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Mechanoemission and mechanochemistry of molecular organic crystals

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Abstract. Data on the emission phenomena and chemical processes occurring in molecular organic crystals capable of rapid exothermic decomposition when subjected to mechanical influences are surveyed. The influence of the nature, composition, and pressure of the gaseous medium on the probability of initiation of the mechanical decomposition of single crystals is examined. The existing concepts concerning the initiation of fast reactions in organic crystals are analysed. A general scheme is proposed for the electrophysical phenomena and chemical reactions occurring when solids are subjected to mechanical influences. The bibliography includes 132 references.

I. Introduction

The study of the physical phenomena and chemical reactions occurring in solids subjected to mechanical influences may play a notable role in the search for nontraditional ways of carrying out technological processes and in the selection of new methods for controlling the activation of chemicals and materials.

The mechanical stresses acting from outside on a solid can lead to irreversible consequences when they have attained certain values: plastic deformation of the crystal lattice and decomposition of the crystal.

In the course of the decomposition of solids, chemical bonds are broken and active centres are formed, whereupon streams of electrons and ions and electromagnetic radiation are generated. These include X-rays with a wide spectral range[1-7] and various electrophysical phenomena due to the formation on the fresh surfaces of an uncompensated charge that relaxes relatively slowly and persists for a fairly long time (up to several hours in the case of dielectric materials). Naturally, the physicochemical properties of the solid (especially its conductivity) influence the intensity and kinetics of the electrophysical phenomena. Such influence is most marked in the case of dielectric materials. The forms of radiation noted above may be combined under the term cold plasma.[8] The idea of the transition of a substance to a plasma state when a solid is subjected to mechanical influences was first proposed by Thiessen.[9,10] Subsequent experimental studies confirmed the validity of this hypothesis.[1-7]

The emission phenomena and chemical reactions observed when solids are subjected to mechanical influences are summarised in the generalised scheme in Fig. 1.

Fig. 2 presents a scheme of the possible consequences of subjecting polymers to mechanical stresses. The mechanical degradation of polymer macromolecules is also accompanied by the rupture of chemical bonds: reactive free radicals (paramagnetic centres) and low-molecular-mass compounds (fragments of macromolecules down to the monomer) are generated. The mechanochemical transformations in polymers have been considered in detail in a number of studies.[1,3,6] A number of electrophysical phenomena are observed on formation of the disintegration surfaces in polymers (as in dielectrics): the appearance of an excess electrical charge, the emission of electrons, gas discharges, luminescence, and other types of emission (IR, radio waves). The characteristic features of their manifestation have been treated systematically in a number of studies.[1-4,6,7]

For a long time, the objects in the study of the mechanoemission and mechanochemistry of solids have been mainly ionic and homopolar crystals as well as polymers (see, for example, Refs 1-4, 6, and 11-13). When these substances are disintegrated, the rupture of chemical bonds is an obligatory consequence.

The structure of the molecular crystals of organic substances has a number of features, which is reflected in their properties. The structural unit in the crystal lattices of organic substances is the molecule, the atoms of which are linked by strong covalent bonds. Only weak van der Waals interactions exist or hydrogen bonds are formed between the molecules. Such a structure of molecular crystals determines many of their physical and mechanical properties: the high electrical resistivity ($10^{15}-10^{18}$ Ωm), the low melting point (down to ~600 K), and the poor mechanical strength and hardness.

Molecular organic crystals have found extensive practical applications and the study of the variation of their electrophysical and physicochemical properties when the crystals are subjected to mechanical influences is therefore a problem of current interest.

The mechanoemission phenomena and chemical reactions in molecular organic dielectric materials, which disintegrate rapidly when subjected to mechanical forces, are described in the present review. The authors have devoted special attention to the

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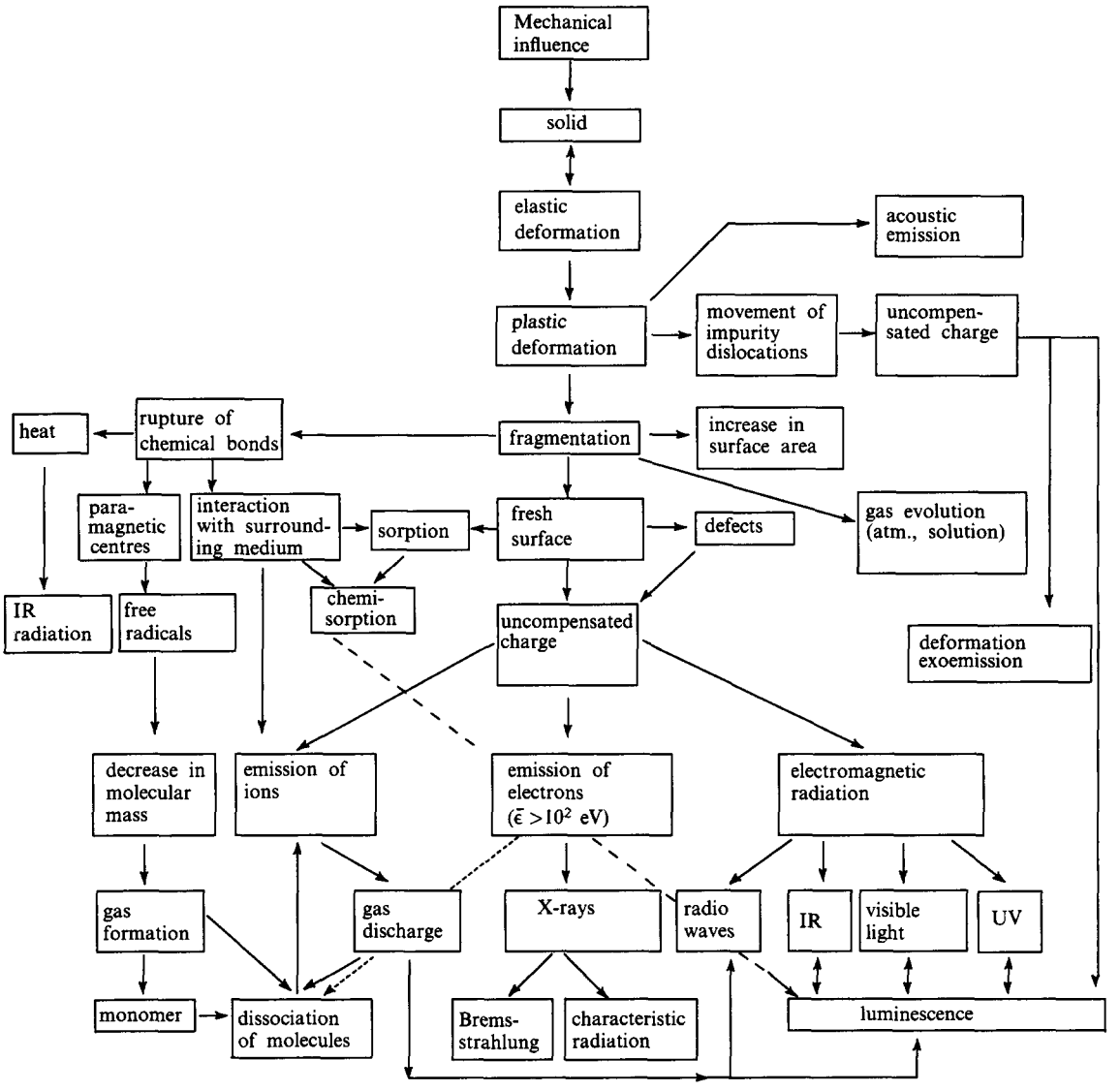


