Russian Chemical Reviews **73** (11) 1121 – 1141 (2004) © 2004 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2004v073n11ABEH000869

Chemical physics of decomposition of energetic materials. Problems and prospects

L P Smirnov

Contents

I.	Introduction	1121
II.	Kinetics and mechanism of decomposition of explosives and oxidisers	1121
III.	Polymer networks as binders for solid propellants	1129
IV.	Mathematical modelling of decomposition of energetic materials	1133
V.	Stability prediction of energetic materials	1136
VI.	Conclusion	1137

Abstract. The review is concerned with analysis of the results obtained in the kinetic and mechanistic studies on decomposition of energetic materials (explosives, powders and solid propellants). It is shown that the state-of-the art in this field is inadequate to the potential of modern chemical kinetics and chemical physics. Unsolved problems are outlined and ways of their solution are proposed. The bibliography includes 235 references.

I. Introduction

The kinetic and mechanistic studies of decomposition of energetic materials (explosives, solid propellants and powders; hereafter, EMs) are first of all necessary for solving practical problems. Design of novel EMs, establishment of safe conditions for their synthesis, storage life calculations and control of the stability, combustion and detonation of EMs require knowledge of the mechanism of thermal decomposition and quantitative data for the description of the process over a wide temperature interval and for different states of aggregation. Studies on the kinetics and mechanism of thermal decomposition are necessary to solve not only technical problems but also some fundamental problems of chemical physics, *e.g.*, establishment of interrelations between the structure and reactivity of EMs, development of theoretical concepts of solid-phase reactions, understanding of the mechanism of combustion and detonation of EMs, *etc*.

Intensive research on the kinetics and mechanism of decomposition of explosives and powders began in the 1950s. Investigations on thermal decomposition of particular classes of explosives and model compounds, *viz*., aliphatic nitro compounds,[1] secondary nitramines,[2–4] nitro esters,[3,5] ammonium perchlorate,[6,7] *etc*., have been well documented. The results of thermal decomposition studies of the explosives mentioned above and some other compounds (organic difluoroamino compounds, furazans, furoxans, tetrazoles, ammonium nitrate and metal nitrates, hydrazinium and hydroxyammonium salts, metal perchlorates, nitric acid and perchloric acid) were summarised in a monograph.[8]

High demand for preparation of solid propellants and other polymeric materials including polymeric composite materials (PCMs) for civil purposes gave an impetus to studies on the physical chemistry of polymers. Considerable advances in this field were made by researchers belonging to the scientific schools headed by V A Kargin, N M Emanuel and N S Enikolopov; the most important results were reported earlier.[9–15]

In regard to design of solid propellants, studies on decomposition of explosives and powders were followed by investigations of destruction of polymer networks that are also widely used in national economy. The authors of monographs[9,15] also analysed the results of kinetic and mechanistic studies of molecular destruction of various classes of unfilled polymers (mostly linear carbochain polymers) exposed to heat treatment, various kinds of radiation, mechannical load and corrosive media and formulated the physical and chemical principles of stabilisaiton of these compounds. Studies of destruction processes showed that distinctions between linear polymers and polymer networks cause marked differences in character of molecular destruction of these compounds.[16–31]

In writing this review the author tried to present a critical analysis of the results obtained in the kinetic and mechanistic studies of decomposition of EMs in order to reveal unsolved problems and to compare the state-of-the-art in this field and the potential of modern chemical kinetics and chemical physics. Such a critical assessment for EMs has not been reported as yet, though it would be useful for outlining prospects for the development of this branch of chemical physics and for formulating and planning further research of decomposition of EMs.

II. Kinetics and mechanism of decomposition of explosives and oxidisers

1. Explosives and model compounds

A chemical reaction can be characterised both qualitatively by dividing into elementary stages (mechanism) and quantitatively by determining the corresponding rate constants; therefore, interrelations between the kinetics and mechanism are of great importance. At present, the mechanism of a complex chemical reaction is usually established using experimental data on the composition of the reaction system obtained from thermochemical measurements, while the rate constants for elementary stages of the process are determined from the results of measurements of changes in the concentrations of the starting compounds, inter-

L P Smirnov Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-096) 515 54 20. Tel. (7-096) 522 10 74.
E-mail: lsmirn@icp.ac.ru

Received 12 January 2004
Uspekhi Khimii **73** (11) 1210 – 1232 (2004); translated by A M Raevskiy

mediates and end products in the course of reaction. Usually, the reaction kinetics and mechanisms are studied in relation to the reactant concentrations and state of aggregation, temperature and other external factors. A combination of this approach and modern physicochemical methods (EPR, IR and NMR spectroscopy, gas-phase electron diffraction, gas-phase neutron diffraction, positron annihilation, *etc.*) has been successfully employed in, *e.g.*, studies on thermal destruction and oxidation of linear carbochain polymers.[9,15]

To date, hundreds of explosives and model compounds belonging to various chemical classes have been studied. Usually, the mechanisms of their decomposition are multistage. A characteristic example is provided by the decomposition of 1,1,1-trinitroethane vapours, which involves the following elementary stages:[1,8]

$$CH_3C(NO_2)_3 \longrightarrow CH_3\dot{C}(NO_2)_2 + NO_2, \quad (1)$$

$$CH_3\dot{C}(NO_2)_2 \longrightarrow CH_3\dot{C}O + NO + NO_2, \quad (2)$$

$$CH_3\dot{C}(NO_2)_2 + NO_2 \longrightarrow CH_3\dot{C}O + NO + 2NO_2, \quad (3)$$

$$CH_3\dot{C}(NO_2)_2 + NO \longrightarrow CH_3C(NO)(NO_2)_2, \quad (4)$$

$$CH_3C(NO)(NO_2)_2 \longrightarrow CH_3CN + NO_2 + NO_3, \quad (5)$$

$$CH_3\dot{C}O \longrightarrow \dot{C}H_3 + CO, \quad (6)$$

$$CH_3\dot{C}O + NO_2 \longrightarrow CH_3CO\dot{O} + NO, \quad (7)$$

$$CH_3CO\dot{O} \longrightarrow \dot{C}H_3 + CO_2, \quad (8)$$

$$CH_3CO\dot{O} + RH \longrightarrow \mathbf{CH_3COOH} + \dot{R}, \quad (9)$$

$$CH_3CO\dot{O} + \dot{C}H_3 \longrightarrow \mathbf{CH_3COOCH_3}, \quad (10)$$

$$\dot{C}H_3 + NO_2 \longrightarrow \mathbf{CH_3NO_2}, \quad (11)$$

$$\dot{C}H_3 + NO_2 \longrightarrow CH_3\dot{O} + NO, \quad (12)$$

$$\dot{C}H_3 + NO \longrightarrow CH_3NO, \quad (13)$$

$$CH_3NO \longrightarrow \mathbf{HCN} + H_2O, \quad (14)$$

$$CH_3NO + 2NO \longrightarrow \dot{C}H_3 + N_2 + NO_3, \quad (15)$$

$$CH_3NO + NO_2 \longrightarrow \mathbf{CH_3NO_2} + NO, \quad (16)$$

$$CH_3\dot{O} + RH \longrightarrow \mathbf{CH_3OH} + \dot{R}, \quad (17)$$

$$CH_3\dot{O} + NO_2 \longrightarrow \mathbf{CH_3ONO_2}, \quad (18)$$

$$CH_3\dot{O} + NO_2 \longrightarrow CH_2O + HNO_2, \quad (19)$$

$$CH_3\dot{O} + NO \longrightarrow \mathbf{CH_3ONO}, \quad (20)$$

$$CH_3\dot{O} + NO \longrightarrow CH_2O + HNO, \quad (21)$$

$$2HNO \longrightarrow H_2O + N_2O, \quad (22)$$

$$CH_2O + NO_2 \longrightarrow H_2O + NO + CO_2. \quad (23)$$

However, the actual decomposition mechanism of 1,1,1-trinitroethane vapours is more complex than that described by Eqns (1)–(23). For instance, Eqn (23) is unbalanced and seemingly describes several stages simultaneously. A number of compounds treated as end reaction products in Eqns (1)–(23) (they are given in bold) differ only slightly in stability from the starting compound (similarly to NO_3 and HNO_2) and react with other components of the reaction system (*e.g.*, CH_3OH reacts with NO_3 and HNO_2). According to Refs 1 and 8, at least twenty-six reactions are needed to schematically describe the decomposition of CH_3NO_2 up to ignition, the primary stage being a homolysis of the C–N bond. However, there is no consensus of opinion concerning the decomposition mechanism of even such a simple compound as nitromethane.[32] It was established that at temperatures below 700 °C the initial stage of the reaction involves cleavage of the C–N bond accompanied by rearrangement of CH_3NO_2 to give methyl nitrite and by decomposition of the last-mentioned compound.[33–35]

Decomposition of explosives is usually a complex process that involves at least several tens of elementary stages. Therefore, determination of the true rate constants for all these stages is a complicated task. The compositions of explosives, oxidisers of solid propellants and powders also contain carbon, hydrogen, oxygen and nitrogen and chlorine or fluorine (more rarely; the oxidation states of nitrogen and chlorine can vary over a wide range). The decomposition mechanisms of these compounds are hardly simpler than the destruction and oxidation mechanisms of carbochain polymers. Because of this, studies on decomposition of explosives, oxidisers of solid propellants and powders should be *a priori* carried out using modern methods. Up to date, almost all studies on thermal decomposition of explosives (with few exceptions) are carried out by sufficiently sensitive and simple methods of formal kinetics.[8] Abroad, research in recent ten to fifteen years has been carried out using improved methods of isotope mixing, pulsed laser irradiation, mass spectrometry with modulation of gas beam, fast IR spectroscopy and other dynamical methods of detection of products, which allows the temporal evolution of chemical compounds in the gas phase to be followed.[4]

Studies on the kinetics of thermal decomposition of explosives and model compounds using gas manometric technique involve determination of the pressure of gaseous compounds in the course of a reaction performed in a closed volume. The degree of decomposition of explosives (η) is calculated as the ratio of the current pressure of gases $p(t)$ to the pressure corresponding to complete cessation of the increase in the pressure in the course of decomposition (p_∞),

$$\eta = \frac{p(t)}{p_\infty}.$$

The decomposition of 1,1,1-trinitroethane [see Eqns (1)–(23)] is characterised by a $\sim 35 : \sim 25 : \sim 40$ ratio (in per cent with respect to the total number of stages) between the reaction stages accompanied by an increase in, a decrease in and constancy of the number of moles of gases. This ratio remains nearly the same for other explosives.[1–8] Therefore, the major drawback of the manometric technique is that it introduces an element of uncertainty and provides incomplete kinetic data. This method cannot in principle provide information on the stages proceeding without changing the number of moles of gases. Generally, it can be used to obtain generalised information on the stages accompanied by changes in the number of moles of gases because usually the kinetic curves of decomposition of explosives are described by relatively simple reaction equations (first-order reaction or first-order autocatalysis equations) containing one or two empirical rate constants. Often, a certain equation can describe only a portion of rather than the whole kinetic curve. The temperature interval for kinetic studies of thermal decomposition of explosives is usually no wider than 40–50 °C. The complete gas evolution, ΔV_∞, is related to the pressure p_∞ and is expressed in units of reduced volume (volume of gaseous products evolved under normal conditions per 1 gramme of explosive under study). Usually, the parameter ΔV_∞ is only determined at elevated temperatures in spite of the fact that the ΔV_∞ value considerably increases with temperature. The dependence of ΔV_∞ on temperature and changes in the composition of gaseous products in the course of reaction introduce errors in the determination of the rate constants, activation energy, E_a, and pre-exponent, k_0, in the Arrhenius equation. By and large, the method is characterised by low accuracy so that determination of the activation energy with an error of at most 4 kJ mol^{-1} in a temperature interval of 40 °C requires a series of 10–12 runs.[36]

Solving some practical problems at least requires knowledge of the true rate constant for the initial stage of a complex reaction (k_{in}). Usually, it is believed that k_{in} can be determined using methods of formal kinetics provided that the rate of the overall reaction is limited by the first step[36] or that the k_{in} value much exceeds the rate constants for the subsequent stages. Thus, to determine k_{in}, one should know all the rate constants for the subsequent stages. If the manometric technique is employed, it is also necessary that the initial stage of the reaction be accompanied

by a change in the number of moles of gases and irreversible. Yet another necessary condition is the absence of competing concurrent reactions. However, these conditions are far from being met.[8, 37, 38] For instance, the primary stages of the decomposition of 1,5- and 2,5-disubstituted tetrazoles proceed without evolution of gas.[37, 38] Decomposition of some nitro derivatives of cyclic compounds containing strained bonds also involves no formation of gaseous products in the first step. A conventional assumption that the experimental rate constant (k_{exp}) equals the rate constant for the primary (limiting) step of a successive reaction is qualitative in character. To assess feasibility of this assumption, information on the kinetics and mechanisms of further steps is required, because the accuracy depends on the number of stages and on the corresponding rate constants. However, relations between k_{exp} and the rate constants for elementary stages were established only for relatively simple reactions.[37, 39] An example is provided by the decomposition of 1,5-disubstituted tetrazoles, which involves a reversible formation and decomposition of azidoazomethines:[37]

$$k_{exp} = k_1 k_2 (k_{-1} + k_2)^{-1},$$

where k_1, k_{-1} and k_2 are the rate constants for the direct and reverse formation of azidoazomethine from tetrazole and for the decomposition of azidoazomethine with evolution of N_2, respectively. The rate constants for a concurrent decomposition channel involving no intermediate formation can also contribute to k_{exp}.[37] The rate constant, k_{exp}, for the radical-chain decomposition of 2,4,6-trinitrotoluene can be expressed as the sum:[39]

$$k_{exp} = a_1 k_1 + a_2 k_1 k_2 k_5^{-1} + a_3 k_1 k_3 (k_2 k_5)^{-1},$$

where k_1, k_2, k_3 and k_5 are the rate constants for the chain initiation, propagation, transfer and termination steps, respectively, and a_1, a_2 and a_3 are constants.

The primary step of decomposition of explosives can be directly studied in the gas phase by suppressing secondary reactions. Detection of gaseous products of primary decomposition in the condensed phase is a much more complicated task compared to gas-phase studies, because diffusion even through thin layers of explosives takes a finite time, which is responsible for a finite degree of conversion with respect to secondary reactions.[4] It is believed [8] that the possibility of changing gas-phase reaction conditions over a wide range allows the first monomolecular stage of a complex decomposition reaction to be distinguished and its kinetic characteristics to be determined by the manometric technique. This approach was employed in studies of gas-phase decomposition of nitroaromatic compounds. However, the radical-chain mechanism of these reactions was not proved, the amounts of inhibitors (I_2, NO_2, NO) introduced were comparable with the amounts of compounds under study and the kinetic chain length was not determined. Clearly, the assumption mentioned above is inapplicable to those explosives for which the primary step of decomposition is due to competition between a number of reactions proceeding by a radical or molecular mechanism.

Often, the molecules of energetic compounds contain a number of (different-type) active reaction centres. These atomic groups interact with one another and compete in the initial stages of thermal decomposition reactions. In this connection the most reactive centre must be determined. The interaction of atomic groups causes the electron density to be redistributed between them as a result of the donor–acceptor interaction, which manifests itself in specific properties of complex energetic compounds (structural elasticity and conformational mobility of atomic groups), electron density redistribution in the transition state of a chemical reaction, *etc.*[40, 41] Extensive literature on manifestation of the mutual influence of atomic groups in various complex organic molecules is available. Combining a number of experimental methods (IR and Raman spectroscopy, X-ray diffraction and neutron diffraction, measurements of dipole moments, *etc.*) allows reliable information on the structural features of complex molecules and intramolecular dynamics to be obtained. Unfortunately, interrelations between different characteristics are still poorly studied. Because of this, many correlations can only be applied to structurally similar compounds.[42]

At present, a number of stubborn problems related to the presence of and donor-acceptor interaction between several reaction centres in the molecules of explosives can be solved only experimentally.[36, 43] For instance, the decomposition of compounds $RN(NO_2)CH_2C(NO_2)_2X$ begins with homolysis of the $C-NO_2$ bond ($X = NO_2$) and the $N-NO_2$ bond ($X = F$).[36] The inductive effect of substituents causes a decrease in the bond dissociation energies by 4–8 kJ mol^{-1}. Experiments showed that at least in those cases where the molecules of explosives contain unstable functional groups some rate constants for the subsequent stages of decomposition are comparable with k_{in} in magnitude. This can lead to the formation of rather stable products which can still undergo further decomposition.[43] This phenomenon called a stepwise (two-stage) decomposition has long been known;[44–46] recently, it again attracted considerable attention.[36, 43, 47]

A few studies concerned with comparison of the kinetic parameters of decomposition obtained by methods of formal kinetics and by direct analytical techniques have been reported. For instance, liquid chromatography and UV spectroscopic studies of decomposition of trinitrophenylmethylnitramine (**1**) showed [46] that the concentration of this compound decreases down to zero before the evolution of gaseous products ceases (Table 1). The composition of gaseous products changes in the course of the process, *viz.*, the NO_2 content passes through a maximum and decreases down to zero nearly simultaneously with full consumption of compound **1**, which decomposes into three condensed compounds, *N*-methyltrinitroaniline (**2**), trinitroanizole (**3**) and picric acid (**4**). It seems likely that the primary step of decomposition is characterised by three rate constants, the ratios between them being varied with temperature because the fraction of compound **2** in the condensed phase increases as temperature increases. Products **2** and **3** undergo a slow decomposition to give compound **4**, so the exact rate constants for the primary step of decomposition of compound **1** can be determined by studying not only the kinetics of comsumption of **1** but also the kinetics of accumulation of the condensed products **2**–**4**. Thus, the true rate constant, k_{in}, for the initial stage of decomposition of explosives cannot be determined using methods of formal kinetics.[46] Changes in the ratios between the rates of particular stages of 1,1,1-trinitroethane decomposition are also indicated by the dependence of the composition of decomposition products on the degree of decomposition η (Fig. 1).

Table 1. Composition of reaction system (in moles of product per mole of starting compound) for thermal decomposition of trinitrophenylmethylnitramine at 433 K.[46]

t/min	Gaseous products [a]	Content of system's components			
		1	**2**	**3**	**4**
25	–	0.832	0.030	0.073	0.037
40	0.450 (0.021)	–	–	–	–
50	0.667 (0.018)	–	0.039	0.230	–
55	–	0.494	0.045	0.265	0.094
70	1.118 (0.031)	–	–	0.295	0.113
90	1.550 (0.021)	0.227	0.072	0.412	0.131
110	1.808 (0.016)	–	–	0.503	–
145	2.030 (0.004)	0.029	0.065	0.525	0.160
200	2.149 (0.001)	–	–	–	–
300	–	0.019	0.047	0.478	0.204
400	2.280 (0.000)	–	–	0.463	–
1440	2.674	0	0.031	0.110	0.524

[a] NO_2 is given in parentheses.

