and determination of the true rate constants for elementary steps of decomposition. If an attempt to describe a self-oscillating process using a kinetic model derived from a hypothetical mechanism fails, the mechanism either includes no appropriate steps or the values of certain rate constants for the steps considered are incorrect.

Investigations of the stability of a reaction system under the action of external factors are of considerable practical interest. The effect of external periodic perturbations on the initially steady-state or oscillating chemical reactions was analyzed.[119] In this case, interesting phenomena are possible, such as frequency locking of the vibrational system, quasi-periodic or stochastic response of the perturbed system, a resonance-type response of variables and their functions (*e.g.*, the dissipation rate), the formation of new saturated rings under the action of particular external noise and the appearance of transitions similar to phase transitions.

The shape of the kinetic curves of liquid-phase chemical reactions is significantly affected by the supramolecular structure of the liquid phase. Using mathematical modelling methods for the first- and second-order reactions and radical-chain reactions, the observed kinetic regularities were analyzed taking into account the effect of association of reactant molecules on their reactivity [124, 125] assuming an equilibrium between the monomer and associate concentrations. As a result of modelling, it was analytically established that the dependences of the apparent rate constant on the rate constants for elementary steps of the process, on the constant of equilibrium between associates and non-associated molecules, on the concentrations of the reactants and solvent and on the degree of conversion are nonlinear. The apparent rate constant (k_{ef}) can be significantly different from the true rate constants (k_n) for elementary steps of the reaction involving the monomer A_1 ($A_1 \rightarrow$ product) and dimer A_2 ($A_2 \rightarrow A_1 +$ product), whose concentrations are in equilibrium ($2A_1 \rightleftharpoons A_2$) characterized by the equilibrium constant K (Fig. 5). The main factors governing the kinetic regularities of the reaction include the type of the associate (self-associate, hetero-associate) and the number of types of associates. The temperature dependence of the apparent rate constant is described by a more complicated expression than the Arrhenius equation. This conclusion is of great importance if one should use a long-range extrapolation of experimental data. If the reaction medium contains not only monomers, but also two types of associates (*e.g.*, dimers and tetramers), this dependence may show an extremal character.

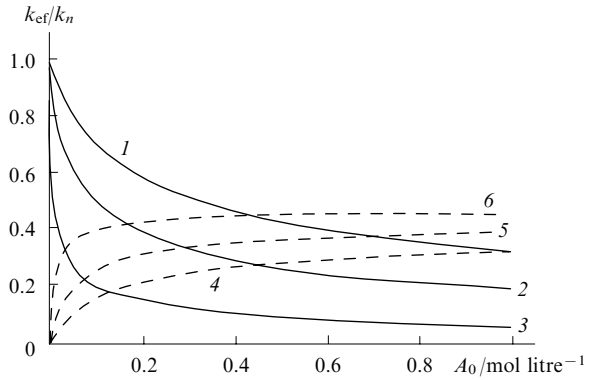


Figure 5. The k_{ef}/k_n ratio plotted *vs.* initial reactant concentration (A_0) at an equilibrium constant K of 3 (*1*, *4*), 10 (*2*, *5*) and 100 litre mol^{-1} (*3*, *6*); $k_n = k_1$ and $k_2 = 0$ (*1–3*); $k_n = k_2$ and $k_1 = 0$ (*4–6*).[124, 125]
Conversion $\alpha = 0$.

This approach allows one to determine the rate constants for elementary steps in the case of both non-associated molecules and associates, which is important for elucidation of the relationships between the reactivity and aggregation state of explosives.

V. Mathematical modelling of transformations of explosives in combustion and detonation

Combustion and detonation of explosives are complex physicochemical processes including multistep chemical reactions and physical processes, such as heat and mass transfer, phase transitions, deformation and destruction of explosives. By and large, the problem of mathematical modelling of combustion and detonation of explosives goes beyond the scope of this review and deserves particular attention because of huge body of information; therefore, we will dwell only on those aspects of this problem which are immediately related to the effect of the complex decomposition kinetics and mechanism of explosives on the regularities of combustion and detonation.