Figure 1. Generalised scheme of the emission phenomena and chemical reactions occurring when solids are subjected to an external mechanical influence.

electrophysical phenomena accompanying the appearance of new disintegration surfaces. These phenomena may induce mechanochemical reactions in the molecular organic substances. The mechanoemission phenomena accompanied by the rupture of bonds of different nature are in our view not only responsible for the chemical reactivity of the fresh surface but also activate the gaseous medium in its vicinity.

II. Electrophysical phenomena

1. Charges on the fresh cleavage surfaces of ionic crystals

In the disintegration of dielectric solids, uncompensated charges having different signs appear on the walls of the developing crack. The very strong electric fields arising under these conditions are the cause of various emission phenomena leading also to chemical changes in the test substance.

The study of the electric fields on the freshly formed surface and especially in a developing crack is fairly complex owing to the rapid relaxation of the excess charge in the initial instant of the lifetime of the fresh surface and the small size of the electrically active regions. Thus the nonstationary electric field in the cleavage crack (the rate of propagation of which is several hundreds of metres per second) in the case of alkali metal halides (a lithium fluoride single crystal) does not exceed 20% of the initial value ($\sim 60\ \mu Cm^{-2}$) after only 10–20 s.[14]

In real crystals, defects are always present as a consequence of their deviation from the ideal periodicity. One distinguishes point defects (impurity atoms or ions, vacancies, atoms or ions of the test substance itself localised in the intestices, etc.), linear defects (dislocations — breakdown in the regular arrangement of atomic planes, in particular of boundaries between regions with different orientations of the crystal structure) and bulk-phase defects (accumulation of vacancies, pores, gas bubbles, etc.). The defectiveness of the crystal lattice as well as the process involving the rupture of an ionic bond (i.e. the very chemical nature of the ionic crystal) are responsible for the nonuniformity of the distribution of electrons between cations and anions. It must be emphasised that the electrically active structure of real crystals has been pre-programmed, i.e. specified, by the nature and characteristic features of the growth of the nuclei of the future crystals with particular defects,[15] while the process involving the disintegration of crystalline substances itself leads to the additional formation of new charged defects on the fresh cleavage surface.