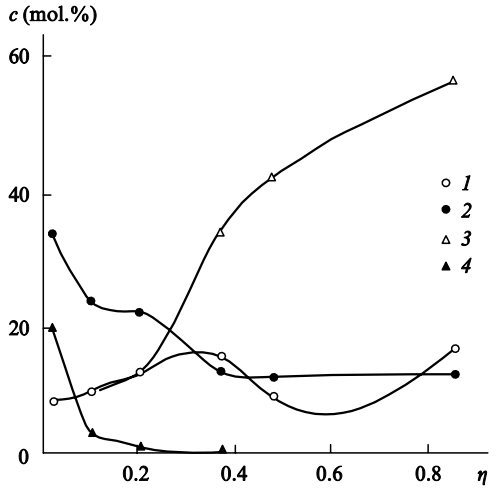


Figure 1. Yield of decomposition products of 1,1,1-trinitroethane at 443 K plotted *vs.* degree of decomposition;[1,8]
CH_3NO_2 (*1*), CH_3ONO_2 (*2*), CH_3CO_2H (*3*), CH_3NO (*4*).

Usually, calorimetric or gravimetric methods of studies on the kinetics of complex chemical reactions are also inappropriate for the determination of true rate constants. Indeed, the decomposition of explosives involves both exothermic and endothermic stages that can strongly differ from one another in thermal effects. Generally, different elementary stages of a complex reaction are accompanied by different changes in the mass of the condensed phase. Despite the fact that methods of formal kinetics do not allow the true rate constants for thermal decomposition to be determined, they can be useful for comparing the stability of functional groups with strongly different reactivities.[48]

However, often the activation parameters (E_a and k_0) determined using methods of formal kinetics differ even for the same compound.[4,8,49] Scatter of data can be explained by inadequacy of procedures employed that makes it impossible to distinguish between the initial steps and catalytic stages and between different phase states of a compound under study and by the influence of side effects on the decomposition. Large scatter of data can be a reason for incorrect conclusions concerning the influence of the structure on the stability of explosives. For instance, the nitramine N–N bonds are only slightly influenced by the inductive effect of substituents; in this case, the geometry of the nitramine group is of great importance, namely, the N–N bond dissociation energy, D(N–N), is 169.5 kJ mol^{-1} for planar nitramine groups and 157.5 kJ mol^{-1} for pyramidal ones. Different degree of structural distortion of pyramidal nitramine group caused by steric strain results in different degree of conjugation between nitrogen atoms in this group, which in turn influences the N–N bond length and, hence, strength. Since it is this bond whose cleavage is the primary step of the decomposition of nitramines, a change in the N–N bond length affects the activation energy, E_a, for the initial stage of the reaction. It was found that the E_a value increases rather than decreases as the N–N bond elongates.[49,50] Thus, it does not always happen that the results obtained by methods of formal kinetics permit estimation of the thermal stability ratios of related compounds.

Usually, it is appropriate to generalise the results of kinetic studies of various classes of explosives and to reveal relations between the reactivity, structure and physical characteristics of explosives using the Hammett–Taft equations that relate different rate constants to one another.[51–53] Correlations between the activation energy, E_a, for decomposition of nitro compounds and their structural characteristics were established using home-made codes.[54,55] These correlations are to some extent useful for systematisation of experimental data on the rate constants; however, detailed analysis of the reactivity problem can be performed only for groups of related reactions. Moreover, interpretation of the physical meaning of the correlation coefficients is arbitrary. In addition, because we don't know with certainty whether the experimental rate constant for decomposition, k_{exp}, is the true rate constant for the primary elementary step, the scientific value of the relations between the structure of explosives and their reactivities characterised by methods of formal kinetics seems to be doubtful.

In solving a number of practically important problems one should know the rate constants for not only initial stages of decomposition. Determination of all the rate constants for multistage reactions is a complicated task. The situation is simplified if the case in point is a study on in-service explosives because decomposition of related explosives involves a number of identical stages. Knowledge of the rate constants for many elementary stages of decomposition of explosives is also necessary to solve other problems.[56,57] Obtaining detailed kinetic information requires the use of modern methods that allow one to monitor changes in the reactant concentrations directly in the reaction system, to establish position of the reaction centre, to obtain information on transient structures, *etc.*[58–62]

However, these techniques are scarcely employed in the decomposition studies of explosives. Because of this, neither the mechanisms of nor rate constants for elementary stages are known even for in-service explosives. In this case, the decomposition of cyclic nitramines near the melting temperature was studied in most detail.[63] Generally, thermal decomposition of 1,3,5-trinitro-1,3,5-triazacyclohexane in the liquid phase can follow four reaction paths in the primary stage. These are HNO_2 release (30%), N–N bond cleavage (10%), formation of a mononitroso compound in the reaction of the explosive with NO (35%) and, finally, autocatalysis of the decomposition of the explosive (or the mononitroso compound) with the end product containing amide groups (25%). A similar composition of products was observed for the decomposition of molten 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane, but the decomposition mechanism of this compound was not established because of the lack of quantitative data.[4] In addition to the reactions considered above there is a number of examples that suggest unreliability of at least particular stages of the decomposition mechanism of explosives and model compounds.[3,4] This can likely be explained by the fact that the mechanism of a complex decomposition reaction of an explosive is usually studied in isolation from the studies on the kinetics of elementary stages of the reaction. For instance, compounds **2** and **3** were not included[8,64] in the scheme of decomposition of compound **1**, though they were experimentally detected among the decomposition products.[46]

Reliability of a reaction mechanism can be established by performing a complex study on the kinetics of elementary stages and by comparing the experimental and calculated kinetic curves plotted for intermediates and end reaction products. In this case, computer simulation can offer considerable advantages (Fig. 2).

Data on the elementary stages and corresponding rate constants for decomposition of explosives in the condensed phase are scarce and less reliable compared to similar data for the gas phase.[3,4,8] For instance, no well-substantiated chemical schemes of liquid-phase decomposition of some classes of explosives are available and there is no consensus of opinion of the reasons for the fact that some nitro compounds decompose in the liquid phase faster than in the gas phase.[39,65] It should be kept in mind that passage from the gas phase to the liquid phase can be accompanied by a change in the reaction mechanism.[3,4] Here, even if the elementary reactions remain unchanged, physics of reactions in the condensed phase is significantly different from physics of gas-phase reactions. Namely, the ratios between the rates of competing processes, the limiting stages and the physical meaning of the kinetic constants are often changed. Studies on the decomposition kinetics in the condensed phase are complicated by the appearance of the gas phase. Differences between the mechanisms of decomposition in different phases and ignoring the distribution of

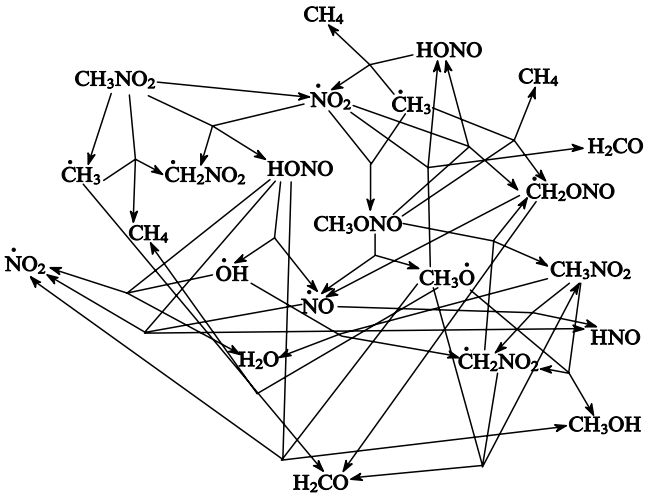


Figure 2. Nitromethane decomposition graph obtained by computer simulation.[32]

reaction products and sometimes reactants between phases cause the reaction kinetics to be dependent on the ratio of the mass, m, of the sample to the volume, V, of the reaction vessel. The influence of experimental conditions on the results of studies carried out using methods of formal kinetics has been the subject of a wide but unsuccessful speculation.

Many explosives are polar compounds. A reason for a possible change in the decomposition mechanism of explosives on going from the gas phase to the liquid phase is intermolecular interaction. Recently, supramolecular chemistry has been intensively developed. The subject of this branch of science is physical chemistry of systems that are (i) more complex than single molecules and (ii) connected to one another through intermolecular (non-covalent) interactions.[66] Supramolecular systems can be characterised by the spatial arrangement and architecture (supramolecular structure) of their components and by types of the intermolecular interactions responsible for interconnection of the components. Liquids whose molecules contain centres of intermolecular interactions can form hydrogen, dipole–dipole and other strong bonds with energies ranging between 10 and 60 kJ mol^{-1}. Association of liquid molecules is a consequence of the formation of labile intermolecular bonds, the equilibrium concentration of which increases as temperature decreases. Association of molecules can influence their reactivities [67] due to (i) a change in the structure of valence electron shells, (ii) such a mutual arrangement of the molecules, which favours (or precludes) a chemical reaction and (iii) a decrease in the molecular mobility. The higher the concentration of intermolecular bonds, the greater the decrease in the molecular mobility in the system on the time scale comparable with the lifetimes of the labile bonds.

Molten trinitrotoluene contains both free molecules and trimolecular associates.[68] Intramolecular oxidation of a CH_3 group proceeds *via* transformation of a transient cyclic complex, resulting in 4,6-dinitroanthranyl. In the associate a CH_3 group of one trinitrotoluene molecule is oxidised owing to NO_2 groups of other molecules in the associate, which are reduced to give azoxy and azo compounds. On going from vapour-phase decomposition to liquid-phase decomposition a number of high-melting thermally stable explosives (nitropyrroles, nitro derivatives of pyridine, pyrazole and triazole, furazans, benzofuroxans and pyridofuroxans) exhibit a dramatic decrease in E_a (by up to 125 kJ mol^{-1}) and in thermal stability (by 50–140 °C). This can be explained by the formation of associates, which allows the radical mechanism of decomposition to be replaced by the molecular mechanism.[69] IR spectroscopic studies revealed self-association in dimethylnitramine [70] and nitroglycerine.[71] At room temperature, nitroglycerine monomers, dimers, trimers and tetramers are in 1 : 1 : 4 : 5.5 ratio.

Despite the fact that association of molecules can affect their reactivities (and, hence, should be taken into account in the kinetic and mechanistic studies of decomposition of explosives), the role of molecular association in the course of decomposition of explosives is still to be clarified. Based on indirect data (feasibility of Trouton's rule), it was assumed[8] that association has no effect on thermal decomposition of explosives, because no association possibly takes place at corresponding elevated temperatures. However, this assumption does not simplify the situation because data obtained at elevated temperatures cannot be used for stability prediction of explosives under the working and storage conditions if uncorrected for molecular association. Self-association of the molecules of explosives both at low and at elevated temperatures has not been studied in detail as yet, though this phenomenon and formation of clusters of associates can be directly quantitatively studied by IR and NMR spectroscopy. If inhomogeneity of a system is due to the presence of associates, an exchange between the associated and non-associated states must affect the transverse magnetisation decay. NMR spectroscopy allows the rate of magnetisation exchange between nuclear spin subsystems with different mobilities and/or different resonance frequencies to be evaluated.[72] This technique can be used in the kinetic studies of complex chemical processes involving transitions from high-populated ground states to less populated but kinetically more active states.[73] To follow structural changes in molecular and supramolecular systems on the picosecond and shorter time scales, a number of multidimensional nonlinear coherent NMR, IR, Raman and EPR spectroscopic techniques were developed.[60–62, 74, 75]

According to modern concepts,[76] multistaginess of the mechanism of a chemical reaction, which involves reversible, concurrent and successive stages and catalysis by gaseous or condensed products, causes the appearance of spatial and temporal dissipative structures (DS). In the former case the distribution of reactants and, hence, the rates of elementary stages and of the overall process is nonuniform in space, the nonuniformity being microheterogeneous in character. In this case, traditional methods of kinetic studies providing volume-averaged values of measured parameters are inapplicable and local methods should be developed. A rather high spatial resolution (a few nanometres) can be obtained in spin diffusion studies.[72, 77]

In the case of temporal DS the concentration of intermediates and the corresponding rates of formation are characterised by oscillations, which can be either regular of chaotic in character. The discovery of oscillations of the heat release rate in studies [78] of thermal decomposition of moist nitrocellulose (Fig. 3) was followed by observations of this phenomenon in the course of decomposition of explosives in the presence of water and in the decomposition of aqueous HNO_3 solutions.[79, 80]

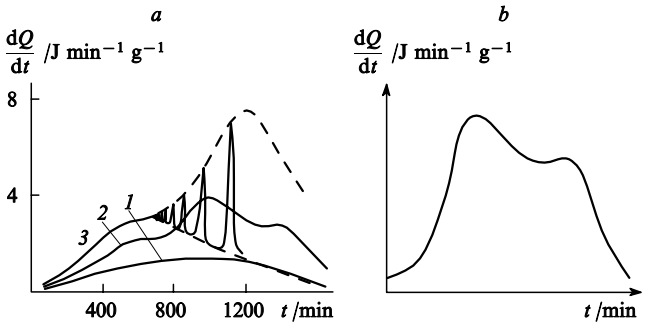


Figure 3. Heat release rate, dQ/dt, plotted *vs.* time for decomposition of nitrocellulose at 423 K (*a*) and total oscillation profile (*b*);[79] open system (*1*); $mV^{-1} = 0.5 \times 10^{-3}$ g cm^{-3}, humidity 1% (*2*); $mV^{-1} = 0.5 \times 10^{-3}$ g cm^{-3}, humidity 23% (*3*).

Detailed studies on the stability of a reaction system require methods that permit the determination of the concentrations of intermediates in the course of reaction and provide a reasonably high temporal (for monitoring) or spatial resolution. A calorimetric technique [78–80] allows the sum of the rates of the changes in the enthalpies due to the occurrence of chemical and physical processes rather than the reactant concentrations to be measured, so oscillations of the total rate of heat release (absorption) can be significantly different from oscillations of the concentrations of intermediates. When using manometric technique, the pressure of gaseous products of decomposition of explosives is usually measured manually in relatively long time intervals (as a rule, tens and hundreds of minutes). Therefore, small pressure oscillations remain undetected in the course of decomposition, though the method permits detection of dramatic changes in pressure in the case of low-frequency, large-amplitude oscillations.

Stability studies of reaction systems are of importance for both elucidation of reaction mechanism and determination of true rate constants for elementary stages of decomposition. If an attempt to describe a self-oscillation reaction using a kinetic model based on a hypothetical mechanism fails, either the reaction mechanism involves no appropriate stages or some constants for the stages under study are incorrect. In this connection theoretical methods [81–83] seems to be promising. For instance, oscillations in the course of decomposition of aqueous HNO_3 solutions cannot be explained in the framework of the mechanism proposed in Ref. 8. Reversibility of HNO_3 decomposition has not been experimentally proved as yet. Probably, the following reactions proceed at rather high temperatures

$$HNO_3 + NO \longrightarrow HNO + NO_3,$$

$$2\,HNO \longrightarrow H_2O + N_2O,$$

therefore, the overall decomposition of HNO_3 is irreversible. The rate constants calculated [8] from the data of calorimetric experiments do not correspond to elementary stages because the calculation procedure ignores the presence of HNO_3 monohydrates and trihydrates in aqueous HNO_3 solutions and the enthalpy changes upon the formation of hydrates.[84] The need of determination of the rate constants for elementary stages of decomposition of HNO_3 and nitrogen oxides is also due to the fact that these compounds are intermediates of decomposition of many explosives.

Experiments showed that solid-phase thermal decomposition of explosives is a spatially inhomogeneous process.[8,85] Corresponding studies of liquid-phase thermal decomposition have not been reported so far. NMR spectroscopy is an efficient method of DS studies in the condensed phase, which allows the appearance of microheterogeneous species to be detected and their size and concentration to be determined.[77,86,87]

Information on the mechanisms of solid-phase decomposition of explosives and oxidisers of solid propellants and corresponding rate constants for elementary stages is scarce. It was repeatedly pointed out that the determination of low degrees of conversion (a few tenths of a per cent) in studies of solid-phase decomposition is precluded by the fact that some products remain solid and cannot thus be determined gravimetrically and manometrically. For instance, it was established [88] that the pressure of gaseous decomposition products in microcavities of ammonium perchlorate crystals reaches 2–3 MPa. It is assumed [89] that accumulation of gaseous products in a crystal having cavities filled with gas leads to the formation of two zones differing in reactivity, namely, a near-surface zone (here, the compound is under tension) and an internal zone where the compound is under uniform compression.

It was proposed to characterise the effect of the lattice of molecular crystals on the reactivity of explosives by the ratio of the apparent rate constants for gas-phase [90] (or liquid-phase [91]) and solid-phase [$k_{exp,(s)}$] decomposition, or the so-called retardation effect of the crystal lattice.[90,91] This effect ignores both the concentration and type of defects. Studies [90,91] were carried out without evaluation of crystal defectivenesses; the $k_{exp,(s)}$ values obtained were low (up to nearly 10^{-12} s^{-1}) and not corrected for dissolution of gases in the explosives under consideration and for the absence of quasi-stationary concentrations of intermediates (this is of importance at low degrees of decomposition), so the parameters $k_{exp,(s)}$ seem to be determined with a low accuracy. In addition, no proofs were presented that the reaction mechanism remains unchanged on going from the gas-phase to the solid-phase reaction, though such a change is possible.[3,68,69] In particular, mention may be made that the energy barrier to interconversion of 1,3,5-trinitro-1,3,5-triazacyclohexane conformers in the gas phase is low (6 to 20 kJ mol^{-1}) and the results of kinetic measurements of gas-phase decomposition of this compound correspond to the dynamically averaged structure.[92] Based on comparison of similar experimental data with the conclusions drawn using an approximate theory that ignores many essential factors, it was concluded [8] that the decomposition of all plastic crystals and compounds with the melting temperatures below 100 °C proceeds as a homogeneous bulk reaction.[8] This conclusion seems to be not proved and the criteria for reaction homogeneity (plasticity of crystals and $T_m < 100$ °C) lack substantiation.