1. Mathematical modelling of transformations of explosives in combustion

Analysis of the results obtained in mathematical modelling of combustion of explosives showed that the Zel'dovich model, which assumes a single-step reaction kinetics and similarity between the temperature and concentration fields, cannot correctly describe specific features of the process,

which are due to complexity of the decomposition mechanism of explosives.[126] Moreover, in recent years, mathematical modelling of combustion of explosives has been more often carried out using multiphase models with detailed kinetic mechanisms rather than the models based on the kinetics with a small number of stages.[4, 126] It is assumed that in the future a complete combustion model should allow one to study not only the changes in the combustion rate, but also other characteristics, such as the spatial-temporal distributions of energy release, concentrations of the starting reactants, intermediates and final products, *etc*.

Most models for combustion of explosives with detailed kinetic mechanisms describe the process in the one-dimensional steady-state approximation.[4, 126] Flame structure modelling included 47 components and 283 elementary steps for hydrazinium nitroformate (a complex of nitroform with hydrazine),[127] 45 components and 232 steps for octogen, 35 components and 178 steps for nitroglycerol, 33 components and 179 steps for ammonium perchlorate and 33 components and 180 steps for ammonium dinitramide.[4] The gas-phase reaction mechanisms used provide quite a correct description of the combustion of many explosives. Owing to the lack of experimental data, chemical reactions in the condensed phase are represented by a few global steps; however, it is believed that they have a relatively little effect on the results of mathematical modelling because heat release mainly occurs in the gas phase.[4] The proposed mechanisms of chemical reactions in combustion of hexogen, octogen, nitroglycerol, ammonium perchlorate and some other explosives allow one to calculate the combustion rates, the temperature and concentration profiles for reactants, intermediates and final products in flame at variable pressure.[4]

However, it should be noted that the calculated and experimental concentration distributions in the combustion wave obtained for intermediates are qualitatively different. For instance, the results of modelling of combustion of hydrazinium nitroformate obtained assuming that the primary step involves a dissipative evaporation of this compound resulting in hydrazine and nitroform were reported.[127] Only monomolecular channels of nitroform decomposition were analyzed assuming that the rate-limiting step is the elimination of NO_2 from nitroform or its isomer $C(NO_2)_2N(O)OH$. A significant qualitative difference between the experimental data and theoretical results (Fig. 6) probably suggests that the mechanism and kinetic parameters of nitroform decomposition should be refined. In particular, oscillations on the experimental concentration distributions for intermediates can be explained by the formation of temporal dissipative structures.

Experimental studies of combustion of some explosives and model fuels (*e.g.*, the system 'hexogen – glycidyl azide polymer') also revealed random or periodic oscillations of the temperature and a region with the temperature exceeding the adiabatic temperature of flame.[128, 129] The authors of those studies believe that the observed phenomena are due to random reasons, such as the changes in the local oxidant/fuel ratio, inhomogeneity of the burning surface, formation of gas bubbles. A regular character of oscillations of the temperature distribution functions (Fig. 7), which represent a spatial scan of temporal oscillations, suggests that they are due to the same reasons as the oscillations of the concentration of intermediates. The reasons why the maximum temperature in the combustion is higher than the adiabatic equilibrium temperature were studied in more

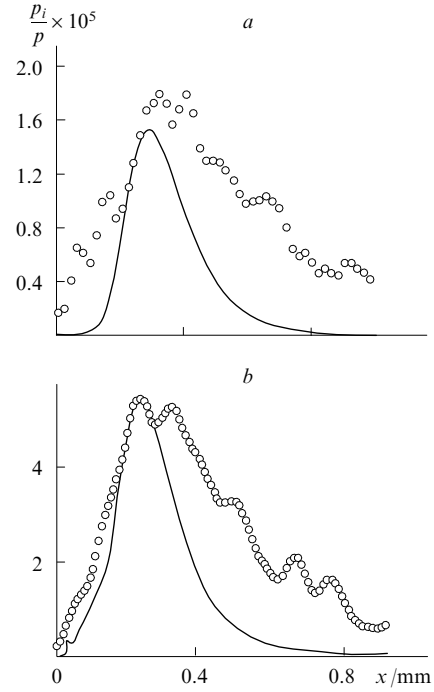


Figure 6. Distribution of CN (*a*) and NH (*b*) in hydrazinium nitroformate flame.[127]
Pressure is 10 MPa and the surface temperature is 623 K. Open circles denote experimental data, solid curves denote the results of calculations; p_i and p are the partial and overall pressure, respectively.