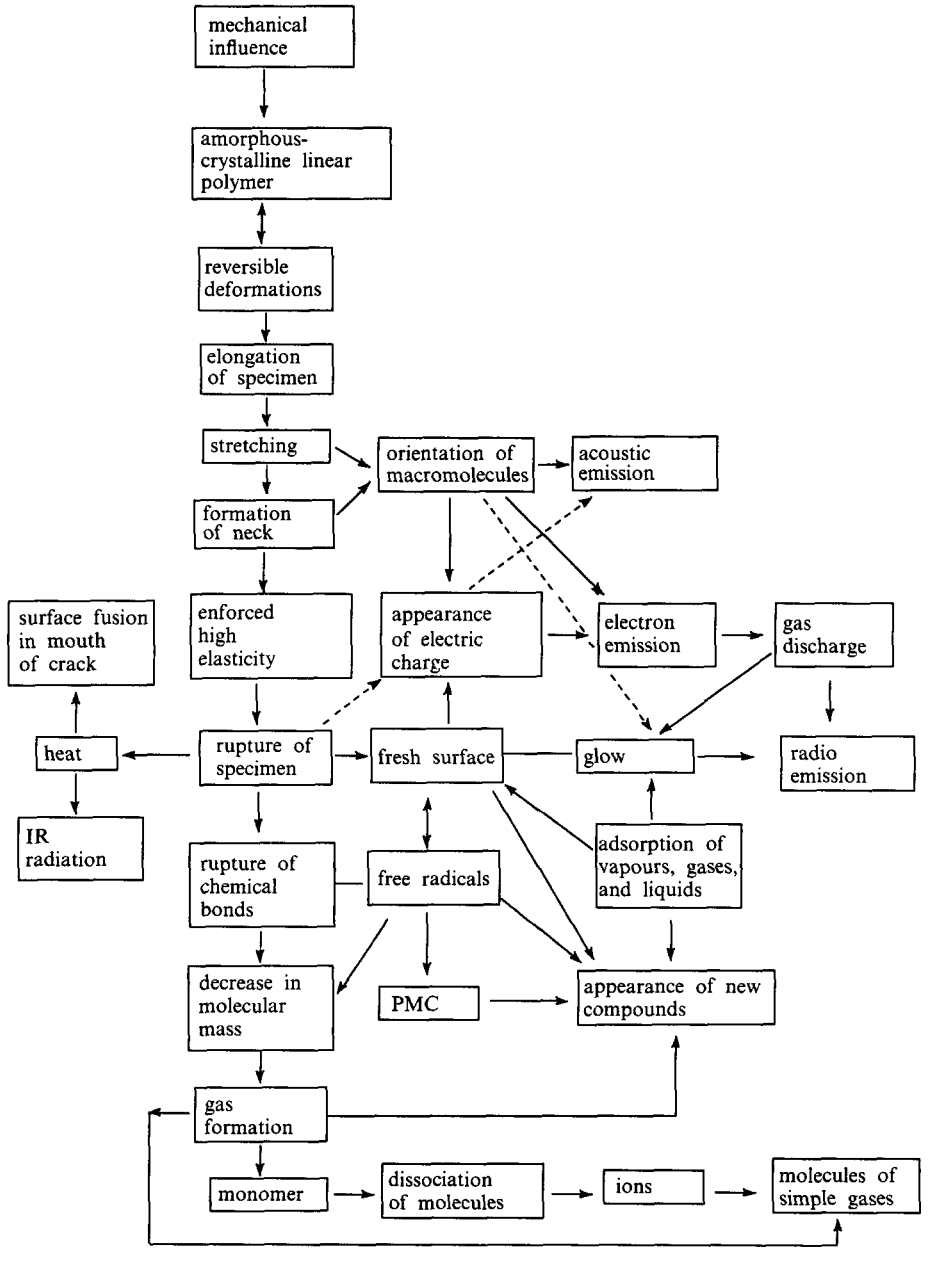


Figure 2. Scheme of possible mechanoemission phenomena and mechanochemical reactions occurring when polymers are subjected to external stresses.

The defective sites constitute electrically active centres and uncompensated ruptured chemical bonds on the disintegration surface of the crystal. Such active centres are frequently detected by the decoration method, where a decorating substance is deposited from the vapour (or liquid) phase (such substances are usually gold, silver chloride, anthraquinone, latexes, etc.). The nuclei are then formed and grow predominantly on the negatively charged section of the surface. The decoration patterns — the topographies of the surfaces and, in particular, of the cleavage surfaces with point defects and their accumulations — are investigated by optical and electron microscope methods.[15] In the case of ionic single crystals, the density of the charged active centres usually attains values of $10^{10} - 5 \times 10^{11}$ cm^{-2}. The results of the study of the electrical nonuniformity (defectiveness) of the cleavage surfaces of various solids by the decoration method have been surveyed in a monograph.[15]

Distler et al.[15] actually observed by the decoration method the electrical breakdowns between positively and negatively charged microregions on the fresh cleavage surface of a quenched sodium chloride crystal for a field strength of $\sim 10^8$ V m^{-1} (see also Deryagin et al.[1]). The decorating gold particles were condensed at the instant of the disintegration of the specimen, i.e. during the growth of the main crack. It has been noted that the charging of the cleavage surface in lithium fluoride does not influence greatly the crack propagation velocity.[16] It is believed[17] that the rate of movement of the main crack can be regulated up to its arrest with the aid of externally applied electric fields.

It has been established by modern physical research methods that the growth of the main crack in ionic crystals, in particular in alkali metal halides, proceeds nonuniformly — in jumps.[17-20] It has been claimed[20] that the power of the emission of the charged particles from the mouth of the crack exceeds by 6 - 10 orders of magnitude the power of the emission of particles from the edges of the crack. It is of interest that the low-temperature chemical reactions occurring on brittle disintegration of solid systems are also of the pulsating type.[21]

Scanning of the surface by means of a special probe electrode using the familiar vibrating capacitor principle may serve as another method for the determination of the electrical surface microrelief, for example of the mirror cleavage plane of the crystal.

Distler et al.[15] concentrated attention on the study of the point defects inducing the appearance of charged microregions on the cleavage surface, i.e. after the fragmentation of the specimen. Among the models of the mechanisms of the generation of a charge in the crack on plastic deformation and disintegration of ionic (in particular, alkali metal halide) crystals, the dislocation model proposed by Molotskii has come to be most widely used.[22] The dominant role of the dislocation mechanism in the charging of a freshly formed disintegration surface in alkali metal halides has been demonstrated.[23] The relaxation of the charge makes it possible to account for the mechanochemical dissociation of the walls of the crack (for example the emission of lithium ions from lithium fluoride).[23,24] The dislocation concept has been supported also by other workers.[18,25,26] Other defects can likewise promote the formation of a charge on the fresh cleavage surface of an ionic crystal.

A possible mechanism for the appearance of deformation luminescence and electron emission in alkali metal halides has been provided[25] by the intersection of dislocations in the course of the plastic deformation of the specimens, where there is a probability of electronic transitions which result in the appearance of electron and hole centres. The recombination of these active centres leads to the emission of electrons and photons. The movement of the dislocations at low rates of deformation (down to 10^{-5} s^{-1}) in a single slip of annealed lithium fluoride specimens leads to the accumulations of charges on the surface of the specimen up to electrical breakdown.[26]

2. Uncompensated charges on the cleavage surfaces of organic crystals

It has been established experimentally at the optical level by the method involving decoration with anthraquinone[27] that electrically charged regions, differing in the sign and magnitude of the potential, are present on the cleavage surfaces of cyclotrimethylenetrinitramine (C3MNA) and trinitrophenylmethylnitramine (3NPNA) crystals. Since the decoration was carried out several minutes after the breakdown of the crystals, the observed mosaic microrelief of the electrically active regions reflects only partially the distribution of the charge density of the electric fields on the fresh cleavage surface and in essence represents the residual charge distribution pattern despite the strong dielectric properties of the test crystals.