2. Decomposition of explosives under fast initiation

Recently, considerable progress has been made in studies of pre-explosion phenomena under fast initiation of explosives [93–97] due to the use of equipment with submicrosecond and nanosecond time resolutions. The results obtained using fast pulse radiolysis and flash photolysis techniques allowed conclusions about the mechanism of an elementary act of explosive decomposition of metal azides and a chain nature of the process to be drawn.[94] The decomposition of metal azides involves the following stages: hole localisation on a cationic vacany, reconstruction of a reactive site *via* a chemical reaction resulting in the formation of a quasi-local hole state in the valence band, hole delocalisation from the reconstructed reactive site, generation of charge carriers by impact ionisation by 'hot' holes and recovery of the local state in the forbidden band, which provides conditions for repetition of this sequence of stages. Propagation velocity measurements for explosive decomposition of a silver azide whisker were reported.[95] The results obtained ($\sim$1500 m s^{-1}) were associated with the propagation velocity of the diffusion front of holes generated in the course of decomposition.

Pre-explosive phenomena in secondary explosives studied taking 1,3,5-trinitro-1,3,5-triazacyclohexane as an example are characterised by a larger number of stages compared to similar phenomena in metal azides.[96] Initiation of an explosive involves a destruction stage, which is necessary for subsequent efficient supply of energy and is local in character. Energy dissipation occurs in the so-called hot spots. Dislocations or associations of dislocations play an important role in the hot spot nucleation stage. A key feature of this stage are electronic excitations. Local narrowing of the forbidden band near dislocations on compression of explosives dramatically increases the probability of electronic excitation and cleavage of the $N-NO_2$ bond.[4,93]

The decomposition kinetics of explosives under fast initiation was studied by direct detection of gaseous decomposition products on the millisecond time scale using time-resolved mass spectrometers with a performance of up to a hundred of scans per second.[96] More than ten neutral and ionised particles (NO_2, NO, HCN, CN, *etc.*) were detected near the surface of the sample 40 μs after application of a 20 ns pulse of an excimer (KrF) laser with a fluence of 5 J cm^{-2} to a 1,3,5-trinitro-1,3,5-triazacyclohexane single crystal.[96] Photon emission in the near UV and visible regions, delayed by 200 ns to 1.2 μs relative to the laser pulse was also detected. An increase in the laser fluence was accompanied by the appearance of long-lived excited neutral species identified as NO.

In discussing the results of studies on laser-initiated decomposition of explosives it was hypothesised that optical breakdown can compete with chemical decomposition of explosives. Mani-

festation of a particular mechanism is governed by the porosity, dispersion and reactivity of explosives. The problem of extraction of kinetic information from the data obtained under fast initiation of decomposition is still to be solved. In this connection time-resolved magnetic resonance spectroscopy based on detection of the nuclear polarisation of diamagnetic reaction products offers great prospects for research on the spin dynamics and chemical kinetics of short-lived radical species in photochemical reactions.[98]

3. Ammonium perchlorate

Among oxidisers of solid propellants, ammonium perchlorate (AP) has undoubtedly been studied in most detail. Nearly a thousand of publications concerned with the properties of this compound have been reported (see, *e.g.*, Ref. 7 and references cited therein). The results of studies carried out in the 1960s and 1970s changed our concepts of the mechanism of AP decomposition, though researchers still have contradictory opinions of some important issues.[88,99–101] In particular, it was established that the primary act of solid-phase decomposition of AP involves transfer of a proton followed by the formation of ammonia and perchloric acid.

The topographical features of thermal decomposition of AP were studied by optical microscopy.[88] Note that optical microscopy has a limited spatial resolution, which prevents structural elements smaller than 0.2 μm from being observed. The decomposition was accompanied by the appearance of spherical mobile 'nuclei' at depths greater than 5 μm (below dislocation outcrops), which grew until a size of nearly 1 μm. As time passed, the nuclei formed an ellipsoidal decomposition centre elongated along the ⟨010⟩ crystallographic direction. The number of decomposition centres in the crystal can vary over a wide range (from one or two to several tens), being (probably) dependent on uncontrollable factors influencing the sample in the course of preparation; the defectiveness of AP crystals on the nanolevel was not assessed prior to the experiments.

Based on the results of studies on the topographical features of AP decomposition,[88] a dislocation-chain mechanism (DCM) of reaction was proposed.[8] According to this mechanism, dislocations can be generated in the course of reaction under the action of mechanical stress produced on accumulation of gaseous decomposition products in the bulk of the crystal and the motion of dislocations favours the decomposition reaction owing to rearrangement of the AP lattice. This is a phenomenological concept, because experimental data[88] provide no unambiguous proof of the effect of dislocations on the decomposition of AP crystals. For instance, a substantial increase in the starting dislocation density (from 10^2 to 10^6 cm^{-2}) affects only slightly the induction period in the curves of relative mass change in the course of thermal destruction, which becomes nearly three times shorter; however, the change in the dislocation density has no effect on the acceleration stage (Fig. 4).

Preliminary deformation of a crystal to saturate it with dislocations is accompanied by a nearly 105 kJ mol^{-1} increase rather than a decrease in the activation energy for the formation of a decomposition centre. As a result, the induction period of the formation of decomposition centres increases by a factor of nearly 25 even at 230 °C. The increase in the activation energy can be explained by the fact that the formation of a potential nucleation centre in the crystal lattice involves polygonisation and interaction between the newly formed dislocations and is followed by vacancy diffusion from the deformation zone towards the dislocations.[88] Thus, contrary to the basic principles of the DCM concept, the newly formed dislocations are inactive. It is believed that ellipsoidal shape of reaction centres is an argument in favour of the mechanism proposed.[88] [This shape is associated with the fact that the motion and generation of dislocations along the ⟨010⟩ direction occur much easier than in perpendicular directions due to anisotropy of mechanical properties of AP crystals.] For instance,

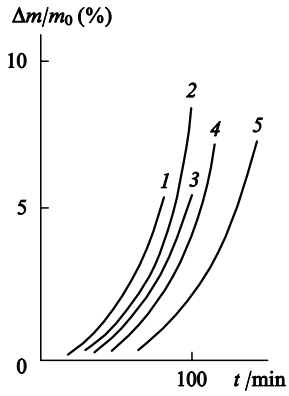


Figure 4. Relative mass change, $\Delta m/m_0$, of ammonium perchlorate crystal in the primary stage of decomposition at 503 K plotted *vs.* time at different dislocation densities.[88]
Initial dislocation density: 10^6 (*1*), 10^5 (*2*), 10^4 (*3*), 10^3 (*4*), 10^2 cm^{-2} (*5*).

it was found that the mechanical characteristics of an AP crystal under tensile stress along the ⟨100⟩ and ⟨001⟩ axes are better than the those of the same AP crystal under tensile stress along the ⟨010⟩ axis. However, it is known that the action of both external forces and the pressure of gases filling microcracks[102] cause the microcracks to grow along the direction perpendicular to the force direction. In other words, growth of the reaction centre along the ⟨010⟩ direction is caused by the forces acting along the ⟨100⟩ and ⟨001⟩ axes. We can agree with the authors of Ref. 100 who said that the available data are insufficient to establish the growth mechanism of an AP decomposition centre. It seems likely that the DCM concept underestimates the role of point defects and overestimates the role of dislocations in the AP decomposition. It should be noted that the starting AP crystals had pores up to 100 nm in diameter, but their prehistory was unknown and the pore size distribution and its evolution in the course of AP decomposition were not characterised.

To gain a better insight into the role of defects in the decomposition of AP and other solid explosives and oxidisers, the formation of vacancy pores of size 1–10 nm and the evolution of the pore size distribution should be studied using, *e.g.*, ^{1}H, ^{15}N or ^{129}Xe NMR spectroscopy (see Refs 103–105). For instance, ^{14}N NMR spectroscopy can be lifted to a level of high usefulness in chemistry and materials science.[105]

The results of studies on AP decomposition indicate an important role played by the kinetic and diffusion factors, exchange with the environment and peculiarities of the crystal structure of AP in localisation of thermal decomposition reaction. A study on topokinetic regularities of low-temperature decomposition of AP crystals as functions of the concentration of additives and temperature suggested that the nucleation rate of decomposition centres is governed by the content of ClO^{3-} impurity ions and by the concentration of free protons, while the growth rate of decomposition centres is nearly independent of the presence of additives.[100] A mechanism of the formation and growth of the AP decomposition centres was proposed.[99] It is assumed that the appearance of spatial and spatial-temporal DS is promoted by the phenomena caused by the pressure of gaseous reaction products. The equation for the reaction front velocity (μm min^{-1}) obtained using a simplest model with allowance for diffusion of perchloric acid has the form

$$u \approx 10^{12.4}\exp\left(-\frac{128\,000}{RT}\right).$$

The results of calculations were found to be similar to the observed 'slow' rates.

4. Hezanitrohexaazaisowurtzitane

Recently, hezanitrohexaazaisowurtzitane (HNIW) first obtained in the USA in 1987 has been the subject of intensive research. This energetic compound belongs to cage-type polynitramines and is of practical interest as a high explosive and a component of solid propellants.[106] The cage structure of HNIW is responsible for high density and enthalpy of formation (ΔH_f = 416 kJ mol^{-1}) and for structural strain. X-Ray diffraction, spectroscopic and quantum-chemical studies revealed [107] violation of the close packing principle in the nitramine crystals. A feature of the polynitramine molecules is the possibility of orbital interaction between the lone electron pairs of amine nitrogens. The variety of interactions of the lone electron pairs in the molecules of conformers is in excellent agreement with the diversity of polymorphs of cyclic and cage-type nitramines. Crystals of the ε-phase are characterised by the highest density (d = 2.062 g cm^{-3}).

The mechanism of thermal decomposition of HNIW has not been established as yet. Data on the kinetics and composition of gaseous decomposition products are contradictory.[108–112] The kinetic parameters of HNIW decomposition exhibit a large scatter (Fig. 5). Solid-phase thermal decomposition of α-, β-, γ- and ε-polymorphs and liquid-phase thermal decomposition of ε-modification were studied in detail by thermogravimetry, manometric technique, IR spectroscopy and optical microscopy.[108, 109] It was shown that decomposition of crystalline HNIW is a pure solid-phase process characterised by self-acceleration due to nucleation and growth of reaction centres. Decomposition follows the phase transitions α → γ, β → γ and ε → γ. The ε → γ transition occurs in the temperature range 180–220 °C and is endothermic in character.[106] The thermal stability of HNIW depends on the initial polymorph state and changes as follows: α < β < γ < ε. The kinetic parameters of decomposition of particular samples are governed by the size, size distribution and crystal morphology. The molecule of a solid product of ε-HNIW decomposition at temperatures below 210 °C contains one of the six nitro groups. The solid product is comprised of transparent microporous particles whose sizes correspond to the sizes of the initial crystals. Heating of the solid product to 600 °C results in a solid residue with a network structure composed mainly of carbon and nitrogen atoms.

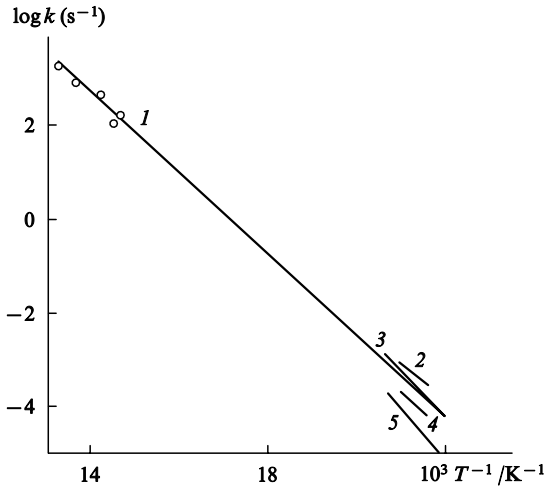


Figure 5. Temperature dependences of the rate constants for decomposition of HNIW.
Rate constants for the leading stage of combustion (open circles) calculated using the Zel'dovich combustion model for a first-order reaction [106] (*1*); rate constants determined from changes in the νNO_2 vibrational intensity in the IR spectrum [110] (*2*) and rate constants for mass change [108, 110] (*3*)–(*5*).

5. Nitrocellulose

Nitrocellulose has a rather complex structure. This is a polymer characterised by some distribution trinitrate, dinitrate and mononitrate units along the polymer chain. Nitro groups can be bonded to both primary and secondary carbon atoms of the monomer unit. A method of assessing structural inhomogeneities in nitrocellulose was developed.[113]

Decomposition of nitrocellulose involves a number of concerted and successive reactions, namely, initial cleavage of the O–NO$_2$ bond, redox interaction between nitrogen oxide (nitrogen dioxide) and macroradicals that are formed in the decomposition of nitrocellulose, hydrolysis of nitrate and glycoside groups, *etc*. However, the mechanism of decomposition has not been completely established as yet. In the early studies carried out in the 1950s and 1960s, the decomposition of nitrocellulose was studied by methods of formal kinetics, *viz*., using the complete gas evolution, loss of the sample mass and formation of the so-called 'condensing' and 'hardly condensing' gases.[114–117] The composition of gaseous products in the initial stage of nitrocellulose decomposition was assessed indirectly;[116, 117] it is inconsistent with the results of more recent mass spectrometric studies.[118] It should be noted that the authors of Refs 116 and 117 pointed that their conclusions about the mechanism of nitrocellulose decomposition are tentative and that the numerical data (E_a and k_0 values) cannot be used in calculating the kinetic parameters of particular stages. The results of IR spectroscopic study of nitrocellulose decomposition are available;[119] however, the reactivity ratios of the primary and secondary ONO$_2$ groups in the dinitrate and trinitrate units was not reported.

The mechanism of decomposition was detailed and the rate constant for the primary step determined in Refs 120–122. Thermal decomposition of nitrocellulose with a nitration degree of 2.7 was studied [120] by UV and IR spectroscopy, gravimetric and photometric methods, gas chromatography and gel permeation chromatography (GPC). It was shown that the reaction begins with cleavage of the O–NO$_2$ bond at a secondary carbon atom in the trinitrate unit. The temperature dependence of the rate constant for loss of secondary nitrate groups in the trinitrate unit (according to IR spectroscopy data) in a system with running medium and the temperature dependence of the rate constant for NO and NO$_2$ formation (according to UV spectroscopy data) in a closed system (at $mV^{-1} \leqslant 5 \times 10^{-4}$ g cm^{-3}) are described by an Arrhenius equation with the same parameters (E_a = 149 kJ mol^{-1} and k_0 = 13.9 s^{-1}). The kinetics and mechanism of subsequent transformations of nitrocellulose are to a great extent determined by conditions for removal of gaseous products. An EPR study of thermal decomposition of nitrocellulose in inert runnimg medium [121] revealed accumulation of free iminoxyl radicals in the primary step. This indicates that the decomposition mechanism involves a stage of formation of a nitroso compound, which subsequently isomerises into an oxime, which then readily decomposes to give an iminoxyl radical.

The average number of breaks of the nitrocellulose polymer chain in the course of decomposition was determined [123] assuming a constant molecular mass. Changes in the molecular mass distribution (MMD) in the course of nitrocellulose decomposition were determined more recently.[120, 122] The conditions for removal of gaseous products from the reaction volume affect the character of the changes in the MMD in the course of thermal decomposition of nitrocellulose. In the system with running medium the MMD becomes narrower due to breakdown of chains with large molecular masses. Terminal macroradicals thus produced undergo partial recombination within the same cage. However, by and large the molecular mass of nitrocellulose decreases due to evolution of gaseous products. In a closed system, the MMD is broadened (Fig. 6) because of production of middle-type macroradicals that recombine to give macromolecules with the molecular masses exceeding that of the starting nitrocellulose.

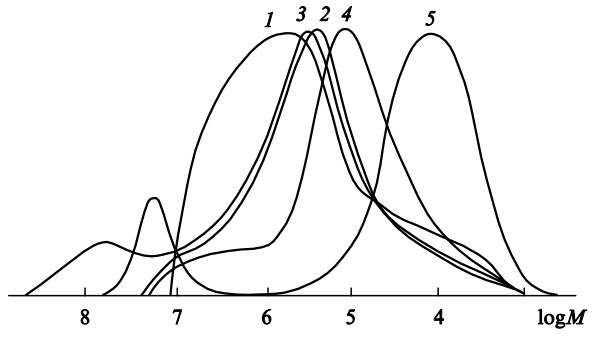


Figure 6. Changes in the MMD of macromolecules in the course of thermal decomposition of nitrocellulose in closed system at $mV^{-1} = 0.02$ g cm^{-3} and $T = 373$ K.[122]
Duration of decomposition /h: 0 (*1*), 48 (*2*), 104 (*3*), 612 (*4*), 1096 (*5*); *M* is the molecular mass of nitrocellulose.

III. Polymer networks as binders for solid propellants

A solid propellant can be treated as a composite material composed of a polymeric binder (10 mass % – 20 mass %), which is usually based on a sparse polymer network containing distributed oxidiser and metal particles of preset dispersion. The compositions of solid propellants depend on the requirements imposed on the specific momentum, stress – strain behaviour, burning rate and the dependence on pressure. A promising way is to prepare binders possessing improved adhesive properties (see Ref. 124).†

1. Structure of polymer networks

A polymer network can be considered as a system comprised of two subsystems, *i.e.*, molecules and the free volume. Each subsystem has a complex multilevel structure.[14] The chemical level of the structure of polymer networks is governed by the structure of the monomer unit. Abstracting of the chemical composition of polymer networks, the topological level of their structure characterises the connectivity of the network structure. The topological structure of a polymer network is characterised by the MMDs of its elements, *viz.*, chain fragments between cross-link points, dangled chains attached to the network through one end, loops formed through end attachment to the initial point of the same chain and free chains. In addition to stable chemical branchings, polymer networks contain labile physical nodes ('entanglements'). The nature of the nodes of physical network and its role in the macromolecular dynamics has been comprehensively reviewed.[126, 127]

The properties of a material are strongly affected by self-organisation on the supramolecular level.[128] This level of structural organisation of polymer networks is characterised by the presence of both highly cross-linked and sparser domains of size of a few nanometres and more. The formation of microheterogeneous domains in polymer networks can be due to various reasons including diffusion and kinetic factors.