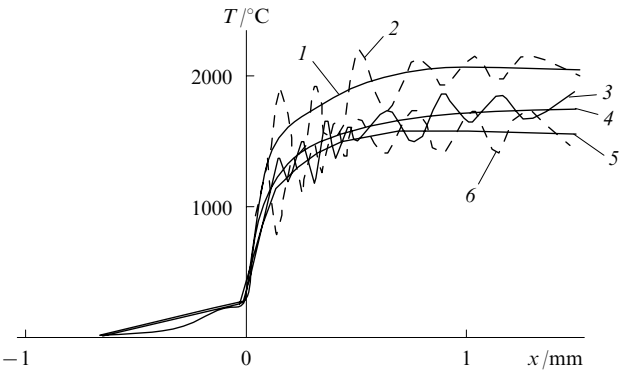


Figure 7. Averaged and real temperature profiles in the gas phase at combustion of hexogen at pressures 0.1 (*1*, *2*), 0.075 (*3*, *4*) and 0.5 MPa (*5*, *6*); initial temperature is 293 K.[129]

detail taking low-temperature flame of rich hydrocarbon – air mixtures as examples.[130–132] It was shown[132] that the nature of this phenomenon consists in the formation of an intermediate (atomic hydrogen), which diffuses from the zone containing no oxygen to the oxidation zone of flame and is oxidized there faster than the starting hydrocarbon. Note that the hybrid DFT method is used for detailed investigations of the mechanisms of chemical reactions in combustion of oxygen – hydrocarbon mixtures with allowance for chain branching.[133]

The assumption of relation between the temperature and concentration oscillations and the kinetics and complex mechanism of decomposition is also probably substantiated by the results of experimental studies of the effect of

sonication on the combustion rate. It was established that sonication leads to acceleration of combustion and the acoustic resonance is clearly pronounced. As was shown theoretically, the dependence of the amplitude of the changes in the rate of powder combustion on the frequency of changes in the pressure is described by a resonance curve.[134–136] The model used in these studies is based on the postulate that the fire bed is a vibrational system characterized by some eigenfrequency and that the action of external factors at a frequency close to the eigenfrequency leads to resonance. This is a phenomenological model because the physicochemical nature of oscillations is usually omitted. According to modern theory of complex chemical processes, the vibrational eigenfrequency of the fire bed depends on the reaction kinetics and mechanism.[119]

Thus, no complete description of combustion of explosives is available as yet, because the kinetics and mechanisms of decomposition reactions have been insufficiently studied not only for the condensed, but also the gas phase. A possible source of valuable information on the mechanism and kinetics of decomposition of explosives at combustion is a combination of experimental and theoretical approaches to investigations of non-steady-state combustion.[126]

2. Mathematical modelling of reactions of explosives at detonation

Studies of shock-initiated reactions of explosives make it possible to formulate an idea of the behaviour of these compounds at the molecular level at extremely high temperatures and pressures. In particular, this is necessary for better insight into the nature of detonation, elucidation of the mechanism of its action on matter at the molecular level and for detailed description of conversion of explosives into final products.

Detonation can be treated as a shock-initiated reaction wave propagating through the sample of an explosive at ultrasonic velocity. The physics of detonation has been substantiated theoretically and experimentally. The description of the kinetics and mechanisms of chemical reactions of explosives under shock, which leads to detonation, is unavailable owing to severe experimental difficulties and uncertainty in theoretical concepts of initiation of chemical reactions under these conditions. The main theory that explains experimental data on the shock initiation of detonation is based on the assumption that the leading role in this process is played by multiphonon pumping.[137, 138] The process begins with heating of phonons belonging to a continuum of low-frequency crystal lattice vibrations or to normal modes of the liquid. These phonons multiply annihilate, thus exciting high-frequency modes through intramolecular transfer of vibrational energy, which continues until localization of energy necessary for the reaction in the reaction centre of the molecule. Many theoretical studies (see, *e.g.*, Refs 139–141) are devoted to mathematical modelling of transfer of normal-mode vibrational energy in nitromethane because this compound has been best studied owing to small size of its molecule.