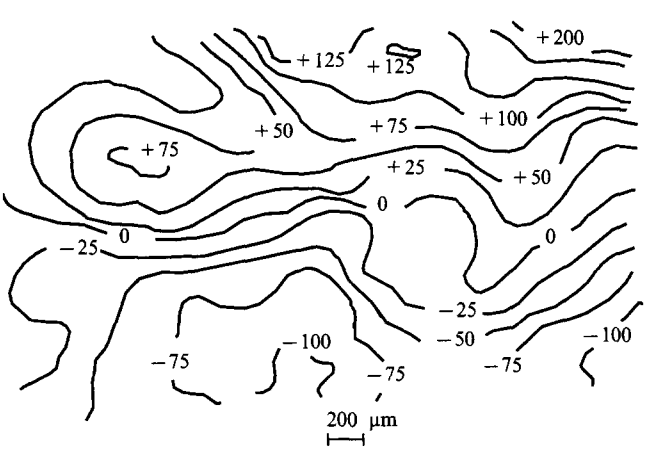


Figure 3. Electric relief of the local fields on the cleavage surfaces of a C3MNA crystal.[27]

The nature of the distribution of the electrical charges on the cleavage surfaces of the same crystals has been investigated by the scanning probe method based on the dynamic capacitor principle.[27] Topograms with a linear resolution of ~50 μm obtained (Fig. 3) show that the positive and negative potentials of individual sections of the cleavage surface may reach 10^3 V.

The considerable external similarity between the topograms of the electrical microrelief and the geometrical relief of the breakdown surface, which can be observed visually under a microscope with a magnification by a factor of 50–100, is noteworthy.[27] Polishing of the cleavage surface of the crystal by a solvent, which to a large extent removes the microrugosities, entails the virtually complete disappearance of the electrical microrelief. Rubbing of the solvent-etched surface with a cotton cloth again induced the appearance of an electrical potential up to 10^3 V. The subsequent relaxation of the potential depends significantly on the pressure (the rate of relaxation diminishes on rarefaction) and the humidity (Fig. 4).

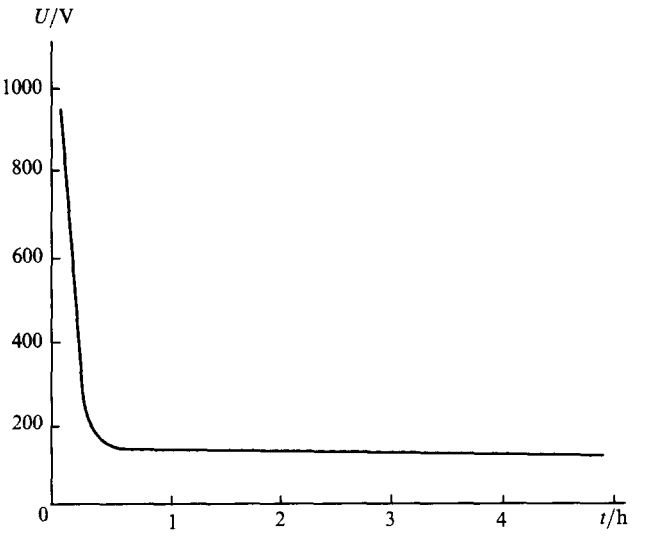


Figure 4. Relaxation of the potential (U) on the surface of a C3MNA crystal after polishing and rubbing against a fabric.[27]

3. Different ways leading to the formation of the electrical microrelief on the breakdown surfaces of organic crystals

The formation of an electrical microrelief on the breakdown surface of an organic crystal may be a consequence of a change in the geometry of the defective surface — the appearance on it of dislocations.

It has been demonstrated experimentally that the cleavage surfaces in the test crystals contain numerous steps and other imperfections.[27] These substances have dipole moments of 3–5 D.[28,29] The microrugosities may generate, in the direction of the measuring electrode, fields of different sign and potential depending on the orientation of the molecular dipoles on the cleavage steps. An experimental test on flat and point electric field sources showed that the dependence of the electrical output signal on the distance between the sources and the electrode (r) is close to exponential for $r > 0.2$ mm.[27]

The presence of steps on the cleavage surface of a sodium chloride single crystal as well as the appearance of new planes, uncharacteristic of the cubic form of the crystals, in particular the [111] plane, has been established.[30]

Thus the microrugosities on the cleavage surface of the crystal investigated may influence significantly the magnitude of the potential determined by the scanning probe method. Consequently the topography of the electrical surface microrelief

represents an electrical map of its geometry. This is also indicated by the disappearance of electric fields after the surface has been etched with a solvent.

The dislocations on the cleavage surface, giving rise to steps, are electrically charged. They distort the pattern of the electron distribution in the crystal lattice. The accumulation of electrons on the cleavage surface become the cause of the appearance of a potential at the fresh surface, where their density is three orders of magnitude higher than for the main bulk of the crystal which has been little deformed.[27]

Experiments have shown[27] that the external pressure and concentration of water vapour play a notable role in the relaxation of charges on the cleavage surface. This is evidently associated with the adsorption and desorption processes on the fresh cleavage surface, which alter the electrical relief.

It is difficult to say which of the mechanisms examined above is decisive because they are manifested simultaneously.