The most important operating characteristics of polymer networks including stability and stress – strain characteristics depend not only on the chemical, topological and supramolecular levels of the molecular subsystem but also on the structure of the free volume subsystem. The pore distribution in polymer networks and in other materials with pore sizes from a few tenths of nanometre to a few nanometres can be characterised using positron annihilation method or NMR spectroscopy with hyperpolarised ^{129}Xe or water as probes.[129 – 131]

Some characteristics of the topological structure, *viz.*, the density of cross-links and the average molecular mass of the chain fragments between cross-link points are related to the elastic modulus of a network polymer by a known relation. Direct methods of studies of the supramolecular design of polymers including polymer networks are unavailable as yet. Attempts to construct supramolecular models of linear polymers were reported.[9] Inequality of traditional concepts of the non-crystalline phase of linear polymers as a high-molecular-mass homogeneous liquid disturbed by fluctuations to the task of relevant description of the phase has been exemplified[132] and a framework-micelle model of structural organisation of this phase proposed. QSPR studies of glassy polymers are carried out using principles of synergetics of nonequilibrium systems and fractal analysis.[133] The model of the polymer structure includes a sparse matrix with cross-links represented by entanglements comprised of close-packed segments (the entanglements form a cluster network).

The effect of fillers on polymers manifests itself in variations of the physicomechanical, structural, thermodynamic and chemical properties of binders.[13, 134, 135] Adsorption bonds are formed between the polymeric binder and disperse filler. These bonds are intermediate between the intermolecular and chemical bonds in strength. Filler particles act as polyfuntional nodes; the amount of the 'bound' binder can exceed 40% of the total mass of the binder. A decrease in the molecular mobility of elastomers upon introduction of fillers can be detected by NMR spectroscopy.[135, 136] An NMR-based method of determination of the network structure of filled elastomers135 allows the total concentrations of physical nodes and chemical cross-link points, the fraction of polymer in nearly immobile adsorbed layer at the filler – polymer interface and the fraction of topological nodes that are formed by the polymer chains present between filler particles (Fig. 7) to be determined.

The molecular mass distribution is an important structural characteristic of polymer networks. Methods of determination of the MMDs of linear polymers are based on analysis of the

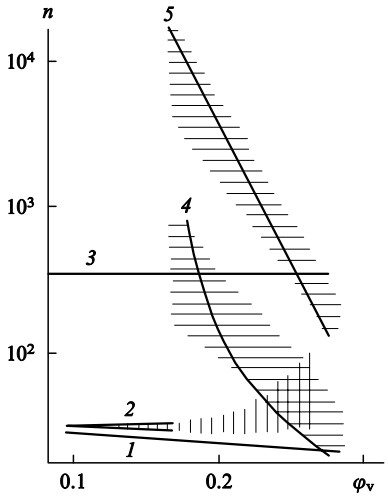


Figure 7. Number, *n*, of repeating units in the chain fragments between cross-link points plotted *vs.* filling degree, φ_v, in polydimethylsiloxane – aerosil mixtures.[135]
Total number of units (*1*); contribution of obstacles created by filler (*2*); contribution of physical nodes (*3*); contribution of adsorption sites (*4*); contribution of cross-links (*5*).

† In contrast to solid propellants, binders for PCMs are usually linear polymers containing 30 mass % – 40 mass % of reinforcing fibres (or mineral filler), antipyrene and other additives.[13] The main operating characteristics of PCMs are improved strength, rigidity, impact strength and incombustibilty. The properties of PCMs depend on particular field of applications.[12, 13] For instance, aviation PCMs must have a heat resistance of 300 – 400 °C and be stable at 500 – 520 °C.[125] For fundamentals of preparation of PCMs with preset properties, see a monograph.[13]

properties of dilute polymer solutions. The MMDs of many insoluble polymers cannot be evaluated using these techniques. Methods based on the degradation of those polymers [137] appeared to be impracticable because they are time-consuming and destructive in character. In this connection recently attempts have been undertaken at using the relaxation properties of polymers for MMD evaluation because the relaxation time spectrum is related to MMD.[16–19, 138–141]

Investigations of the kinetics and mechanism of decomposition of polymer networks and solid propellants based on them are necessary to solve two problems, namely, service life assessment and control of items made of these materials and mathematical modelling of corresponding combustion processes. The service life of the items mentioned above usually depends on the stress–strain properties of polymer networks and solid propellants. Its determination requires knowledge of kinetic data and information on the mechanism responsible for changes in the topological and supramolecular structures of polymer networks and on adhesive properties of solid propellants. Mathematical modelling of combustion of solid propellants requires information on the kinetics and mechanism of thermal decomposition of these compounds.

2. Molecular degradation of polymer networks

Polymer degradation is governed by the chemical and physical transformations of these materials under action of temperature, mechanical stress, aggressive media (water, acids, alkali, oxygen, ozone, *etc.*), various kinds of radiation (photoemission, radioactivity, laser radiation, cosmic rays).[9, 142] In practice, polymeric materials are subject to a number of factors simultaneously. Complexity of studies on the chemical degradation processes is due to diversity of the mechanisms and reactive particles (radicals, ions, unstable molecules) responsible for the development of these processes. The key role in the degradation of linear polymers is played by the radical and radical-chain mechanisms. Ionic mechanisms are of importance for the degradation in acid-base media and in the presence of strong oxidisers; molecular mechanisms are less-common.[9]

Thermal degradation mechanism of polymer networks is to a great extent similar to the degradation mechanism of corresponding linear polymers. For instance, a radical-chain degradation mechanism of polymer networks and the degradation mechanism of linear polymers involve the same elementary stages, *viz.*, chain initiation, propagation, transfer and termination. The molecular mechanism of degradation of polymer networks usually involves a relatively small number of elementary stages. Therefore, studies on the degradation kinetics and the determination of true rate constants for the elementary stages can be performed using methods of formal kinetics. Mathematical formalism developed to analyse the kinetic curves in the case of radical-chain mechanism of degradation of linear polymers [143] can with some variations be applied to polymer networks. When analysing kinetic data for molecular mechanism of degradation, one should take into account that every act of evolution of volatile products (change in the mass of the sample) requires two acts of degradation of chain fragments between cross-link points.

Usually, thermal degradation of polymer networks is studied by simpler methods, namely, thermogravimetry and differential thermal analysis in the dynamic heating regime [144, 145] rather than methods of formal kinetics. Often, assuming a simple one-step degradation mechanism, the thermal stability is characterised by the empirical parameters determined from the experimental data, *viz.*, the degradation onset temperature, maximum mass loss rate temperature and integrated decomposition temperature rather than the activation energy E_a.

The results obtained in studies of the temporal dependence of the charactetistics of the topological structure (*e.g.*, density of cross-links, MMD of chain fragments between cross-link points) can be used for the determination of true rate constants for degradation. In this case, account must be taken of the fact that the chain scission and cross-linking can occur simultaneously.

Mechanical stress is an important factor affecting the rates of chemical reactions of polymers.[15, 142] Often, it is responsible for changes in the reactivities of strained macromolecules, that is, stress influences the kinetics of those reactions that involve structural rearrangements in the reaction centre.[15] If these changes are similar in character to spontaneous structural changes occurring in the course of reaction, the process is accelerated. Otherwise, retardation occurs. Tensile stress causes activation of C–H bonds in the reactions accompanied by proton abstraction.[15] If the hybridisation of a main-chain atom changes, the rate constant, k_σ, for an elementary stage under stress and the rate constant, k, for the same elementary stage in the absence of stress are related as follows

$$k_\sigma = k \exp[\gamma\sigma(RT)^{-1}],$$

where the coefficient γ, or the reaction sensitivity to stress, can be considered as the product of two independent coefficients, $\gamma = \gamma_a\beta$. The coefficient γ_a depends on the energy capacity of the strained structural fragment and on the extent of structural changes in this fragment in the transition state; the sign of the coefficient γ_a depends on the type of stress (tensile or compressive) and on the type of the hybridisation change ($sp^3 \rightarrow sp^2$ or $sp^2 \rightarrow sp^3$). The coefficient β depends on the nonuniformity of stress distribution over the system of bonds. Under tensile stress, chemical reactions accompanied by the $sp^2 \rightarrow sp^3$ rehybridisation of two neighbouring carbon atoms (*e.g.*, addition to the main-chain double bond) are characterised by acceleration of the addition of all reactants to the *trans*-C=C-bond; in the case of addition to the *cis*-isomer, this is only valid for those reagents that have the reaction coordinate $\delta^{\neq} > 0.68$. At $\delta^{\neq} < 0.68$, tensile stress has a retardation effect on the reaction. Compressive stress causes the opposite effect.

The reaction rate sensitivity to mechanical stress can be used to study the reaction mechanism and to determine the constants for elementary reactions.[142] The influence of stress on the reaction kinetics is detected not only in the case of external mechanical stress but also in the presence of internal structural strain in, *e.g.*, polymeric composites, swelled polymer networks, *etc.*

3. Kinetic regularities of decomposition of cross-linked polymers

Kinetic regularities of decomposition of cross-linked polymers have been studied in most detail taking polyurethanes (PUs) as examples.[16–24, 26, 27] Sparse PUs have, on the one hand, a number of valuable service properties typical of elastomers and, on the other hand, a significant drawback, because they are readily degradable at elevated temperatures.

Thermal decomposition of linear PU and model low-molecular-mass urethanes has been the subject of extensive literature. In studies of the degradation of linear PUs the emphasis was placed on analysis of reaction products. Only a few publications concern the degradation kinetics. It was established that the most unstable structural unit of linear PU is the urethane group, which can dissociate into initial alcohol and isocyanate or decompose *via* formation and subsequent decomposition of an intermediate cyclic complex following a molecular or quasi-ionic mechanism.[146–148] Degradation of linear PUs and low-molecular-mass urethanes results in the same products,[149–151] but the data on the degradation kinetics of linear PU are nonsystematic, namely, the Arrhenius equation parameters were usually determined from the rate constants measured at three or four temperatures while the effect of the chemical structure on the thermal stability was characterised using the results obtained only at one temperature.

Calorimetric and gravimetric studies of the degradation kinetics of sparse PUs showed that the parameters, E_a and k_0, of the process depend on the sample synthesis conditions (temperature, presence of catalyst, solvent).[20, 21, 26, 27, 152] This can be explained as follows. Polyurethanes are synthetised in the presence of a catalyst at relatively low temperatures. The process is accompanied by association of reactants, which results in the

formation of nonequilibrium network structures containing systems of strained bonds. Studies on the evolution of structural characteristics of PU networks in the course of PU degradation became possible owing to the use of modern methods of determination of the sol fraction MMD,[21,27] the MMD of chain fragments between cross-link points [16–20] and the microheterogeneity of the sparse polymer networks.[22]

The MMD evolution of the sol fraction in the course of thermal degradation of sparse PU networks was studied by GPC.[21,27] The sol fraction has a trimodal molecular mass distribution with two peaks at $M \approx 300$ and 600 corresponding to the low-molecular-mass fraction and a peak with a maximum at $M \approx 10^4$ corresponding to the 'polymeric' fraction (Fig. 8). It was shown that the urethane groups near cross-link points are the most probable chain scission sites and that the MMD of the 'polymeric peak' of the sol fraction characterises the MMD of the chain fragments between cross-link points in the PU network. The results of computer simulation [27,153] showed that the reactivity of the most stable (urethane) functional group depends on its position in the polymer chain. The formation of a cross-link point of a network based on 1,1,1-trimethylolpropane causes a strong deformation of the neighbouring urethane groups. Steric hindrances to arrangement of three bulky diisocyanate units in the cross-link point lead to the formation of urethane groups with less stable strained bonds compared to the urethane groups in the linear chain fragments. Thus, the primary step of degradation of cross-linked PUs mainly involves breakdown of the urethane groups near the cross-link points.

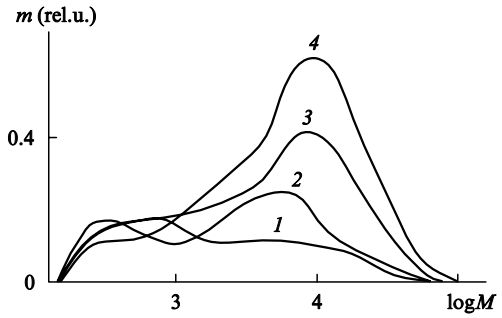


Figure 8. Molecular mass distribution of sol fraction for *in vacuo* thermal destruction of cross-linked polyurethane at 393 K.[21,27]
The amount of the sol fraction in the initial sample was 2.89 mass % and the initial density of cross-links was 2.13×10^4 cm^{-3}. Duration of destruction, days: 0 (*1*), 8 (*2*), 15 (*3*), 35 (*4*); *M* is the molecular mass of the sol fraction.

A theory was developed, which relates the molecular mobility of the chain fragments between cross-link points in sparse polymer networks to the MMD of these chains.[18,24] The MMD evolution of the chain fragments between cross-link points of cross-linked PUs in the course of thermal degradation of these compounds was studied by NMR spectroscopy.[17–20,24] The results obtained are illustrated in Fig. 9. As can be seen, in the initial stage of the process the unimodal MMD is transformed into a broader bimodal MMD and not only longer but also short chain fragments between cross-link points appear; *i.e.*, breakdown of cross-links and cross-linking occur simultaneously. The longest chain fragments between cross-link points are also the most unstable, which is seemingly due to microheterogeneous character of the supramolecular structure of sparse PU networks.[22]

Studies on the MMD evolution of the chain fragments between cross-link points of sparse PU networks under permanent tensile stress or strain showed [17,19] that in this case the network structure changes long before the macroscopic degradation of the sample, the structural changes being similar to those observed in the course of thermal degradation (Fig. 10). Distinctions between

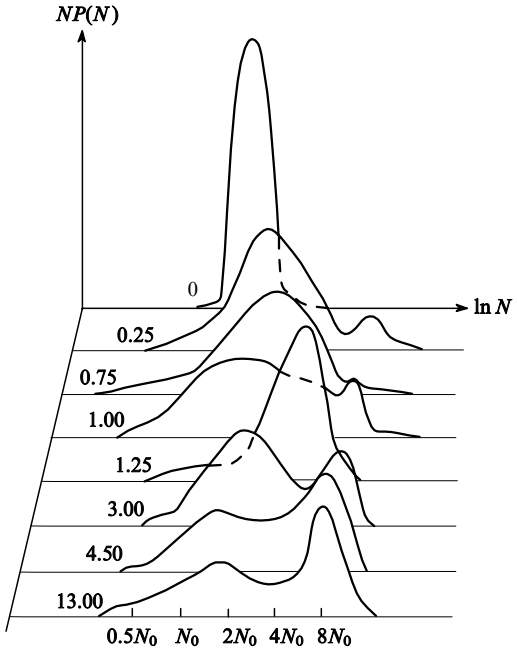


Figure 9. Molecular-mass distribution in the chain fragments between cross-link points for *in vacuo* thermal destruction of cross-linked polyurethane at 498 K.[19]
Figures near curves denote the duration of destruction /h; N_0 is the average length of a chain fragment connecting cross-link points in the starting sample.

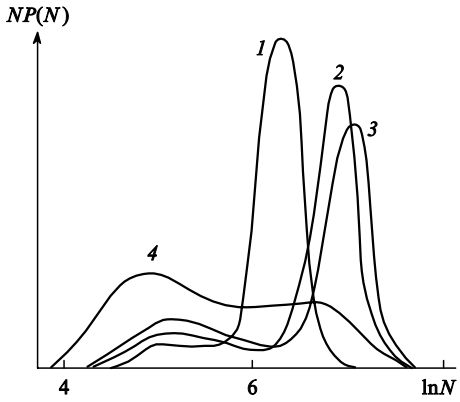


Figure 10. MMD of chain fragment connecting cross-link points in cross-linked PU after storage of the sample for 21 days at 300 K at constant tensile stress σ.[17]
σ /MPa: 0 (*1*), 0.75 (*2*), 1.0 (*3*), 1.25 (*4*).

the character of changes in the MMDs of the chain fragments connecting cross-link points under permanent stress and strain were revealed. The results obtained allowed the degradation mechanism of strained elastomers to be clarified because opposite views of this mechanism were reported.[9,142,154,155]

This nondestructive method of studying the MMD evolution of the chain fragments between cross-link points in the course of thermal degradation of elastomers under stress and strain is of importance for estimation of accumulated defects. However, the technique has not been employed in studies of solid propellants as yet.

The kinetic regularities of the degradation of three highly cross-linked polymers, *viz.*, dimethacrylate triethylene glycol (DMATG), cross-linked and 'hyper-cross-linked' polystyrene (HPS) and poly(epoxyamine) (PEA) have been studied in sufficient detail.[23–26,29,30]

DMATG has a microheterogeneous supramolecular structure formed by highly cross-linked 'granules' distributed in a highly defect matrix. Degradation of DMATG was studies by NMR and gravimetry.[23–26] The kinetic regularities of the degradation depend on the initial degree of conversion (Γ_0) of the sample and dramatically change at $\Gamma_0 = \Gamma_m$ (Γ_m is the degree of conversion at which highly cross-linked granules contact one another and the polymer becomes monolithic). Degradation of the samples with $\Gamma_0 < \Gamma_m$ is characterised by cleavage of the weak, strained matrix bonds and a decrease in the total mass of granules; the density of cross-links remains unchanged. The process proceeds by a radical-chain mechanism and involves partial formation of new cross-links. At $\Gamma_0 > \Gamma_m$, degradation follows the molecular mechanism *via* decomposition of the ester groups of DMATG and formation of polymethacrylic anhydride.

The character of PEA and HPS degradation depends on the density of cross-links.[29,30] The process proceeds by the mechanism of radical-chain depolymerisation at relatively low values of this parameter and by the molecular mechanism in the case of more cross-linked samples. The degradation of the HPS samples with the density of cross-links greater than 40% obeys a more complex pattern and proceeds much lower than in the case of the samples characterised by lower densities of cross-links (Fig. 11). The presence of strained network fragments in HPS affects the shape of the initial portions of the dependences of the specific degradation rate on the degree of degradation. An increase in the thermal stability of the networks with higher density of cross-links can be explained by a decrease in the chain initiation probability and by an increase in the kinetic chain termination probability for radical-chain depolymerisation of the short, and therefore, nearly immobile chain fragments connecting cross-link points. The fact that fullerenes inhibit the degradation of these samples confirms the radical-chain degradation mechanism of the cross-linked polymer networks with a density of cross-links less than 40%.

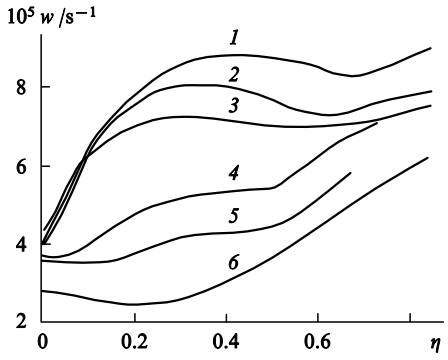


Figure 11. Specific rate of change in mass (w) plotted *vs.* degree of decomposition η for *in vacuo* destruction of cross-linked polystyrene samples at 613 K.[30]
Initial density of cross-links (%): 11 (*1*), 17 (*2*), 25 (*3*), 43 (*4*), 66 (*5*), 100 (*6*).