There are also a number of alternative theories. According to one of them, the key point in solid-state stage of a shock wave-initiated chemical decomposition of solid explosives are electronic excitations initiated by molecular distortions.[142] This theory is substantiated by the conclusions drawn in modelling of the effect of shock waves on molecular crystals. In particular, narrowing of the forbidden band under compression of explosives within the shock wave front was considered.[143] Electronic structure calculations for hexogen revealed a local narrowing of the forbidden band near dislocations and an additional narrowing at compression in the shock wave front, which leads to a significant increase in the probability of electronic excitation.[144] The results obtained agree with those of a molecular dynamics simulation[2] of electronic band structure of a compressed explosive, namely, it was shown that the loss of bond covalency under compression should be considered as the primary step of the sequence of reactions leading to detonation. Structural changes in pentaerythrytol tetranitrate crystals under hydrostatic compression were studied by the Hartree–Fock method.[145] It was established that crystals of this explosive are flexible, they accommodate the lattice contraction by shortening the bonds and by twisting and thus changing the bond angles.

Theoretical and experimental studies of the influence of static compression, twisting, plastic deformation on the structure and reactivity of inert compounds are carried out to elucidate details of post-effects of mechanical action on the chemical reaction. A ^{1}H NMR study[146] revealed intramolecular motions under plastic deformation of a molecular crystal; this can be related to jumps between enantiomers of distorted molecules. The energies of planar and nonplanar configurations obtained from DFT calculations suggest that changes in the electron density distribution under plastic deformation of the molecular crystal are accompanied by 50% narrowing of the forbidden band. Experimental investigations of model reactions showed the appearance of new intense absorption bands under adiabatic compression.[147] This was explained by transition from the ground-state (S_0) to excited-state (S_1) molecular geometry. *Ab initio* calculations[147, 148] predict in this case a qualitative redistribution of the electron density with reduction of orbital symmetry of the vibrationally activated molecules due to the Jahn–Teller and Renner–Teller effects. As a consequence, reactions forbidden by the Woodward–Hoffmann rule become possible.

Mathematical modelling of the kinetics of processes involving electronic-excited atoms and molecules is a topical avenue of research on the regularities of combustion and detonation.[149, 150] Investigations of the PES of reaction systems allow one to establish possible elementary reactions with electronically excited species and their rate constants. However, the technique is time-consuming and the PES calculations of excited species are difficult to perform even for small reaction systems including a few atoms. An approximate approach[150] based on the model of electronic-vibrational term allows one to estimate the energy barrier to reactions with excited molecules and their rate constants from the known rate constants for related reactions with ground-state molecules.

At the molecular level, a shock-initiated chemical reaction is described[151, 152] as a nonequilibrium non-thermal process whose rate is determined by the average vibrational velocity of radical pairs produced on molecular breakdown in 10^{-14}–10^{-12} s. The model is substantiated by the results of molecular dynamics calculations.[153]

Kinetic models for decomposition of explosives in a detonation wave based on the possibility of direct rupture of chemical bonds in molecules were proposed.[151, 154, 155] These models are based on the admission that a possible mechanism of cleavage of the chemical bond in a molecule in the shock wave front can involve direct transfer to the

bond of a kinetic energy higher than the bond dissociation energy.[151, 154] A molecular dynamics simulation of the destruction of TNT, hexogen, octogen, pentaerythrytol tetranitrate, 1,3,5-triamino-2,4,6-trinitrobenzene and nitromethane molecules under high-energy collisions was reported.[156] The times of kinetic energy redistribution over intramolecular vibrational modes were calculated. The probability of collisional destruction of the molecules of explosives in the detonation wave front was estimated. A possible breakdown mechanism (so-called accumulation mechanism) was considered. It assumes the possibility of localization of the kinetic energy of collision on a particular bond in the molecule. Conditions required for this mechanism to occur were established. Modelling of the destruction of TNT, hexogen and octogen molecules gave the threshold collision velocities, where the time taken to destroy the molecules is shorter than the intramolecular vibrational relaxation time. At particular orientations of colliding molecules, the minimum collision velocity corresponding to bond dissociation is $\sim 1.8-2$ times higher than the average mass velocity of matter in the chemical peak of strong detonation waves. It was assumed that the considered bond dissociation mechanism is realized in the interaction of a shock wave with micropores and crystal lattice defects in explosives, because when the shock wave reaches a free surface, its mass velocity is doubled.