4. Electron emission and electromagnetic radiation emitted from the fresh cleavage surface

When organic molecular crystals of pentaerythritol tetranitrate (PETN), C3MNA, cyclotetramethylenetetranitramine (C4MNA), and 3NPNA were cleaved in a vacuum chamber at a residual pressure of $10^{-3}-10^{-5}$ Pa, the emission of electrons from the cleavage surface was recorded.[31-35] The maximum emission intensity was recorded immediately after the disruption of the specimen, decreasing by a factor of 3–6 after 2–5 s.[34,35] Bearing in mind that the delay in the recording of the emission after cleavage in the experiments of different workers[31-35] was 0.05–1 s, it follows that the initial emission intensity should have been several orders of magnitude higher than the observed value, since the rate of its decrease is nearly exponential.

The electron flux depends on the nature of the substance and the crystallographic orientation of the disrupted specimen. For example, a low electron emission has been noted for 3NPNA compared with other crystals (Fig. 5).[34,35] In C3MNA specimens the maximum electron intensity is higher by a factor of three (6×10^3 counts s^{-1} cm^{-2}) on disruption along the (010) plane than along the (001) plane. Several minutes after disruption, the electron flux as a rule exceeded the background value only by a factor of 1.5–2. In parallel experiments, the variation of the emission flux was 20%–30%. An estimate of the energy of the electrons, by the method involving tunneling through barriers, showed that it can reach values in the range 10^3-10^4 eV for organic molecular crystals.[34,35]

The intensity of the electron emission from PETN decreases by approximately two orders of magnitude 5×10^{-2} s after disruption of the specimen (Fig. 6).[31,32] Unfortunately the method used to disrupt the specimens (crushing of the crystal between two planes) precluded the recording of the emission directly from the fresh surface.

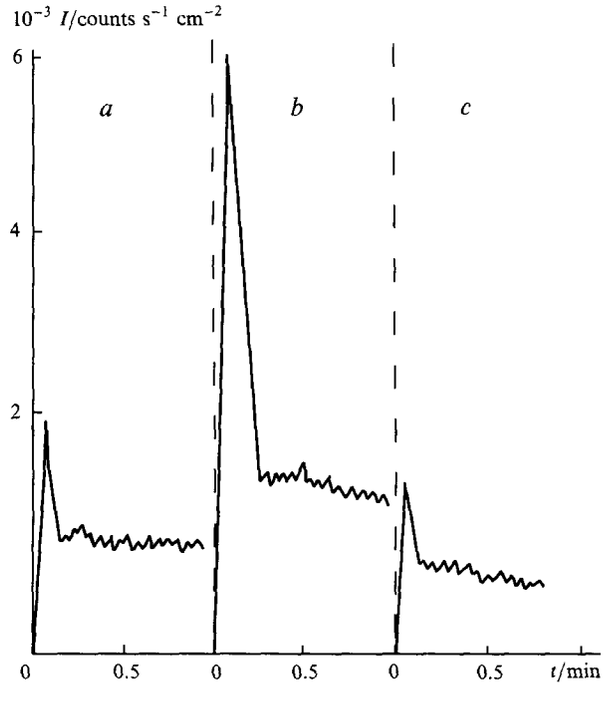


Figure 5. Kinetics of the decrease in the intensity of the emission of high-energy electrons from fresh cleavage surfaces of various crystals:[34] (*a*) C3MNA, (001) plane; (*b*) C3MNA, (010) plane; (*c*) 3NPNA (010) plane.

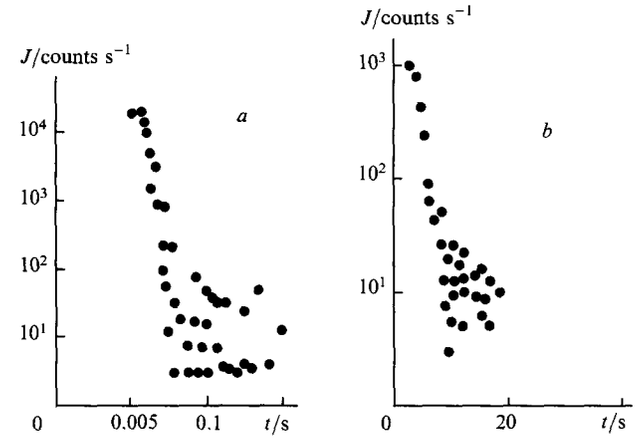


Figure 6. Decrease in the intensity of the emission of electrons (*a*) and protons (*b*) on fragmentation of PETN crystals.[31]

The proton flux was also recorded simultaneously with the electron flux,[31] but its magnitude proved to be an order of magnitude less (Fig. 6). The formation of protons is probably not always related directly to the disruption of the organic crystal, i.e. is not a result of the appearance and development of the cracks leading to the disruption of the specimen. It may be that in effect analogous to that described by Gai et al.[36] was observed in the experiment: the electrons emitted from the breakdown surface of the specimen bombard the metallic surfaces between which the crystal was contained or the metallic surfaces of the vacuum chamber, inducing the dissociative ionisation of the water molecules adsorbed on them to yield protons.

On cleavage of crystals of organic substances in the dark in the immediate vicinity of a highly sensitive photographic film in air, a compact group of individual spots exposed on the film was observed, indicating a nonuniform nature of the emission from the fresh cleavage surface.[34] Since the specimens were disrupted in air, the exposed spots reflected the pattern of the local electric gas discharges in the vicinity of the charged regions of the fresh surface. Furthermore the glow may be due to the interaction of the molecules and ions of the gaseous medium on an initial excited nonequilibrium potential surface.[37,38] The radio emission pulse in the centimetre range recorded on disruption of the crystals in air, confirms the probability of the gas-discharge processes.[34] Nor can one rule out also the possibility that the photographic film is exposed by X-rays, which was observed when crystals of organic substances were cleaved. Apparently this emission represents bremsstrahlung.[35] It is to be expected that the interaction of electromagnetic radiation arising over a wide spectral range (optical, X-ray, etc.) on disruption of a freshly formed surface may be an additional cause of electron emission.