The formation of polymer networks is usually accompanied by noticeable reaction shrinkage. Sometimes this results in the polymer networks with a large nonequilibrium excess free volume and sometimes causes defect formation (micropores appear and cracking occurs). The kinetic regularities of the PEA degradation are affected by the value of the excess free volume and, in partiular, by the excess free volume distributions over the *n*-defects, clusters and microcavities and across the width of the sample.[31,156]

Degradation of polymeric composite materials based on linear polymers is usually studied by thermogravimetry and differential thermal analysis in the dynamic heating regime. Statistical treatment of experimental data is often carried out assuming a simple one-step kinetics. Because of this, the results obtained and conclusions drawn are, as a rule, qualitative in character. Clearly, the reasons for contradictory results of many studies on thermal and oxidative degradation of PCMs are differences between the experimental methods and procedures employed.[157]

There are a few studies on the degradation of filled polymers based on polymer networks. The decomposition kinetics of these compounds is significantly different from the decomposition kinetics of binders and depends on the type of the filler used (Fig. 12).[28,31] An increase in the decomposition rate in the presence of chemically inert fillers cannot be explained by the chemical interaction between the binder and filler. An increase in the binder decomposition rate can be attributed to the action of internal stress that depends on the type of filler, adhesion strength of the filler and binder, and the difference between the thermal expansion coefficients of the filler and binder. Residual shrinkage stress should also be taken into account because the formation of polymer networks is usually accompanied by noticeable shrinkage. A procedure based on pulsed NQR technique was developed for the determination of internal stress in polymers and polymeric composites.[158]

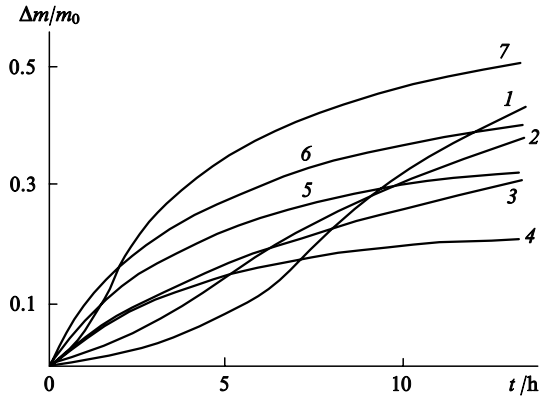


Figure 12. Relative mass change, $\Delta m/m_0$, of PEA samples for *in vacuo* destruction at 543 K.[28,31]
Unfilled samples (*1–3*), filled samples (*4–7*); particles of size 1–2 mm (*1*), film 0.2 mm thick (*2*), particles of size 0.09–0.16 mm (*3*); filler: boron fibre (*4*), organic fibre (*5*), glass fibre (*6*), carbon fibre (*7*).

Highly cross-linked polymers can be considered as best model systems suitable for establishment of the effect of microheterogeneity, restricted molecular mobility of binder with an increase in the density of cross-links, the excess free volume and its distribution over the structural elements and the stressed state of the binder (due to the difference between the thermal expansion coefficients of the binder and filler) on the thermal stability of polymer networks.

4. Effect of decomposition products of solid propellant oxidisers on the degradation of polymeric binder

Often, oxidisers or some other components of solid propellants decompose faster than binders. The decomposition products of a given component can interact with the binder. The kinetics and mechanism of this interaction depend on the nature of the oxidiser decomposition products and on the type of the polymeric binder. Oxidative degradation of linear polymers has been studied in most detail.[9,15] A monograph [15] is concerned with peculiarities of this process, supramolecular and conformational effects in the oxidation kinetics of oriented polyolefins, changes in the structure and properties of polymers under stress and analysis of the degradation regularities of polymers exposed to aggressive media under mechanical stress. Among numerous studies on the ozone ageing of strained cross-linked rubbers based on natural rubber, polyisoprene, polybutadiene, butadiene–styrene or butadiene–acrylonitrile copolymers, *etc.*, most are applied in character and

mainly concern cracking assessment and the time to rupture measurements (see monograph [15] and references cited therein). The critical strain observed during the ozone degradation of elastomers (maximum crack growth rate and minimum sample durability under nearly 20% tensile strain) can be explained [15] by a change in the reactivity of the strained C=C bond.

The kinetics and mechanism of oxidative degradation of the elastomers used as binders for solid propellants have almost not been studied. For instance, studies on the oxidative degradation of a PU elastomer based on polybutadiene containing terminal hydroxyl groups and diisocyanate were aimed at solving practical problems, *viz*., elucidation of the reasons for embrittlement of elastomers and deviation of the experimental data on thermal ageing from the Arrhenius equation.[159–163] The temperature dependences of the oxidation products of the elastomer samples containing and containing no antioxidant was studied by IR and NMR spectroscopy, GPC and oxygen uptake measurements.[162] Dynamic and chemical heterogeneity of size nearly 20 nm was found in the aged samples. The major oxygen-containing products are alcohols (~60%). Ester and acid groups were found but no ketones were detected. It was shown that chain scission is cross-linking of macromolecules occur simultaneously during degradation. The gel content increases from 60% to 90% during the oxidation, the density of cross-links in the gel substantially increases and the sol molecular mass decreases. Nevertheless, the reason for cross-linking was not established. Probably, this is due to radical-chain polymerisation of the polybutadiene fragment at the double bonds.[152]

Undoubtedly, the decomposition products of solid propellant oxidisers that intensely interact with polymeric binder are nitrogen oxides and chlorine oxides, perchloric acid and nitric acid. The interaction of nitrogen oxides and nitric acid with low-molecular-mass organic compounds and polymers was mainly investigated in relation with the kinetic and mechanistic studies of nitration of organic compounds.[164–168] It was shown that nitration of aromatic compounds is an ionic process and that nitration of paraffinic hydrocarbons is a free-radical process initiated by nitrogen dioxide. Nitration of cellulose only proceeds under the action of a nitric acid pseudoform ($HONO_2$) present at HNO_3 concentrations greater than 70%.[168] At concentrations below 60%, HNO_3 is present in the form of a trihydrate which causes oxidative degradation of cellulose. Liquid-phase oxidation of decane by nitrogen dioxide proceeds by the mechanism of degenerate branched-chain reaction.[169] Gas-phase oxidation of glyoxal by nitrogen dioxide follows a radical-chain mechanism.[170]

The effect of nitrogen oxides on polymers was mainly studied in relation with the problem of maintenance of the operating characteristics of polymeric materials exposed to aggressive media (see a review [171] and references cited therein). Degradation of various classes of polymers in NO, NO_2 and $(NO_2)_2$ atmospheres was usually studied phenomenologically without determining the rate constants and parameters of the Arrhenius equation. It was shown that at temperatures similar to room temperature NO_2 is capable of abstracting mobile hydrogen atoms from polymers to produce side nitro and nitrite groups. These processes are accompanied by scission of the main polymer chain. Nitrogen dioxide can also add to the double bonds of carbochain polymers to generate macroradicals and thus initiate free-radical ageing of the polymers. Exposure to nitrogen dioxide causes not only degradation but also cross-linking of polyisoprene and polybutadiene macromolecules. At elevated temperatures ($T \geqslant 373$ K), NO_2 also reacts with less responsive methylene C–H bonds. Interacting with alkyl, alkoxy and peroxy macroradicals, NO_2 can inhibit free-radical transformatins of polymers to give macromolecular products of different thermal stability.

Nitrogen monoxide is much less reactive compared to nitrogen dioxide. It is incapable of abstracting mobile hydrogen atoms from organic molecules and cannot add to isolated double bonds to produce free radicals at temperatures similar to room temperature. Being an efficient acceptor of free radicals, nitrogen monoxide inhibits free-radical processes.

A few phenomenological studies on the oxidation of polymers with the decomposition products of ammonium perchlorate are available.[172–174] It was shown that at high temperatures oxidative pyrolysis of polymers [poly(methyl methacrylate), polystyrene, butyl rubber, polyethylene, SKDN rubber, *etc*.] in perchloric acid vapours and in mixtures with AP becomes the predominant process proceeding with an effective activation energy of 200–240 kJ mol^{-1} (*cf*. 140 kJ mol^{-1} for the decomposition of pure AP). The kinetic and mechanistic aspects of the interaction between the oxidiser decomposition products and the binder on the topological and supramolecular levels, the effect of stress on the kinetics and mechanism of this interaction and the adhesive properties of the binder towards the filler have almost not been studied so far, though this is of great importance for well-warranted stability control of solid propellants. In this context the use of NMR, IR and EPR spectroscopies can play a significant role.[62, 74, 75] For instance, two-dimensional IR Fourier spectroscopy allowed one to study fine details of the oxidative degradation mechanism of polymer networks that cannot be established using one-dimensional spectroscopy in the frequency domain.[62] It is also possible to study the evolution of the structural characteristics of filled polymer networks in the course of binder degradation to reveal the most unstable block in the composite structure. In particular, nanolayer spectroscopy seems to be promising for studies of degradation of filled polymer networks. This method permits measurements of temporal intervals corresponding to the appearance of different types of radicals in nanolayers of a compound and establishment of the sequence of elementary acts of a chemical reaction up to the formation of molecular products.[175] However, these techniques have not been employed in studies of filled polymer networks including solid propellants as yet.

IV. Mathematical modelling of decomposition of energetic materials

1. Modelling of structure – reactivity relations

The strategy of development of weapon systems involves design of new and improvement of the existing EMs. At present, the problem of development of a cheap, efficient and fast method for testing newly designed EMs is topical in connection with enhanced requirements for the service properties of EMs.[176] An improved screening methodology is required to avoid expensive tests of inappropriate materials. This can be realised using methods of mathematical modelling that are divided into two main classes: (1) classical Monte Carlo (MC) simulation and molecular dynamics (MD) modelling and (2) quantum-chemical calculations. Quantum-chemical calculations are based on fundamental principles of quantum chemistry; solving quantum chemistry equations provides a complete and exact description of an atomic system. MD modelling using realistic models allows the reaction dynamics of large atomic systems to be described correctly.

A basic problem of theoretical chemistry is establishment of relations between the electronic structure and reactivities of reactants (rate constant for an elementary reaction can be considered as a measure of reactivity). The methodology and computational procedures employed for calculating the potential energy surfaces, dynamics and rate constants for gas-phase reactions were developed in the 1970s.

At present, quantum-chemical calculations can be carried out only for the simplest explosives and their models.[177–182] The molecular geometries in the equilibrium and transition states, Mulliken atomic charge distributions and electric dipole moments were calculated for, *e.g*., the simplest nitramines.[177, 178] These characteristics, as well as their changes caused by intramolecular motions are of importance in discussing the chemical properties of compounds. Quantum-chemical calculations of the force field,

analysis of vibrational spectra of several nitro compounds and the force constants of stretching vibrations, internuclear distances and spectral characteristics of the simplest nitramines were reported.[179]

Ab initio (including multiconfigurational) quantum-chemical methods were employed to calculate the potential energy surfaces of nitroso compounds in the ground state and in the lowest excited electronic state and to determine the equilibrium geometric parameters, vibrational frequencies and the potential functions of internal rotation of molecules.[180] The structures of nitroso compounds were calculated and the Y—NO (Y = C, N, O, S) bond dissociation energies determined.[57] The bond lengths and bond angles in ammonium dinitramide $NH_4N(NO_2)_2$ in the gas phase were obtained from *ab initio* MO calculations.[181,182]

No substantiated assumptions of the molecular geometries of 1,5- and 2,5-substituted tetrazoles, furazans and furoxans in the transition states of thermal decomposition of these compounds are available; therefore, the principle of least motion cannot be used.[183] For instance, the ground-state parameters characterising those bonds in the heterocycle that are involved in thermal decomposition were used[184] as reactivity indices. The relations established are consistent with the assumptions[37,38] of the mechanism of thermal decomposition of tetrazoles.

Quantum-chemical methods offer great computational potentials and are employed in calculations of the properties of particular molecules. Much less attention has been paid to the interpretation of results obtained in terms of the chemical bonding, molecular structure and mutual influence of molecular fragments. A quantum-chemical procedure for analysis of the electronic structure and physicochemical properties of complex molecules in terms of the interactions between the fragment orbitals was reported.[185] This approach has long been known[186] but was not systematically employed in the analysis of intramolecular interactions in order to distinguish between the key mechanisms of the mutual influence of structural fragments in complex organic molecules (inductive effect, conjugation, *etc.*) and in studies of their relations to the physicochemical properties of compounds.

Using quantum-chemical methods, it is possible to calculate the rate constant for a certain individual reaction;[187] however, generalisaiton of kinetic data for different classes of chemical reactions and the problem of establishing relations between the reactivity and structure (and physical characteristics) of reactants remain unsolved. Two empirical models (a model of intersecting parabolas and a model of intersecting Morse curves) for hydrogen abstraction reactions have been reported.[188] It was shown that the activation energy of such a reaction depends on ten parameters. These models allows the transition-state geometry (interatomic distances in the reaction centre and bond angles) to be calculated from experimental data.[189]

Recently, considerable attention has been paid to studies on the reactions dynamics in the condensed phase. Detailed consideration of the main methods of theory of liquid-phase reactions, *viz.*, numerical simulation by the Monte Carlo and molecular dynamics methods, numerical and analytical studies of the Langevin stochastic equations, Focker–Planck equation and Bohm–Gross kinetic equation has been given.[190–192] The potentials and limitations of moderm methods were exemplified by calculations of the rate constants for particular isomerisation, substitution, addition and electron transfer reactions.

Attempts at calculating the activation energy, E_a, for a dissociation reaction from the IR spectra using a relation between the anharmonicity constant and the dissociation energies of those diatomic molecules in which the interatomic interaction is described by a Morse function were undertaken.[193,194] The dissociation energies of the C—N bond in CH_3NO_2 and of the N—N bond in solid *N*-nitrodimethylamine and in CCl_4 and CH_3NO_2 solutions were calculated.

Studies[195,196] concerned more rigorous mathematical modelling of the primary steps of thermal decomposition of explosives. Density functional calculations of the initial stages of decomposition of 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one dimer were reported.[195] The reaction is characterised by an activation energy of 369 kJ mol^{-1}; its elementary stages involve the formation of four intermediates and five transition states and result in CO_2 evolution.

The initial decomposition process of urea nitrate were studied by the Hartree–Fock, density functional and second-order Müller–Plesset perturbation theories.[196] Calculations revealed the sequence of elementary stages of urea nitrate decomposition which involves one intermediate and two transition states (TS1 and TS2) with successive formation of NH_3, HNCO and HNO_3. A potential energy profile for the urea nitrate decomposition is shown in Fig. 13 *a*. The decomposition begins with intramolecular proton transfer from one NH_2 group to another to produce NH_3. The optimised geometry of TS1 corresponding to the beginning of intramolecular proton transfer is shown in Fig. 13 *b* (arrows

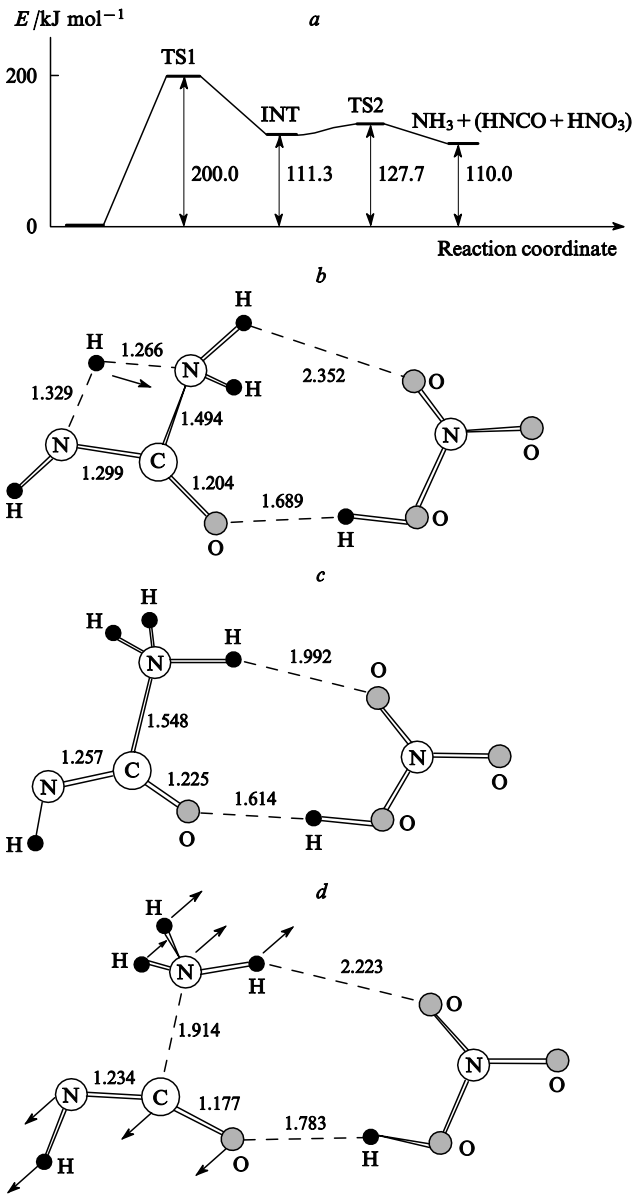


Figure 13. Results of mathematical modelling of primary stages of thermal decomposition of urea nitrate.[196]
Changes in potential energy (*a*), optimised geometry of TS1 and displacement vectors of the normal mode at 1762.7 cm^{-1} (*b*); optimised geometry of (*c*), optimised geometry of TS2 and displacement vectors of the normal mode at 319.2 cm^{-1} (*d*). Bond lengths are given in Å.

denote the displacement vectors). Transition state 1 is a four-membered ring. The intermediate formed after proton transfer goes to TS2. The directions of the displacement vectors in TS2 correspond to the decomposition with production of NH_3, HNCO and HNO_3. Transition state 1 is formed only based on the optimised structure of urea nitrate. In the case of $(NH_2)_2COH^+$, which is the ground state of the crystal structure of urea nitrate, no formation of the four-membered ring N–H–N–C occurs. Therefore, it is assumed that the two-dimensional network of strong hydrogen bonds in the crystal needs to be destroyed by external stimuli (*e.g.*, heat or impact) to begin the decomposition reaction of urea nitrate.