Studies on mathematical modelling of shock wave-initiated decomposition of explosives with allowance for the mechanisms of chemical reactions are carried out. The pathways of monomolecular decomposition of hexogen, octogen and nitromethane under shock were studied by the DFT method.[34] A scheme of shock initiated decomposition of hexogen was proposed; it is based on experimental observations and results of quantum chemical calculations.[157] It is assumed that shock-initiated decomposition of hexogen involves dissociation of the $N-NO_2$ bond and formation of an N-centred radical, which then decomposes to NO_2 and HCNH radicals. This monomolecular scheme provides an explanation for some features of the process that are observed at low pressures in the shock wave and for the primary steps at high pressures in the shock wave. At long times and at pressures >10 GPa, a bimolecular reaction between hexogen and free-radical products is observed.

A number of studies on mathematical modelling of the macrokinetics of gas-phase detonation processes are based on model kinetic equations, because the use of the kinetics of detailed mechanism of a chemical reaction increases the computing time.[158] The results of modelling of detonation process in hydrogen–air mixtures for the kinetic reaction mechanism including 10 main components and 40 elementary chemical reactions were reported.[159] Conditions for the formation of a detonation structure and a cellular structure of the shock wave were established.

In mathematical modelling of the macrokinetics of shock wave-initiated decomposition of solid explosives one should keep in mind that these substances actually have a heterogeneous structure because they usually consist of polycrystals and their properties at the mesolevel differ from those of a single crystal due to the presence of internal boundaries. Three-dimensional modelling of shock effect on an ensemble of individual 'crystals' was carried out to study the compaction, deformation and chemical reactions in porous explosives.[160] Rapid deformation of particles at contact points was revealed; this causes large-amplitude fluctuations (wavelength of the order of a few particle diameters) of the stress-strain state. Localization of energy leads to the appearance of hot points. The chemical reaction is responsible for the formation of multiple wave structures governed by the particle size distribution.

Thus, at the molecular level the initiation mechanism of shock-wave induced decomposition of explosives is still unknown. Seemingly, its details can be elucidated using the notions and methods of femtochemistry, in particular, coherent chemistry methods involving experimental studies of nonequilibrium, non-thermal femtosecond and subpicosecond processes with participation of electronically excited molecules. According to concepts in femtochemistry,[161, 162] an elementary step of a reaction involving electronically excited molecules is a totality of intramolecular processes including intramolecular energy redistribution, transfer of an electron or proton, dissociation and formation of chemical bonds, conformational rearrangements, *etc.*, which occur on the femtosecond and subpicosecond time scales. These time scales are used in studies of intermediates for measuring their absorption spectra and lifetimes. For some types of intramolecular processes, the characteristic time scales were determined. Absorption of a femtosecond light pulse is followed by creation of a coherent vibrational wave packet in the reactant molecule. The wave packet is characterized by synchronous nuclear motions and localization of the excitation energy in a particular configuration space of the molecule (Fig. 8). If vibrations involved in a chemical reaction are excited, the reaction can proceed faster than stochastization of nuclear motions and 'spread' of the excitation energy over the entire molecule (coherent reaction), *i.e.*, it takes times shorter than 10^{-13} s. Otherwise, one deals with stochastic rather than regular nuclear motions and the reaction proceeds by a conventional mechanism. One can expect that stochastization of nuclear motions under detonation of solid explosives is difficult because high pressure and shear impose limitations on the number of degrees of freedom of nuclear motions owing to orientation of molecules and a decrease in the free volume. This assumption agrees with the experimental results reported by Enikolopov (see review [163]) who showed that shear deformation leads to considerable (by 3–8 orders of

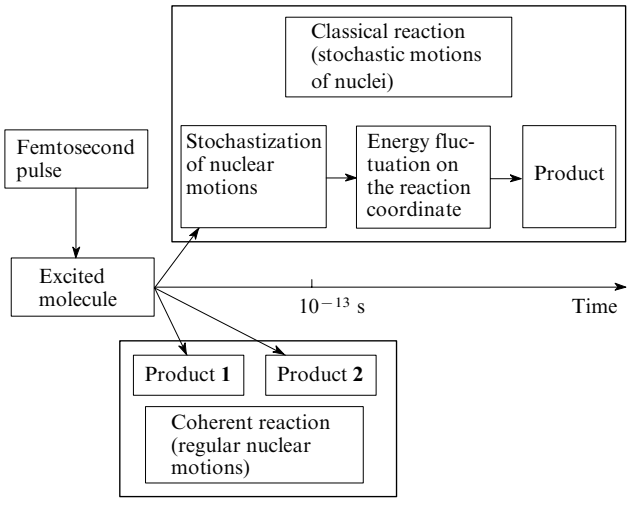


Figure 8. Scheme illustrating the position of coherent processes and reactions on the time scale of chemical reactions.[161]