The recording and study of the electromagnetic radiation arising on disruption of rocks and crystals have been examined in a monograph.[39]

We suggest that the very strong electric fields in the developing crack 'accelerate' free electrons, imparting energies up to 10^2-10^4 eV to the latter. Such electrons have in fact been recorded in experiments on the disruption of organic substances.[34,35] The elucidation of the cause of the appearance of the energy necessary to expel an electron from the surface of the crystal remains perhaps the main question to which so far there has been no unambiguous answer.

There exist a series of approaches which explain the appearance of the additional energy in an electron (present at a local level in the vicinity of the surface of the solid) needed to exceed the electronic work function. For example, Krylova[40,41] noted the following possibilities: the utilisation of the high-energy component in the Maxwell distribution, the Auger effect in the electron–hole recombination, the acceleration of the electrons by the internal electric field of the surface layer of the dielectric material. (For further details concerning the acceleration of electrons in internal fields, see Deryagin et al[1]). The energy promoting the expulsion of an electron, for example on photostimulation, can be induced by an external photoeffect.

If the molecule is a component of a condensed phase containing identical molecules, then additional forces begin to operate, which alter the ionisation energy to a considerable extent. In the case of organic crystals, this is the polarisation energy in the crystal (it may be compared with the solvation energy of ions in solution).[42] It has been shown by UV photoelectron spectroscopy that the ionisation potential for different crystalline organic substances is lower by 1.1–3.0 eV than the ionisation potential in the gas phase.[42]

The application of the band theory to the description of electronic processes is justified both experimentally and theoretically for many solids. It constitutes the basis of a qualitative description of the rules governing charge transfer in readily conducting materials, semiconductors with a high mobility of carriers, and dielectric materials of the ionic crystal type. However, the employment of methods of band theory for the description of the physical processes in molecular crystals, a characteristic feature of which is the small overlap of the electronic wave functions and the low mobility of the charge carriers, is by no means always valid.[43,44] For example, in anthracene and naphthalene the temperature dependence of the electron transfer process is consistent with band theory but not in all the crystallographic directions.[44] Band theory describes adequately the properties of organic crystals such as charge-transfer complexes and radical-ion salts with high electrical conductivities in the dark.[42]

It is noteworthy that the nature of the transfer of charge carriers in organic crystals is determined by the presence of capture and scattering centres, the role of which may be assumed by the crystal lattice defects.[45] For this reason, various mechanical, thermal, and radiation influences, altering the concentration and nature of the defects and their distribution, change within certain limits the electrophysical properties of the molecular crystals and thus promote or hinder the charge transfer processes, which is probably a preliminary stage in the appearance of electron emission on disruption.

III. The formation of free radicals

It was noted above that the mechanical disruption of polymers entails the rupture of interatomic bonds with formation of free radicals.[3,6,11–13,46,47] The cleavage and dispersion of crystalline substances with covalent polar bonds leads to the appearance of unsaturated bonds (free radicals).[48–52] The appearance of free radicals on disruption of the cohesion of crystals of organic substances was believed for a long time to be impossible, since it had been postulated that this entails the rupture of only weak van der Waals bonds, the energy of which are lower by one–two orders of magnitude than that of covalent bonds.[53]

An attempt was made[54] to investigate the destruction of PETN during the insertion of a chisel into the crystal under high vacuum conditions at room temperature. Unfortunately, the authors[54] did not present concrete results on the measurement of the mass spectra and merely published their conclusion that the $\dot{C}H_2-O-NO_2$ radicals are formed on rupture of the carbon–carbon bonds and are decomposed further to NO and CO. The claim that the mass spectra of the PETN decomposition products which they obtained on mechanical disruption differ from the mass spectrum of the thermal degradation products is in our view rather unconvincing. The point is that the qualitative and quantitative compositions of the gases evolved on thermal decomposition of unstable substances such as PETN, C3MNA, C4MNA, and 3NPNA depend to a large extent on the temperature range, the heating rate, the external pressure, the amount of impurities, the phase state, and other parameters.[55–60] The absence of thermostatic control or cooling in the experiment[54] on mechanical degradation also do not constitute evidence that thermal degradation did not occur.

Owens and Sharma[61] investigated the changes occurring in trinitrotoluene (TNT) and C3MNA crystals acted upon by weak shock waves. Studies by the EPR method did not permit definite conclusions, since it was not possible to assign the signal due to the paramagnetic centres. Changes in the spectrum of C3MNA subjected to the action of shock waves were detected by X-ray photoelectron spectroscopy. The decrease in the peak with an energy of 407.5 eV, corresponding to the nitrogen atom of the NO_2 group, relative to the 402 eV peak, corresponding to the ring nitrogen atom, showed that ~14% of the N–N bonds in the test substance were ruptured. Such an effect was not observed for the control specimens which had not been subjected to the action of shock waves, i.e. the effect was not induced by the X-rays with an energy of 1.2536×10^3 eV employed in the technique. In the TNT specimens subjected to the action of shock waves, a shift of the 405 eV peaks towards lower energies was observed, which can be accounted for, according to the authors,[61] by the displacement of the hydrogen atom of the $-CH_3$ or $-\rangle CH$ group towards the oxygen atom of an adjoining group.

Analysis of the products obtained under the influence of weak shock waves and the products of the low-temperature decomposition enabled the authors[61] to conclude that different mechanisms operate in the decomposition of the molecules of the initial substance and that high-temperature heating centres probably arise on exposure to shock waves. However, treatment with shock waves involves a series of significant differences from the mechanical treatment.[62] Whereas in the mechanical treatment the time elapsed from the start of the decomposition process to the instant of attainment of the maximum pressure (pulsed influences, impact) or, conversely, the time required for the decrease in the pressure from the maximum value to the end of the removal of the stress (pulsed removal of the stress) is $10^{-3}-10^{-4}$ s, on exposure to shock waves (pressure of 1 – 10 GPa) the time is 10^{-6} s. The passage of the narrow 'peak' pressure front through the bulk of the substance at a rate exceeding the rate of propagation of acoustic waves in the given medium is characteristic of a shock wave.[62] Thus, strictly speaking, treatment with shock waves constitutes a physical process, different from the mechanical process.