To design new low-sensitive EMs with improved service properties, the effect of mechanical stress on the kinetics and mechanism of their decomposition should be studied.[197] Detailed mathematical modelling of stress action on the reactivity of EMs has been carried out only for polymers.[15]

2. Modelling of solid-phase decomposition

Solid-phase decomposition of EMs can produce some products that form individual phases. Mathematical description of the formation of a new phase has attracted considerable attention.[198, 199] In particular, kinetic concepts of the nucleation and growth of vacancy pores in crystals are based on the kinetic equation of formation of a new phase.[200] According to these concepts, vacancy pores are associations of vacancies that form clusters in the form of vacancy voids (negative crystal), the cluster size varying from tens to hundreds of lattice constants. In the vicinity of each pore there is a nonuniform vacancy distribution, which depends on the vacancy size and can be treated as a vacancy-gas cloud. Diffusive motion of vacancies to a pore and settling on it cause pore motion and growth. The higher the curvature of the pore surface area, the higher the concentration of vacancies above this area.

A closed kinetic equation for the description of radiation-induced evolution of vacancy pores in the coordinate space was derived.[199] The stability regions of the vacancy pore lattice with respect to pore growth and pore displacements from the lattice sites were established. The main processes responsible for changes in the pore distribution in supersaturated vacancy gas are condensation, evaporation and surface diffusion of vacancies and coagulation of pores.

Detailed mathematical modelling of the primary step of solid-phase thermal decomposition of explosives is unavailable as yet. Mathematical treatment of decomposition of a model solid compound involving formation of solid and gaseous products was reported [8, 201] assuming deep stages of conversion where the overall steady-state process is governed by production of the solid product isolated in individual phase. Expressions for the interface propagation velocity, characteristic thickness of the reaction zone and concentration distribution were derived for the simplest idealised case of reversible first-order reaction with allowance for diffusion of the solid product ignoring the stress and strain effects on the reaction rate.

A steady-state mathematical model [8, 202] for reaction front propagation in AP crystal was constructed assuming a dislocation-chain mechanism of AP decomposition ignoring diffusion of reaction products. According to the DCM model, AP decomposes on dislocations, multiplication of dislocations being stress induced. However, the kinetic description of dislocations in this model is phenomenological. The dependences of the dislocation multiplication rate on stress applied and on the concentration of dislocations have no substantiation. The model also ignores such important stages of plastic deformation of the crystalline material as dislocation annihilation, mutual entrapment of dislocations in the intersecting slip planes, dislocation absorption at grain boundaries and dislocation multiplication by double cross sliding.[203, 204] In addition, stress distribution was preset arbitrarily and relations between the stress–strain state and fracture micromechanics of the crystal and the pressure of gaseous products were ignored. Linear dependence of the AP decomposition rate on the dislocation concentration postulated in the model is inconsistent with the experimental data. It should also be noted that evaluation of the model is impossible due to the lack of methods suitable for the determination of the constants appeared in the model equations.

N S Enikolopov and co-workers (see a review [205] and references cited therein) showed that shear deformation causes a substantial (by 3–8 orders of magnitude) increase in the rate of solid-phase reactions compared to the rate of liquid-phase reactions. It was assumed that reactions in the detonation regime proceed isothermally at low temperatures due to immediate conversion of chemical energy into mechanical energy.

Theoretical studies of pre-explosive phenomena under shock-wave initiation showed that the key step of the solid-phase stage of the process are electronic excitations. Narrowing of the forbidden band upon compression of explosives at the reaction wave front was considered.[206] Calculations of the electronic structure of 1,3,5-trinitro-1,3,5-triazacyclohexane revealed [207] a local narrowing of the forbidden band near dislocations and additional narrowing of the forbidden band upon compression in the shock front, which leads to considerable increase in the electronic excitation probability (formation of an exciton) and cleavage of the $N-NO_2$ bond. A molecular dynamics study [176] revealed that metallisation (loss of covalency) upon compression of explosives must be taken into account as the primary step of a sequence of reactions leading to detonation. On the molecular level, a shock-initiated chemical reaction is described [208, 209] as a nonequilibrium non-thermal process whose rate is determined by the average vibrational rate of radical pairs produced *via* molecular decomposition on the 10^{-14}–10^{-12} s time scale. This model is consistent with the results of MD calculatios.[210]

Almost all EMs are heterogeneous in nature, being often composed of a polycrystalline material and a binder. The presence of internal interfaces differs the behaviour of EMs from that of pure materials. Compaction (consolidation), strain and a chemical reaction in a porous explosive was studied using three-dimensional modelling of shock action on an 'array of discrete crystals'.[211] It was shown that fast deformation at contact points induces large-amplitude fluctuations of the strain state characterised by a wavelength of the order of a few particle diameters. Energy localisation causes the appearance of 'hot' spots. Chemical reaction produces multiple wave structures depending on the particle size distribution.

Modelling of thermal decomposition of solid propellants on the mesolevel (oxidiser particle — binder layer) was not performed.

3. Modelling of combustion of energetic materials

Combustion of EMs is a complex physicochemical process, which involves decomposition reactions, heat and mass transfer and strain and decomposition. The complexity of the process makes experimental studies and the development of rigorous quantitative theories of EM combustion difficult. It is believed that elaboration and analysis of simplified combustion models with allowance for particular factors only in order makes possible clarification of the physical picture of combustion and a relatively simple mathematical description. The problem of mathematical modelling of EM combustion goes beyond the scope of this review and should be considered separately due to extensive literature on the problem. However, we will dwell on those aspects of mathematical modelling of the process that are immediately related to the influence of the kinetics and mechanism of EM decomposition on the regularities of their combustion.

A number of simple models of linear combustion with allowance for dispersion, foaming, evaporation and sublimation of the solid compound have been analysed.[212–219] Usually, one-step or two-step reactions are considered ignoring differences between the kinetic regularities of heat release and gas evolution in the course of decomposition. For instance, combustion of highly volatile compounds is analysed using a reaction kinetics scheme

involving two concurrent or two successive steps.[215, 216] Combustion studies of individual explosives were carried out assuming a one-step kinetics with allowance for the difference between the activation parameters for the condensed phase and the gas phase.[217, 218] Combustion of mixed systems was analysed in the homogeneous condensed zone approximation taking into account (i) thermal decomposition and sublimation of oxidiser and (ii) binder degradation and oxidation by the oxidiser decomposition products; however, the corresponding reaction kinetics were described by zero-order reaction equations.[219]

As shown above, the decomposition of EMs proceeds by a complex multistage mechanism. The results of the combustion rate calculations obtained in the analysis of simple combustion models are in good agreement with the experimental data of combustion studies of several oxidisers (NH_4ClO_4, $NH_3OH.ClO_4$, NH_4NO_3, $CH_3NH_3ClO_4$) with complex decomposition mechanisms.[8, 220] Because of this, it may appear that complexity of the EM decomposition kinetics and mechanism is insignificant for mathematical modelling and there is no longer need of detailed studies on the EM decomposition. However, this conclusion is incorrect, because mathematical modelling of combustion of EMs often involves an arbitrary closure of the system of equations by introducing one or two arbitrary parameters, *e.g.*, an additional heat flow from the gas phase to the condensed phase and the degree of dispersion (sublimation). These models ignore the mechanical problem; therefore, a relation between the dispersion and combustion conditions is established based on the simplest estimates.[8] Following this way, the interrelation between the stress–strain state of EMs and the regularities of combustion is reduced to the dependence of the burning rate on pressure.

Note that an increase in pressure has almost no effect on thermal decomposition of binder in the case of radical-chain mechanism. The molecular mechanism is characterised by a decrease in the rate of evaporation of high-molecular-mass degradation products.[221] Consideration of the mechanical problem in combustion modelling is also necessary because combustion of charges with actual geometry requires allowance for not only hydrostatic pressure but also the deviator components of the stress tensor. As shown above, these components can strongly influence the decomposition of solid propellants.

Finally, note that in the early 1960s studies on the macrokinetics of exothermic reactions revealed that the reaction front temperature exceeds the adiabatic temperature (Fig. 14). A part of these results obtained in experimental studies of solid propellant block formation was reported some later.[222] Nevertheless, combustion in the condensed phase is usually modelled assuming that reaction front propagation can be described similarly to gas-phase combustion[8, 223] and the steady-state combustion models ignore experimentally detected excess of enthalpy in the combustion wave, which leads to superadiabatic temperatures.

To some extent the simplified mathematical treatment of EM combustion can be explained by the lack of the kinetic parameters relevant to complexity of the multistage EM decomposition over a wide temperature interval. Nevertheless, note that almost all correctly posed problems can be solved using modern powerful computers and experimental techniques. For instance, a modern strategy of modelling well-developed turbulent flows of multicomponent reactive gases with allowance for interrelations between the chemical kinetics and turbulent transfer was reported.[224]

Recently, advances were also made in studies of combustion of mixed fuels. These studies intensively use computer simulation of processes proceeding in the gas phase and condensed phase. Numerical analysis of combustion of a model fuel based on 1,3,5-trinitro-1,3,5-triazacyclohexane and glycidyl azide polymer has been reported.[225] Four oxidiser and binder decomposition reactions were taken into account for the condensed phase while the kinetic scheme for the gas phase included a total of 532 reactions involving seventy-four compounds.

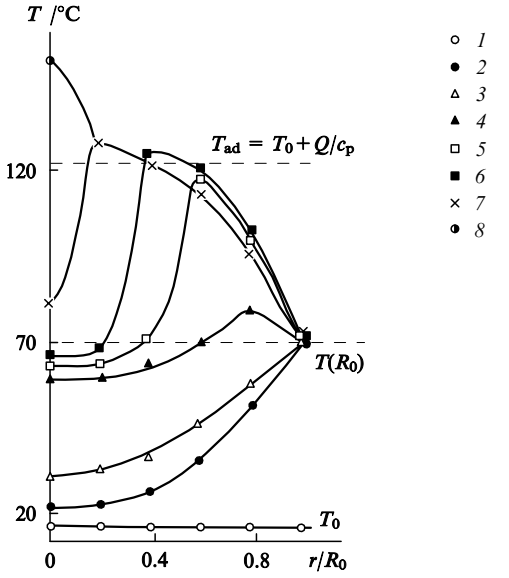


Figure 14. Temperature distribution throughout the cross section of a cylindrical reactor of radius R_0 = 20 cm for polymerisation of a model mixture based on triethylene glycol dimethacrylate.[222]
Dimensionless time, t/t_∞: 0 (*1*), 0.25 (*2*), 0.40 (*3*), 0.86 (*4*), 0.91 (*5*), 0.95 (*6*), 0.99 (*7*), 1.0 (*8*).

V. Stability prediction of energetic materials

Explosives, solid propellants and powders are thermodynamically unstable materials due to occurrence of chemical reactions and physical processes in these substances.[8, 226] This requires the EM service life to be assessed with a rather high accuracy because untimely replacement of items made of EMs causes unreasonable expenditures. Explosive demolition requires that precautions be taken, often being an environmental hazard.

The warranty period of items made of EMs can be determined empirically or semiempirically but mathematical modelling is thought to be more efficient.[9, 226] A scheme of modelling of complex physicochemical processes was first developed to study thermal explosions. It involves phenomenological studies of the process, aimed at identification of the most important factors responsible for the changes in the practically valuable properties of EMs; construction of physicochemical and mathematical models of the process; experimental determination of parameters of particular stages; calculations and comparison of the results obtained with the results of full-scale tests to evaluate the accuracy of prediction, *etc*.

No mathematical model suitable for correct description of all (most important) physicochemical and physicomechanical processes proceeding in the course of production and storage of items made of EMs is available as yet. A relevant procedure for assessment of the warranty period of items made of EMs based on mathematical modelling has also not been elaborated so far. It was proposed[8] to characterise the stabilities of solid fuels and of the cast and pressed charges by the time taken to reach a degree of decomposition of 0.02% during the reprocessing step and storage life of the composition (in this case all gaseous products are dissolved in the condensed phase and development of internal pressure, pore formation and swelling of items are impossible). According to this concept, the extent of changes in the service life of items made of EMs are solely determined by the after-effects of gas evolution in the course of decomposition (increase in internal pressure, pore formation and swelling of items). Calculations of the tolerable degree of decomposition were carried out ignoring gas diffusion and the presence of atmospheric gases dissolved in the condensed phase.

This method of determination of stability criteria for EMs and items made of them has neither practical nor theoretical substantiation. The development of internal pressure, pore formation and swelling of items owing to gas evolution in the course of EM decomposition have not been studied even phenomenologically, the effect of these parameters on the operating characteristics has not been established and no quantitative relationships between them and the degree of decomposition was found, though porosimetry techniques for the condensed phase are well known (*e.g.*, positron annihilation and NMR spectroscopy). A small variation of porosity during decomposition is permissible, because pressed items made of explosives are characterised by a nearly 5% initial porosity. The service life of most solid propellants depends on the changes in their physicomechanical characteristics due to the binder degradation, which often proceeds without gas evolution.[227, 228] If an item made of solid propellants is subject to shrinkage or temperature stress, an increase (within certain limits) in the volume of the solid propellant due to gas evolution and pore formation is useful, because it reduces or even completely relieves stress.

The predictive power of the proposed unexperimented procedure for the determination of stability criterion is low. The authors noted that this criterion can vary within the limits of two orders of magnitude for the same composition. In practice, low accuracy of prediction is to some extent compensated by prolongation of the warranty period based on the results of full-scale tests of the items after expiration date. The 'benefit' from the prolongation of the warranty period is of course imaginary. Nevertheless, for obvious reasons this does not favour improvement of service life assessment procedures.

Temperature is not the sole factor determining the stability of items made of EMs.[226] The rate of a decomposition reaction also depends on different kinds of radiation (X-ray, UV, *etc.*), on the mechanical stress, on the presence of moisture and other compounds in the environment, *etc*. The influence of these factors on the EM decomposition and on the stability of items made of EMs has been studied much poorer than the thermal effects.

Instability of the shape and size of items made of EMs can be due to not only thermal decomposition but also incompleteness of phase separation in the course of crystallisation, thermodynamically nonequilibrium conformation of polymer chains and other physical factors.[226, 229]

Solving the problem of stability prediction for EMs requires a great body of data and takes a long time. For instance, in the USA the service life of rocket engines is evaluated by statistical treatment of the results of accelerated cyclic load tests of engines belonging to groups with different storage lifes. This allows one to attain engine failure in admissible and predictable time.[230, 231] Direct comparison of the results of calculations with the behaviour of the item under operating conditions requires too long time. However, differences between the test results and the life expectancy can be due to not only ignoration of some operation factors but also to a change in the mechanism of the process under operating conditions. For instance, if two competing concurrent processes (breakdown of cross-links and cross-linking) proceed in a polymer network, the dependence of the stress – strain properties on time has the form

$$Y = \alpha\exp(-k_1 t) - \beta\exp(-k_2 t) + Y_0,$$

where k_1 and k_2 are the rate constants for breakdown of cross-links and cross-linking, respectively, and Y_0, α and β are constants. If $k_1 < k_2$ under test conditions, the dependence $Y(t)$ passes through a minimum; otherwise ($k_1 > k_2$), it passes through a maximum. Extrapolation with allowance for the behaviour of the function $Y(t)$ in the initial period of tests can introduce gross errors.[226] Changes in the stress – strain state of the composite due to the difference between the binder and filler thermal expansion coefficients and temperature-induced changes in the mechanism of the interaction between the oxidiser decomposition products and binder can also introduce large errors when using a similar extrapolation.

A combined prediction procedure involving alternate 'placing' of a material or an item under accelerated test conditions and under operating conditions is nearly free from these drawbacks.[9]

At present, NMR imaging techniques have been intensively developed. They permit imaging of internal structure of a material and monitoring of its state immediately under operating conditions.[87, 232–235] NMR images are in essence multidimensional NMR spectra. For instance, NMR imaging permits non-destructive real-time monitoring of the dynamics of physical and chemical processes by measuring the spatial distribution of concentration in any section of the sample. Large objects are studied using surface coils [233] or devices combining an RF coil and a magnetic field source.

VI. Conclusion

The kinetic and mechanistic studies of EM decomposition aimed at solving important practical and theoretical problems are far from being completed. This is to a great extent due to the fact that the scientific and methodological potentials of modern chemical physics (in particular, chemical kinetics) and solid state physics are still little used in the EM decomposition studies. An optimum research strategy must involve joint kinetic and mechanistic studies of complex chemical reactions. This can be done using various efficient methods of determination of the composition of reaction mixtures and the evolution of reactant concentrations in the course of reaction. However, the decomposition mechanism of explosives is usually studied out of the context of the kinetics of elementary decomposition stages while the kinetic parameters are as a rule determined using methods of formal kinetics. However, these methods are little informative and therefore cannot be used for the determination of the rate constants for elementary stages of multistage processes.

Computer simulation of the decomposition of explosives as a means of controlling the mechanism reliability is only coming in practice, being performed taking simple model compounds as examples. The kinetics and mechanism of the decomposition of explosives in the condensed phase are very poorly studied because improved methods of investigation of the supramolecular structure of liquid and solid explosives characterised by rather high spatial and temporal resolution are almost not employed. Information on the supramolecular structure of the condensed phase and its evolution in the course of reaction is ignored. The true rate constants for the primary steps of decomposition (leave alone the rate constants for all elementary stages of the process) have not been determined as yet even for in-service explosives and solid propellant oxidisers and the corresponding decomposition mechanisms are not substantiated. The aforesaid suggests that the available methods of theoretical chemistry have considerable promise for the determination of the kinetics and mechanism of thermal decomposition of EMs. The highest efficiency can be attained in joint studies carried out using these methods and modern experimental techniques.

Usually, solid propellant binders are polymer networks with a complex multilevel structure. The chemical, topological and supramolecular structure of such polymers and composites based on them can be investigated using modern efficient and theoretically substantiated approaches. A number of methods for studying the structure of the free volume subsystem of the polymer network are available. This allows the decomposition kinetics of polymer networks and composites exposed to the action of various external factors to be studied, the most unstable structural blocks to be determined and efficient methods of stability improvement to be elaborated. However, the new techniques are very rarely used in studies of the degradation and stabilisation of solid propellants; the decomposition of solid propellants is studied using methods of formal kinetics.

The most important problem, prediction of stability of EMs, is still to be solved. The proposed criterion for stability of these materials (limitation on the tolerable degree of conversion during the reprocessing time and the storage life to a value of 0.02%) is not substantiated. In this situation the best way is to use of a combined prediction procedure and NMR techniques that allow the state of items made of EMs to be monitored immediately under operating conditions.