magnitude) increase in the rate of solid-phase reaction compared to that of the liquid-phase reaction. It was assumed that under shear the detonation course of solid-phase reactions (even endothermic ones) occurs isothermally at low temperatures owing to interconversion of the chemical and mechanical energies.

An ultrafast laser shock study [142] proved that the shock wave initiated chemical reaction in poly(vinyl nitrate) takes about 10 ps including the primary step, *viz*., nitro group dissociation. This duration of the induction period is expected for the reaction mechanism involving transition of vibrational energy by multiphonon pumping. It also corresponds to the relaxation time of electronic excitation from high-excited vibrational states prior to dissociation. Other fast mechanisms, such as direct shock-wave excitation of high-frequency vibrations or direct electronic excitation and fast dissociation of the excited state, should require subpicosecond times, which contradicts the available experimental data.

Pre-explosion phenomena in secondary explosives were studied taking octogen as an example.[164] It was established that deformation and destruction of explosives in the course of initiation of explosion are local in character. Energy dissipation occurs at the so-called hot points. In the 'nucleation' step, a significant role is played by dislocations or their aggregates. A key role in this step is played by electronic excitations. Local narrowing of the forbidden band near dislocations under compression of explosives abruptly increases the probability of electronic excitation and dissociation of the $N-NO_2$ bond.[102, 165]

Analysis of data obtained by fast pulsed radiolysis and photolysis techniques made it possible to draw conclusions about the mechanism of elementary step of explosive decomposition of heavy metal azides and on the chain nature of the process.[166, 167] The following decomposition steps were proposed: hole localization on a cationic vacancy, reconstruction of the centre as a result of a chemical reaction with the formation of a quasi-local hole state in the valence band, hole delocalization from the reconstructed centre, multiplication of charge carriers as a result of shock ionization by 'hot holes' and recovery of the local state in the forbidden band, which creates prerequisites for repetition of this sequence of steps. The dependence of the critical density of the initiation energy of explosive decomposition of silver azide on the crystal size was studied. This allowed one to reveal an increased recombination frequency of electron–hole pairs on the crystal surface.[168]

The aforesaid suggests that the mechanism of the primary step of decomposition of explosives at detonation can differ from the conventional mechanism due to occurrence of reactions involving electronically excited molecules.

VI. Conclusion

Decomposition of explosives is a multistep redox reaction involving both electron-donating and electron-withdrawing atoms, which in initially are within the same molecule. The use of formal kinetic methods in the early stage of investigations on the decomposition kinetics and mechanism of explosives precluded solution of the most important problems. Recently, domestic researchers and their colleagues abroad have made considerable progress in studies of the decomposition of explosives using a combination of modern experimental methods, concepts of theoretical chemistry and computational facilities.

The use of mathematical modelling in the design of high-power, thermally stable explosives made the screening of chemical compounds faster and cheaper. This approach allows one to study the molecular structure and thermochemistry of explosives, the kinetics and mechanisms of their decomposition and transformations of intermediates to final products. It was established that initially the decomposition of explosives often follows a number of channels; therefore, the possibility of studying competing reactions in the primary step of decomposition by mathematical modelling methods is of great importance.

These methods also are also promising for investigations of the supramolecular structure of explosives: one can calculate the thermal stability of associates of the molecules of explosives in the liquid phase, take into account the effect of molecular association on the kinetics of primary steps of decomposition. Modern concepts of solid state physics have almost not been used so far in modelling the kinetics of primary steps of solid-phase decomposition of explosives; this precludes elucidation of the structure–reactivity relationships for solid explosives and prediction of the storage life of explosive goods.

Mathematical modelling methods are used in the determination of the regimes of transformation of explosives in combustion and detonation. In a number of studies, combustion is modelled with allowance for real complexity of chemical mechanisms. Great prospects in studies of the elementary steps of chemical reactions at detonation with allowance for excited molecules are offered in connection with progress in femtochemistry.

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