When triaminotrinitrobenzene (TATNB) was subjected to shock waves[63] and mechanical[64] influences, the formation of free radicals was observed.

The generation of radicals in arylindanedione dimers (ADD) has been recorded by the EPR method in studies[65,66] involving the shear deformation under a high pressure on Bridgman anvils. The release of pressure led to a rapid and irreversible decrease in the concentration of the paramagnetic centres in the polycrystalline specimen approximately by an order of magnitude. The use of a high-pressure chamber for the recording of radicals under the

conditions of a high hydrostatic pressure led to a completely different result. It was found that radicals are not generated under these conditions.[65,66] Consequently, on rupture of the bonds in ADD, radicals are formed only at high pressure when shear deformation takes place. The kinetic features of the mechanically induced dissociation of molecules under the conditions of shear deformation were established: the pressure dependence of the rate of application of the shear deformation and of the shear angle.[65,66] It was concluded[66] that the rupture of the bonds between the monomers in the dimer, leading to the formation of free radicals, occurs on brittle disruption of the crystalline ADD specimen on newly formed surfaces.

It was established[67] that the fraction of the energy consumed on rupture of the chemical bond in ADD on shear deformation at high pressures does not exceed 1%. On the other hand, most of the mechanical energy (~90%) is dissipated as heat. These data confirmed the above criticism of the study[54] in which a difference was noted between the mass spectra obtained for PETN subjected to mechanical influences and those of the thermal degradation products. Evidently, in the experiments carried out in the above study,[54] the insertion of the chisel into the crystal resulted in the transformation of a large proportion of the mechanical energy into thermal energy. Later it was found[68] that radicals were generated as a result of the mechanostimulated dissociation of the ADD molecules.

It has been established by the EPR technique[35,69] that the dispersion of the PETN, C3MNA, and C4MNA in a vibromill with glass spheres at a frequency of 50 Hz and at the temperature of liquid nitrogen in a helium atmosphere leads to the formation of paramagnetic centres, which were identified as $\dot{N}O_2$ radicals (Fig. 7, Tables 1 and 2). Evidently these radicals are products of the nonthermal decomposition of the test substances. The number of the free radicals is of the order of 10^{16} g^{-1} or 10^{12} cm^{-2}. Thus we observed[69] a fundamentally different pattern in the decomposition of the PETN crystals on disruption from that put forward by Fox and Soria-Ruiz.[54]

Fairly reliable results, indicating the abstraction of the NO_2 group from the PETN molecule, have been obtained by the EPR method, which records the paramagnetic centres directly, in combination with a low temperature (77 K) and thermostatic control. However, the accumulation of 'paired' radicals was not detected.[69] This can be accounted for by their high instability and

Table 1. Parameters of the g-tensor of the NO_2 molecules at 77 K.[35]

Matrix	g_{xx}	g_{yy}	g_{zz}	g_{av}
Ice[a]	2.0066	1.9920	2.0022	2.0003
Argon[a]	2.0037	1.9900	2.0037	1.9991
PETN	2.0065	1.9915	2.0025	2.002±0.0005
C4MNA	2.0065	1.9925	2.0035	2.008±0.0005
C3MNA	2.006	1.992	2.003	2.000±0.001

[a] Values taken from Atkins and Symons.[70]

Table 2. HFS parameters (G) of the EPR signal of the $\dot{N}O_2$ radical at 77 K.[35]

Matrix	$-B_{xx}$	$-B_{yy}$	$-B_{zz}$	A_{iso}[b]
Ice[a]	6.28	2.24	13.33	56.88
Argon[a]	−3.6	7.2	3.6	54.2
PETN	4	7	11	55
C4MNA	5	7	12	56 (±1)
C3MNA	4	8	12	56

[a] Values taken from Atkins and Symons.[70]
[b] $A_{iso} \approx \frac{1}{3}(A_{xx} + A_{yy} + A_{zz})$.

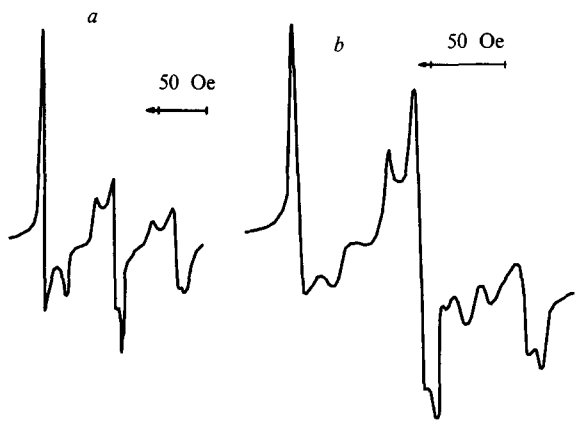


Figure 7. The EPR signals of the $\dot{N}O_2$ radicals in matrices comprising ground PETN (*a*)[69] and C4MNA (*b*)[35] at 77 K.