Mathematical modelling of combustion is performed using simple steady-state models and a number of essential assumptions. This is due to the lack of kinetic parameters relevant to the actual complexity of EM decomposition over a wide temperature interval. Powerful modern computers allow almost all correctly posed problems in the field of mathematical modelling of EM combustion to be solved.

References

1. G M Nazin, G B Manelis *Usp. Khim.* **63** 327 (1994) [*Russ. Chem. Rev.* **63** 313 (1994)]
2. F I Dubovitskii, B L Korsunskii *Usp. Khim.* **50** 1828 (1981) [*Russ. Chem. Rev.* **50** 958 (1981)]
3. R A Fifer, in *Fundamentals of Solid-Propellant Combustion* Vol. 90 (Eds K Kuo, M Summerfield) (New York: AIAA, 1984) p. 177
4. N E Ermolin, V E Zarko *Fiz. Goren. Vzryva* **33** (3) 10 (1997) [a]
5. R Boshan, R T Merrow, R W Van Dolan *Chem. Rev.* **55** 485 (1955)
6. A G Keenan, R F Siegmund *Quart. Rev.* **23** 430 (1969)
7. G B Manelis (Ed.) *Mekhanizm Termicheskogo Razlozheniya Perkhlorata Ammoniya* (Mechanism of Thermal Decomposition of Ammonium Perchlorate) (Chernogolovka: United Institute of Chemical Physics, 1981)
8. G B Manelis, G M Nazin, Yu I Rubtsov, V A Strunin *Thermal Decomposition and Combustion of Explosives and Propellants* (London, New York: Taylor and Francis, 2003)
9. N M Emanuel, A L Buchachenko *Khimicheskaya Fizika Molekulyarnogo Razrusheniya i Stabilizatsii Polimerov* (Chemical Physics of Molecular Destruction and Stabilisation of Polymers) (Moscow: Nauka, 1988)
10. N A Plate, A V Litmanovich, O V Noa *Makromolekulyarnye Reaktsii* (Macromolecular Reactions) (Moscow: Khimiya, 1977)
11. V A Kabanov, V P Zubov, Yu D Semchikov *Kompleksno-Radikal'naya Polimerizatsiya* (Complex Radical Polymerisation) (Moscow: Khimiya, 1987)
12. A L Volynskii, N F Bakeev *Vysokodispersnoe Orientirovannoe Sostoyanie Polimerov* (Highly Dispersed Directed State of Polymers) (Moscow: Khimiya, 1984)
13. Al Al Berlin, S A Vol'fson, V G Oshmyan, N S Enikolopov *Printsipy Sozdaniya Kompozitsionnykh Polimernykh Materialov* (Principles of Creation of Composite Polymer Materials) (Moscow: Khimiya, 1990)
14. V I Irzhak, B A Rozenberg, N S Enikolopyan *Setchatye Polimery: Sintez, Struktura, Svoistva* (Cross-Linked Polymers: Syntheses, Structure and Properties) (Moscow: Khimiya, 1979)
15. A A Popov, N Ya Rapoport, G E Zaikov *Okislenie Orientirovannykh i Napryazhennykh Polimerov* (Oxidation of Directed and Stressed Polymers) (Moscow: Khimiya, 1987)
16. G I Sandakov, V P Tarasov, N N Volkova, Yu A Ol'khov, L P Smirnov, L N Erofeev, A K Khitrin *Vysokomol. Soedin., Ser. B* **31** 821 (1989) [b]
17. L N Erofeev, G I Sandakov, L P Smirnov, A I Sosikov, K T Summanen, N N Volkova, in *Proceedings of the International Rubber Conference IRC'94, Moscow, 1994* Vol. 2, p. 628
18. G I Sandakov, L P Smirnov, A I Sosikov, K T Summanen, N N Volkova *J. Polym. Sci., Polym. Phys.* **32** 1585 (1994)
19. G I Sandakov, L P Smirnov, K T Summanen, N N Volkova *Prog. Colloid Polym. Sci.* **90** 235 (1992)
20. N N Volkova, G I Sandakov, A I Sosikov, Yu A Ol'khov, L P Smirnov, K T Summanen *Vysokomol. Soedin., Ser. A* **34** 77 (1992) [b]
21. E Sh Nudel'man, G A Gorbushina, Yu A Ol'khov, L P Smirnov *Vysokomol. Soedin., Ser. A* **34** 69 (1992) [b]
22. B E Krisyuk, G I Sandakov *Vysokomol. Soedin., Ser. A* **37** 615 (1995) [b]
23. L P Smirnov, N N Volkova *Prog. Colloid Polym. Sci.* **90** 222 (1992)
24. L P Smirnov *Vysokomol. Soedin., Ser. B* **42** 1775 (2000) [b]
25. N N Volkova, A I Sosikov, M P Berezin, G V Korolev, L N Erofeev, L P Smirnov *Vysokomol. Soedin., Ser. A* **30** 2133 (1988) [b]
26. N N Volkova, Candidate Thesis in Chemical Sciences, United Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka, 1984
27. E Sh Nudel'man, Candidate Thesis in Chemical Sciences, United Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka, 1991
28. N N Volkova, E V Summanen, L P Smirnov, E A Dzhavadyan, T I Ponomareva, B A Rozenberg *Mekh. Kompoz. Mater.* 391 (1990)
29. N N Volkova, L M Bogdanova, E V Summanen, B A Shumm, L N Erofeev, L P Smirnov *Vysokomol. Soedin., Ser. A* **43** 1773 (2001) [b]
30. N N Volkova, E V Summanen, L P Smirnov *Vysokomol. Soedin., Ser. A* **45** 1659 (2003) [b]
31. L P Smirnov, in *Heterophase Network Polymers. Synthesis, Characterization and Properties* (Eds B A Rozenberg, G M Sigalov) (London, New York: Taylor and Francis, 2002) p. 235
32. E V Sokerina, D E Lushnikov, T S Pivina, A A Porollo, V P Ivshin, in *The Proceedings of the 21st International Pyrotechnic Seminar, Moscow, 1995* p. 849
33. M J S Dewar, J P Ritchie, J Alster *J. Org. Chem.* **50** 1031 (1985)
34. A M Wodtke, E J Hintsa, Y T Lee *J. Chem. Phys.* **84** 1044 (1986)
35. A M Wodtke, E J Hintsa, Y T Lee *J. Phys. Chem.* **90** 3549 (1986)
36. B L Korsunskii, V G Matveev, L D Nazina, G M Nazin *Izv. Akad. Nauk, Ser. Khim.* 259 (1998) [c]
37. V G Prokudin, V S Poplavskii, V A Ostrovskii *Izv. Akad. Nauk, Ser. Khim.* 2209 (1996) [c]
38. V G Prokudin, V S Poplavskii, V A Ostrovskii *Izv. Akad. Nauk, Ser. Khim.* 2216 (1996) [c]
39. V V Dubikhin, V G Matveev, G M Nazin *Izv. Akad. Nauk, Ser. Khim.* 1977 (1996) [c]
40. S N Bulusu (Ed.) *Chemistry and Physics of Energetic Materials* (London: Kluwer, 1990)
41. G F Adams, R W Shaw *Annu. Rev. Phys. Chem.* **4** 311 (1992)
42. P P Shorygin, N B Lopatina, B V Lopatin, T E Gorodilova *Izv. Akad. Nauk, Ser. Khim.* 304 (1998) [c]
43. V V Dubikhin, G V Lagodzinskaya, A M Korolev, V G Matveev, G M Nazin *Khim. Fiz.* **22** (7) 28 (2003) [d]
44. R C Farmer *J. Chem. Soc.* **117** 1603 (1920)
45. C N Hinshelwood *J. Chem. Soc.* **119** 721 (1921)
46. F I Dubovitskii, G B Manelis, L P Smirnov *Zh. Fiz. Khim.* **35** 521 (1961) [e]
47. B A Lur'e, V P Sinditskii, S P Smirnov *Fiz. Goren. Vzryva* **39** (5) 55 (2003) [a]
48. G M Nazin, V G Prokudin, G B Manelis *Izv. Akad. Nauk, Ser. Khim.* 231 (2000) [c]
49. V P Sinditskii, V Yu Egoryshev, M V Berezin *Khim. Fiz.* **22** (4) 56 (2003) [d]
50. Z Jalovy, S Zeman, in *The Proceedings of the 30th International Annual Conference ICT, Karlsruhe, 1999* p. 104
51. L P Hammet *Physical Organic Chemistry* (New York: McGraw-Hill, 1940)
52. R W Taft *J. Am. Chem. Soc.* **74** 2729 (1952)
53. R W Taft *J. Am. Chem. Soc.* **74** 3120 (1952)
54. M I Kumskov, S E Peshkova, L A Ponomareva, K I Rezchikova *Izv Akad. Nauk, Ser. Khim.* 1942 (1996) [c]
55. T S Pivina, D V Sukhachev, L K Maslova, V A Shlyapochnikov, N S Zefirov *Dokl. Akad. Nauk* **330** 468 (1993) [f]
56. A R Bulter, D L H Williams *Chem. Soc. Rev.* **22** 233 (1993)
57. Y Fu, Y Mou, B-L Lin, L Lin, Q-X Guo *J. Phys. Chem. A* **106** 12386 (2002)
58. M Schütze, H Herrmann *Phys. Chem. Chem. Phys.* **4** 60 (2002)

59. I V Koptyug, R Z Sagdeev *Usp. Khim.* **72** 183 (2003) [*Russ. Chem. Rev.* **72** 165 (2003)]
60. M Khalil, N Demirdöven, A Tokmakoff *J. Phys. Chem. A* **107** 5258 (2003)
61. R R Ernst, G Bodenhausen, A Wokaun *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Oxford: Oxford University Press, 1987)
62. P Musto *Macromolecules* **36** 3210 (2003)
63. S Belusu, R Behrens *Def. Sci. J.* **46** 347 (1996)
64. R S Stepanov, V N Shan'ko, I P Medvedetskaya, L A Kuznetsov, in *Fizicheskaya Khimiya* (Physical Chemistry) Vol. 2 (Krasnoyarsk: Siberian Technological Institute, 1965) p. 3
65. V V Dubikhin, V G Matveev, G M Nazin *Izv. Akad. Nauk, Ser. Khim.* 266 (1995) [c]
66. J-M Lehn *Supramolecular Chemistry. Concepts and Perspectives* (Weinheim: VCH, 1995)
67. H Ratajczak, W J Orville-Thomas *Molecular Interactions* Vol. 2 (New York: Wiley, 1981)
68. Yu Ya Maksimov, E N Kogut *Zh. Fiz. Khim.* **52** 1400 (1978) [c]
69. I F Falyachov, G P Sharnin, N M Safin, I Sh Saifullin, R Kh Fassakhov, in *The Proceedings of the 21st International Pyrotechnic Seminar, Moscow, 1995* p. 187
70. V A Shlyapnikov, L S Khaikin, O E Grikina, N O Cherskaya, L E Maksimova, N F Pyatakov *Izv. Akad. Nauk, Ser. Khim.* 2241 (1998) [c]
71. B Lurie, E Semkiv, in *The Proceedings of the 21st International Pyrotechnic Seminar, Moscow, 1995* p. 547
72. P S Belton, R G Ratcliffe *Prog. Nucl. Magn. Reson. Spectrosc.* **17** 241 (1985)
73. N R Skrynnikov, F W Dahlquist, L E Kay *J. Am. Chem. Soc.* **124** 12 352 (2002)
74. D E Thompson, K A Merchant, M D Fayer *J. Chem. Phys.* **115** 317 (2001)
75. A T Krummel, P Mukherjee, M T Zanni *J. Phys. Chem. B* **107** 9165 (2003)
76. P Gray, S K Scott *Chemical Oscillations and Instabilities. Non-linear Kinetics* (Oxford: Clarendon Press, 1994)
77. M Goldman *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Oxford: Clarendon Press, 1970)
78. L T Abramova, Yu N Rogov, L P Smirnov, in *Tezisy Dokladov Pervogo Vsesoyuznogo Simpoziuma po Makroskopicheskoi Kinetike i Khimicheskoi Gazodinamike, Alma-Ata, 1984* (Abstracts of Reports of the First All-Union Symposium on Macroscopic Kinetics and Chemical Gaz Dynamics, Alma-Ata, 1984) Vol. 2, p. 80
79. L P Smirnov, E V Deyun, E V Summanen, in *Khimicheskaya Fizika Protsessov Goreniya i Vzryva (Tez. Dokl. XII Simpoziuma po Goreniyu i Vzryvu), Chernogolovka, 2000* [Chemical Physics of Combustion and Explosion Processes (Abstracts of Reports of the XXIIth Symposium on Combustion and Explosion), Chernogolovka, 2000] Pt. 3, p. 107
80. L P Smirnov, E V Summanen *Dokl. Akad. Nauk* **386** 359 (2002) [f]
81. A N Ivanova *Kinet. Katal.* **20** 1019 (1979) [g]
82. M Feinberg *Chem. Eng. Sci.* **42** 2229 (1987)
83. M Feinberg, in *Patterns and Dynamics in Reactive Media* Vol. 37 (Eds R Aris, D Ararson, H L Swinney) (Berlin: Springer, 1991) p. 43
84. M J Chedin *J. Chim. Phys. (France)* **49** 109 (1952)
85. Yu Ya Maksimov, E N Kogut *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **20** 349 (1977)
86. I V Koptyug, A A Lysova, V N Parmon, R Z Sagdeev *Kinet. Katal.* **44** 436 (2003) [g]
87. I V Koptyug, R Z Sagdeev *Usp. Khim.* **71** 672 (2002) [*Russ. Chem. Rev.* **71** 593 (2002)]
88. A V Raevskii, in *Mekhanizm Termicheskogo Razlozheniya Perkhlorata Ammoniya* (Mechanism of Thermal Decomposition of Ammonium Perchlorate) (Ed. G B Manelis) (Chernogolovka: United Institute of Chemical Physics, 1981) p. 30
89. S M Ryabykh *Khim. Fiz.* **9** (2) 191 (1990) [d]
90. Yu M Burov, G B Manelis, G M Nazin *Khim. Fiz.* **4** (7) 956 (1985) [d]
91. Yu M Burov, G M Nazin, G B Manelis *Izv. Akad. Nauk, Ser. Khim.* 1261 (1999) [c]
92. T Vladimiroff, B M Rise *J. Phys. Chem. A* **106** 10437 (2002)
93. V I Tarzhanov *Fiz. Goren. Vzryva* **39** (6) 3 (2003) [a]
94. Yu A Zakharov, E D Aluker, B P Aduev *Predvzryvnye Yavleniya v Azidakh Tyazhelykh Metallov* (Preexplosive Effects in Azides of Heavy Metals) (Moscow: TsEI 'Khimmash', 2002)
95. B P Aduev, E D Aluker, A G Krechetov, A Yu Mitrofanov *Fiz. Goren. Vzryva* **39** (6) 104 (2003) [a]
96. J T Dickinson, L C Jensen, D L Doering, R Yee *J. Appl. Phys.* **67** 3641 (1990)
97. B P Aduev, E D Aluker, G M Belokurov, A G Krechetov *Zh. Eksp. Teor. Fiz.* **116** 1676 (1999) [h]
98. E G Bagryanskaya, R Z Sagdeev *Usp. Khim.* **69** 1009 (2000) [*Russ. Chem. Rev.* **69** 925 (2000)]
99. V A Koroban, B S Svetlov, V P Guk, T I Smirnova, in *Mekhanizm Termicheskogo Razlozheniya Perkhlorata Ammoniya* (Mechanism of Thermal Decomposition of Ammonium Perchlorate) (Ed. G B Manelis) (Chernogolovka: United Institute of Chemical Physics, 1981) p. 5
100. E F Khairetdinov, T V Mulina, V V Boldyrev, in *Mekhanizm Termicheskogo Razlozheniya Perkhlorata Ammoniya* (Mechanism of Thermal Decomposition of Ammonium Perchlorate) (Ed. G B Manelis) (Chernogolovka: United Institute of Chemical Physics, 1981) p. 101
101. Yu I Rubtsov, G B Manelis, in *Mekhanizm Termicheskogo Razlozheniya Perkhlorata Ammoniya* (Mechanism of Thermal Decomposition of Ammonium Perchlorate) (Ed. G B Manelis) (Chernogolovka: United Institute of Chemical Physics, 1981) p. 123
102. R V Gol'dshtein, V M Entov, B R Pavlovskii *Dokl. Akad. Nauk SSSR* **237** 828 (1977) [f]
103. Y Ba, D Chagolla *J. Phys. Chem. B* **106** 5250 (2002)
104. V P Shantarovich, Yu A Novikov, Z K Azamatova *Fiz. Tv. Tela* **40** 164 (1998) [i]
105. T Giavani, H Bildsoe, J Skibsted, H J Jakobsen *J. Phys. Chem. B* **106** 3026 (2002)
106. V P Sinditskii, V Yu Egoryshev, M V Berezin, V V Serushkin, Yu M Milekhin, S A Gusev, A A Matveev *Khim. Fiz.* **22** (7) 69 (2003) [d]
107. N I Golovina, G V Shilov, L O Atovmyan, S M Aldoshin, in *Materialy Vserossiiskoi Konferentsii 'Energeticheskie Kondensirovannye Sistemy'* (Materials of All-Russian Conference 'Energetic Condensed Systems') (Chernogolovka, Moscow: Yanus-K, 2002) p. 22
108. B L Korsunskii, V V Nedel'ko, N V Chukanov, T S Larikova, F Fol'k *Izv Akad. Nauk, Ser. Khim.* 815 (2000) [c]
109. V V Nedel'ko, B L Korsunskii, N V Chukanov, T S Larikova, E A Semendyaeva, in *Materialy Vserossiiskoi Konferentsii 'Energeticheskie Kondensirovannye Sistemy'* (Materials of All-Union Conference 'Energetic Condensed Systems') (Chernogolovka, Moscow: Yanus-K, 2002) p. 30
110. D G Patil, N B Brill *Combust. Flame* **87** 145 (1991)
111. S Löbbecke, M A Bohn, A Pfeil, H Krause, in *The Proceedings of the 29th International Annual Conference of ICT*. Karlsruhe 1998. P. 145
112. J C Oxley, A B Kooh, R Szekeres, W Zheng *J. Phys. Chem.* **98** 7004 (1994)
113. V I Kovalenko *Usp. Khim.* **64** 803 (1995) [*Russ. Chem. Rev.* **64** 753 (1995)]
114. L G Browning, G G Gelenter, S R Harris, C M Mason *J. Phys. Chem.* **60** 1260 (1956)
115. G E Kornilova, B A Lur'e, B S Svetlov, in *Trudy MKhTI im. D I Mendeleeva* (Proceedings of D I Mendeleev Moscow Chemical Technology Institute) (Moscow: Vyssh. Shkola, 1969) No. 62, p. 62
116. K K Andreev, B S Samsonov, in *Trudy MKhTI im. D I Mendeleeva* (Proceedings of D I Mendeleev Moscow Chemical Technology Institute) (Moscow: Vyssh. Shkola, 1967) No. 53, p. 7
117. K K Andreev, B S Samsonov, in *Trudy MKhTI im. D I Mendeleeva* (Proceedings of D I Mendeleev Moscow Chemical Technology Institute) (Moscow: Vyssh. Shkola, 1967) No. 53, p. 22
118. V A Mal'chevskii, O F Pozdnyakov, V R Regel', M G Fal'kovskii *Vysokomol. Soedin., Ser. A* **13** 2078 (1971) [b]

119. R W Phillips, C A Orlick, R J Steinberger *Phys. Chem.* **59** 1034 (1955)
120. L P Smirnov, L N Leksina, Yu N Rogov, G A Volkov, in *The Proceedings of the 21st Pyrotechnics Seminar, Moscow, 1995* p. 813
121. V A Silaev, F M Gumerov, V F Sopin, I L Zhuravleva, G N Marchenko *Khim. Fiz.* **10** (1) 70 (1991) [d]
122. Yu N Rogov, L P Smirnov, L N Leksina, V S Ushakova *Vysokomol. Soedin., Ser. A* **31** 352 (1989) [b]
123. B A Lur'e, B S Svetlov, in *Trudy MKhTI im. D I Mendeleeva* (Proceedings of D I Mendeleev Moscow Chemical Technology Institute) (Moscow: Vyssh. Shkola, 1980) No. 112, p. 5
124. A El-ghayoury, H Hofmeier, B de Ruiter, U S Schubert *Macromolecules* **36** 3955 (2003)
125. E N Kablov *Vestn. Ros. Akad. Nauk* **72** (1) 3 (2002) [j]
126. E Ya Davydov, A P Vorotnikov, V P Pustoshnyi, G B Pariiskii *Usp. Khim.* **69** 981 (2000) [*Russ. Chem. Rev.* **69** 899 (2000)]
127. V I Irzhak *Usp. Khim.* **69** 283 (2000) [*Russ. Chem. Rev.* **69** 261 (2000)]
128. Yu D Tretyakov *Usp. Khim.* **72** 731 (2003) [*Russ. Chem. Rev.* **72** 651 (2003)]
129. I L Moudrakovski, V V Terskikh, Ch I Ratcliffe, J A Ripmeester, L-Q Wang, Y Shin, G J Exarhos *J. Phys. Chem. B* **106** 5938 (2002)
130. J H Strang, M Rahman, E G Smith *Phys. Rev. Lett.* **71** 3589 (1993)
131. S G Allen, P C L Stephenson, J H Strange *J. Chem. Phys.* **106** 7802 (1997)
132. Yu A Mikheev, G E Zaikov *Khim. Fiz.* **20** (11) 55 (2001) [d]
133. V U Novikov, G V Kozlov *Usp. Khim.* **69** 572 (2000) [*Russ. Chem. Rev.* **69** 523 (2000)]
134. V P Solomko *Napolnennye Kristallizuyushchiesya Polimery* (Filled Crystallisable Polymers) (Kiev: Naukova Dumka, 1980)
135. V M Litvinov, V G Vasil'ev *Vysokomol. Soedin., Ser. A* **32** 2329 (1990) [b]
136. J W ten Brinke, V M Litvinov, J E G J Wijnhoven, J W M Noordermeer *Macromolecules* **35** 10 026 (2002)
137. H Matsubara, A Yoshido, Y Kondo, Sh Tsuge, H Ohtani *Macromolecules* **36** 4750 (2003)
138. W F Jaeger, A Lungu, D Y Chen, D C Neckers *Macromolecules* **30** 780 (1997)
139. A Lungu, D C Neckers *Macromolecules* **28** 8147 (1995)
140. P E M Allen, G P Simon, D R G Williams, E H Williams *Macromolecules* **22** 809 (1989)
141. T P Kulagina, V M Litvinov, K T Summanen *J. Polym. Sci., Polym. Phys.* **31** 241 (1993)
142. E V Deyun, G B Manelis, E V Polianchik, L P Smirnov *Usp. Khim.* **49** 1574 (1980) [*Russ. Chem. Rev.* **49** 749 (1980)]
143. L Reich, S S Stivala *Elements of Polymer Degradation* (New York: McGraw-Hill, 1972)
144. N A Lavrov, A G Pisarev *Plasticheskie Massy* (1) 28 (2002)
145. S-J Rark, H-C Kim, H-I Lee, D-H Suh *Macromolecules* **34** 7573 (2001)
146. E Dyer, G E Newborn *J. Am. Chem. Soc.* **80** 5495 (1958)
147. E Dyer, G C Wright *J. Am. Chem. Soc.* **81** 2138 (1959)
148. M P Thorne *Can. J. Chem.* **45** 2537 (1967)
149. N Grassie, M Zulfiqar *J. Polym. Sci., Polym. Chem. Ed.* **16** 1563 (1978)
150. N Grassie, M Zulfiqar, M I Guy *J. Polym. Sci., Polym. Chem. Ed.* **18** 265 (1980)
151. S Poti, P Maravigna, G Mantando *J. Polym. Sci., Polym. Chem. Ed.* **19** 1679 (1981)
152. N N Volkova, Yu I Ol'khov, S M Baturin, L P Smirnov *Issledovanie Termicheskogo Razlozheniya Shitykh Poliuretanov* (Investigation of Thermal Decomposition of Cross-Linked Polyurethanes) (Preprint of United Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka, 1983)
153. L P Smirnov, E Sh Nudel'man *Raschet Konfiguratsii Uretanovykh Grupp v Zavisimosti ot ikh Polozheniya v Polimernoi Setke* (Calculation of Configuration of Urethane Groups Depending on Their Position in Polymer Network) (Preprint of Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka, 1991)
154. N N Kausch *Polymer Fracture* (Berlin: Springer, 1978)
155. G M Bartenev *Prochnost' i Mekhanizm Razrusheniya Polimerov* (Strength and Mechanism of Polymer Fracture) (Moscow: Khimiya, 1984)
156. L M Bogdanova, N N Volkova, A V Lankin, L P Smirnov *Vysokomol. Soedin., Ser. A* **40** 297 (1998) [b]
157. M T Bryk *Destruktsiya Napolnennykh Polimernykh Sistem* (Destruction of Filled Polymer Systems) (Moscow: Khimiya, 1989)
158. V P Tarasov, L N Erofeev, E A Dzhavadyan, Yu N Smirnov, B A Rozenberg, in *Heterophase Network Polymers. Synthesis, Characterization and Properties* (Eds B A Rozenberg, G M Sigalov) (London, New York: Taylor and Francis, 2002) p. 301
159. K T Gillen, M Celina, R L Clough, J Wise *Trends Polym. Sci.* **5** 250 (1997)
160. E Földes, J Lohmeijer *Polym. Degrad. Stab.* **66** 31 (1999)
161. G Ahlblad, T Reitberger, B Terselius, P Stenberg *Polym. Degrad. Stab.* **65** 185 (1999)
162. D J Harris, R A Assink, M Celina *Macromolecules* **34** 6695 (2001)
163. M Celina, A C Graham, K T Gillen, R A Assink, L M Minier *Rubber Chem. Technol.* **73** 678 (2000)
164. E D Hughes, C K Ingold, R I Reed *J. Chem. Soc.* 2400 (1950)
165. A V Topchiev *Nitrovanie Uglevodorodov i Drugikh Organicheskikh Soedinenii* (Nitration of Hydrocarbons and Other Organic Compounds) (Moscow: Academy of Sciences of the USSR, 1956)
166. S S Novikov, G A Shveikhgeimer, V V Sevost'yanova, V A Shlyapochnikov *Khimiya Alifaticheskikh Alitsiklicheskikh Nitrosoedinenii* (The Chemistry of Aliphatic and Alicyclic Nitrocompounds) (Moscow: Khimiya, 1974)
167. V A Rafeev, Yu I Rubtsov, T V Sorokina *Izv. Akad. Nauk, Ser. Khim.* 343 (1996) [c]
168. E Farmer *J. Soc. Chem. Ind.* **50** 75 (1931)
169. Yu I Rubtsov, A I Kazakov, E Yu Rubtsova, L P Andrienko, E P Kirpichev *Izv. Akad. Nauk, Ser. Khim.* 1986 (1996) [c]
170. J H Thomas *Trans. Faraday Soc.* **49** 630 (1953)
171. G B Pariiskii, I S Gaponova, E Ya Davydov *Usp. Khim.* **69** 1071 (2000) [*Russ. Chem. Rev.* **69** 985 (2000)]
172. O P Korobeinichev, K K Kovalenko, A I Lesnikovich *Fiz. Goren. Vzryva* **13** 550 (1977) [a]
173. E P Goncharov, A G Merzhanov, A S Shteinberg, in *Gorenie i Vzryv. Materialy 3-go Vsesoyuznogo Simpoziuma po Goreniyu i Vzryvu* (Combustion and Explosion. Proceedings of the 3rd All-Union Symposium on Combustion and Explosion) (Moscow: Nauka, 1972) p. 765
174. A P D'yakov, L I Nikolaeva, V A Strunin, G B Manelis *Khim. Fiz.* **22** (5) 70 (2003) [d]
175. A I Pristupa, V A Sharpatyi *Dokl. Akad. Nauk* **387** 643 (2002) [f]
176. B M Rice, J Hare, S V Pai, W Mattson, G Krasko, S F Trevino, D C Sorescu, D L Thompson *Khim. Fiz.* **20** (10) 9 (2001) [d]
177. L S Khaikin, O E Grikina, L V Vilkov, M A Palafoks, J E Boggs *Zh. Strukt. Khim.* **34** 4 (1993) [k]
178. L S Khaikin, O E Grikina, V A Shlyapochnikov, L V Vilkov, Ch V Bok *Izv. Akad. Nauk, Ser. Khim.* 2135 (1995) [c]
179. L S Khaikin, O E Grikina, V I Perevozchikov, S S Kramarenko, V A Shlyapochnikov, J E Boggs *Izv. Akad. Nauk, Ser. Khim.* 1557 (1998) [c]
180. E K Dolgov, V A Bataev, I A Godunov *Izv. Akad. Nauk, Ser. Khim.* 35 (2003) [c]
181. A M Mebel, M C Lin, K Morokuma, C F Melius *J. Phys. Chem.* **99** 6842 (1995)
182. G F Valardez, S Alavi, D L Thompson *J. Chem. Phys.* **119** 6698 (2003)
183. V I Minkin, B Ya Simkin, R M Minyaev *Kvantovaya Khimiya Organicheskikh Soedinenii. Mekhanizmy Reaktsii* (Quantum Chemistry of Organic Compounds. Reaction Mechanisms) (Moscow: Nauka, 1986)
184. Yu Yu Nikishev, I Sh Saifullin, O R Klyuchnikov *Kinet. Katal.* **34** 969 (1993) [g]
185. V M Promyslov, P P Shorygin *Izv. Akad. Nauk, Ser. Khim.* 1835 (2000) [c]

186. E L Mehler *J. Chem. Phys.* **74** 6298 (1981)
187. K J Leidler *Chemical Kinetics* (New York: Harper and Row, 1987)
188. E T Denisov *Usp. Khim.* **66** 953 (1997) [*Russ. Chem. Rev.* **66** 859 (1997)]
189. T G Denisova, N S Emel'yanova *Kinet. Katal.* **44** 485 (2003) [g]
190. M V Bazilevskii, V I Faustov *Usp. Khim.* **61** 1185 (1992) [*Russ. Chem. Rev.* **61** 651 (1992)]
191. B Ya Simkin, I I Sheikhet *Kvantovo-Khimicheskaya i Statisticheskaya Teoriya Rastvorov. Vychislitel'nye Metody i Ikh Primenenie* (Quantum-Chemical and Statistic Theory of Solutions. Numerical Methods and Their Applications) (Moscow: Khimiya, 1989)
192. P Haggi, P Talkner, M Borkovec *Rev. Modern Phys.* **62** 251 (1990)
193. N V Chukanov, B L Korsunskii, F I Dubovitskii, O V Anan'ina *Dokl. Akad. Nauk SSSR* **265** 1445 (1982) [f]
194. N V Chukanov, B L Korsunskii, F I Dubovitskii, O V Anan'ina *Dokl. Akad. Nauk SSSR* **277** 1181 (1984) [f]
195. Y Kohno, O Takahashi, K Saito *Phys. Chem. Chem. Phys.* **3** 2724 (2001)
196. Y Kohno, O Takahashi, R I Hiyoshi, J Nakamura, K Saito *J. Phys. Chem. A* **107** 6444 (2003)
197. P Politzer, H E Alper, in *Computational Chemistry, Reviews of Current Trends* Ch. 6 (Ed. J Leszezynski) (Singapore: World Scientific, 1999) p. 4
198. A I Olemskoi, I V Kaplyk *Usp. Fiz. Nauk* **165** 1105 (1995) [*Physics-Uspekhi* **38** 1061 (1995)]
199. L A Maksimov, A I Ryazanov *Zh. Eksp. Teor. Fiz.* **79** 2311 (1980) [h]
200. Ya B Zel'dovich *Zh. Eksp. Teor. Fiz.* **12** 525 (1942) [h]
201. G B Manelis, V A Strunin *Zh. Fiz. Khim.* **46** 1987 (1972) [e]
202. G B Manelis, E V Polianchik *Sov. Sci. Rev., Chem. Rev. B* **15** 61 (1991)
203. V I Trefilov (Ed.) *Deformatsionnoe Uprochnenie i Razrushenie Kristallicheskikh Materialov* (Deformation Strengthening and Destruction of Crystalline Materials) (Kiev: Naukova Dumka, 1987)
204. V E Panin, V A Likhachev, Yu V Grinyaev *Strukturnye Urovni Deformatsii Tverdykh Tel* (Structure Levels of Deformation of Solids) (Novosibirsk: Nauka, 1985)
205. N S Enikolopov *Usp. Khim.* **60** 586 (1991) [*Russ. Chem. Rev.* **60** 283 (1991)]
206. J J Gilman *Mechanochemistry* **274** 65 (1996)
207. M M Kuklja, E V Stefanovich, A B Kunz *J. Chem. Phys.* **112** 3417 (2000)
208. F E Walker *J. Appl. Phys.* **63** 5548 (1988)
209. F E Uoker *Khim. Fiz.* **14** (12) 47 (1995) [d]
210. B M Rice, W Mattson, J Grosh, S F Trevino *Phys. Rev. E* **53** 611 (1996)
211. M R Baer *Khim. Fiz.* **20** (10) 21 (2001) [d]
212. V A Strunin *Zh. Fiz. Khim.* **39** 433 (1965) [e]
213. E I Maksimov, A G Merzhanov *Dokl. Akad. Nauk SSSR* **157** 412 (1964) [f]
214. G B Manelis, V A Strunin *Combust. Flame* **17** 69 (1971)
215. V A Strunin, G B Manelis *Fiz. Goren. Vzryva* **19** (2) 89 (1983) [a]
216. B I Khaikin, A K Filonenko, S I Khudyaev *Fiz. Goren. Vzryva* **4** 591 (1968) [a]
217. V A Strunin, A N Firsov, K G Shkadinskii, G B Manelis *Fiz. Goren. Vzryva* **22** (1) 3 (1986) [a]
218. V A Strunin, A N Firsov, K G Shkadinskii, G B Manelis *Fiz. Goren. Vzryva* **22** (1) 40 (1986) [a]
219. V A Strunin, G B Manelis *Fiz. Goren. Vzryva* **15** (5) 24 (1979) [a]
220. F I Dubovitskii *Khim. Fiz.* **1** (1) 127 (1982) [d]
221. A A Koptelov, S V Karyazov *Dokl. Akad. Nauk* **389** 643 (2003) [f]
222. G B Manelis, L P Smirnov *Fiz. Goren. Vzryva* **12** 665 (1976) [a]
223. A G Merzhanov, B I Khaikin *Teoriya Voln Goreniya v Gomogennykh Sredakh* (Theory of Combustion Wave in Homogenous Media) (Chernogolovka: Institute of Structural Macrokinetics, Academy of Sciences of the USSR, 1992)
224. A V Kolesnichenko *Matemat. Model.* **14** (7) 81 (2002)
225. E S Kim, V Yang, Y-C Liau *Combust. Flame* **131** 227 (2002)
226. B D Goikhman, T P Smekhunova *Usp. Khim.* **49** 1554 (1980) [*Russ. Chem. Rev.* **49** 748 (1980)]
227. W N Huang, J J Aklonis *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **16** 88 (1975)
228. J Moacanin, J J Aklonis, R F Landel *J. Macromol. Sci., B* **11** 41 (1975)
229. Ch Lin, S B Chun, P T Mather, L Zheng, E H Haley, E B Coughlin *Macromolecules* **35** 9868 (2002)
230. G J Svob, K W Bills *J. Spacecraft Rockets* **21** 162 (1984)
231. K Kishore, V R P Verneker, V Gayathri, K R Shubha, K Sridhara *J. Spacecr. Rockets* **20** 345 (1983)
232. P T Callaghan *Principles of Nuclear Magnetic Resonance Microscopy* (Oxford: Clarendon Press, 1991)
233. I V Koptyug, L Yu Il'ina, V B Fenelonov, A Yu Derevyankin, R Z Sagdeev, V N Parmon *Dokl. Akad. Nauk* **376** 777 (2001) [f]
234. G Eidmann, R Savelsberg, P Blümler, B B Blümich *J. Magn. Res., A* **122** 104 (1996)
235. J J Ackerman *Concepts Magn. Res.* **2** 33 (1990)

[a] — *Combust. Explos. Shok Waves (Engl. Transl.)*
[b] — *Polym. Sci. (Engl. Transl.)*
[c] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[d] — *Chem. Phys. Rep. (Engl. Transl.)*
[e] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[f] — *Dokl. Chem. (Engl. Transl.)*
[g] — *Kinet. Catal. (Engl. Transl.)*
[h] — *J. Exp. Theor. Phys. (Engl. Transl.)*
[i] — *Phys. Solid State (Engl. Transl.)*
[j] — *Herald Russ. Acad. Sci. (Engl. Transl.)*
[k] — *Russ. J. Struct. Chem. (Engl. Transl.)*