their rapid destruction even at 77 K or by the very great width of their signal, which is difficult to observe owing to the triplet of the anisotropic lines due to the NO_2 species. When C3MNA and C4MNA crystals dispersed at 77 K were heated to 293 K, we observed a decrease in the concentration of the $\dot{N}O_2$ radicals almost to the level of the sensitivity of the EPR apparatus, while heating of the ground PETN crystals even to 373 K did not lead to the complete destruction of the paramagnetic centres.[69] This means that the destruction of the $\dot{N}O_2$ radicals on raising the temperature is not associated with the dimerisation reaction $2\,\dot{N}O_2 \rightarrow N_2O_4$ and is induced by their interaction with the products of the decomposition of the 'paired' radicals and the occurrence of the oxidation-reduction reactions

$$\dot{N}O_2 + \dot{R} \rightarrow CO_2 + CO + H_2O + N_2.$$

Neither nitrogen dioxide nor its dimer were detected in the mass spectrum of the gases evolved after heating to 298 K; the PETN dispersed at 77 K.[35] Only peaks corresponding to the products of the decomposition of the PETN molecule were detected: H_2O, CO, CO_2, N_2. The peak observed at $m/e = 30$ may belong to NO as a side product of the degradation reaction, formed in small amounts when NO_2 and the 'paired' radicals interact. Most of the $\dot{N}O_2$ radicals and the products of their reactions with the unstable fragments of the initial molecules may remain trapped in the matrix of the crystalline test substance, which is indicated by the retention of 30% of the paramagnetic centres in the PETN heated to 373 K.

It has been suggested[35,69] that degradation of the PETN molecules with elimination of the NO_2 groups takes place as a result of the action of different types of radiation (electron emission, X-ray and optical radiations, etc.), arising on disruption of the crystal. The fact that an anomalously high radiation yield has been observed in mechanically activated solids may confirm the validity of this hypothesis.

Delpuech and Cherville[71,72] investigated the electronic structures of a series of organic compounds capable of undergoing a rapid exothermic decomposition and the changes in these substances occurring when they are subjected to pulsed mechanical influences. The stable ground state, the structural features of which determine the absorption and distribution of energy, as well as various unstable states arising as a result of impact stresses were examined. Characteristics such as the radiochemical yield of the $\dot{N}O_2$ radicals (G_R) and the primary radiochemical yield of the excited molecules (G_o) have been compared for three groups of organic substances—nitramines, aromatic nitrocompounds, and nitric acid esters. Here G_R corresponds to the number of NO_2 species for each 100 eV of the absorbed radiation energy determined by the EPR method at 77 K and G_o is the number of excited NO_2 molecules in the specified energy range for each 100 eV of the radiation energy.

Table 3. The radiochemical yields of NO_2 molecules and the yields of excited molecules.[71,72]

Nitro-compound	G_R	G_o(calc.)	G_o(expt)	
		G_o(calc.) [C3MNA]	G_o(expt)[C3MNA]	
			methanol[a]	acetonitrile[a]
PETN	3.80	0.87	0.60	—
C3MNA	0.9	1	1	1
C4MNA				
(δ-modification)	—	1.02	—	—
(β-modification)	0.8	1.03	1.08	1.17
(α-modification)	—	1.03	—	—
EDNA	0.3	1.06	1.08	—
3NPNA	0.006	1.55	1.58	1.45
TNA	$<10^{-3}$	1.56	1.83	1.82
TATNB	0.01	2.01	—	2.15
TNB	$<10^{-3}$	2.09	2.25	2.18

[a] solvent.

The primary radiochemical yield was determined by UV spectroscopy (in the range 195–360 nm) and theoretically by means of the semiempirical CNDO/2 computational method. The advantage of the theoretical calculation was that the quantity G_o for the molecules of organic substances was calculated in relation to the crystalline state (Table 3).

As a rule, substances with a higher probability of the initiation of rapid exothermic decomposition when subjected to a pulsed influence (impact) have a higher value of G_R and a lower value of G_o. This means that the exothermic reaction can be more readily induced by means of a mechanical influence in organic compounds with a low radiation stability.

For their calculations, Delpuech and Cherville[71,72] selected only organic substances whose structures had been reliably demonstrated. The distribution of the electric charge densities, obtained by the semiempirical INDO method, is presented in Table 4, which indicates the asymmetry of the charge per unit bond length $\Delta c^0/l$ for the most polarised $R-NO_2$ bonds as well as the ionisation energies.[71,72] Evidently the asymmetry of the charge distribution varies in the range 0.5–1.1 for all $R-NO_2$ bonds. The nitramine $N-NO_2$ bonds and the ester $O-NO_2$ bonds are more polarised than the $C-NO_2$ bonds, which are stabilised as a result of resonance with the bonds in the benzene ring. Comparison of the data in Table 4 for substances with related functional groups showed that the parameter $\Delta c^0/l$ is insufficient for predicting the probability of the initiation of the rapid exothermic decomposition. Hence one may conclude that the genesis of the decomposition of the molecules of the test substances cannot be adequately assessed solely on the basis of the structural parameters of the stable ground state. The authors[71,72] suggested that the distribution of the energy absorbed when the substances are subjected to a mechanical influence reflects more fully the variation of the parameter $\Delta c^0/l$ in different excited states.

Calculations have also been made for the excited states with the aid of quantum-chemical methods.[71,72] It was found that the classification of nitramines in terms of the asymmetry of the charge per unit $N-NO_2$ bond length in the excited state is identical to the classification in terms of the probability of the initiation of the decomposition for substances subjected to a pulsed stress. The results of the above studies[71,72] made it possible to differentiate two main criteria for the assessment of the behaviour of nitramines and aromatic nitro-compounds when reactions in the latter are initiated by means of pulsed mechanical influences — the electronic structure in the ground state and the way in which the absorbed energy is distributed.

Table 4. The ionisation potentials and maximum charge asymmetries in the ground states of nitramines and aromatic nitro-compounds.[71,72]

Substance	Ionisation potential/eV	Bond	Charge asymmetry	Charge asymmetry per unit bond length
C3MNA	14.83	N_1-NO_2	1.044	0.764
C4MNA (δ-modification)	13.49	N_8-NO_2	0.937	0.673
C4MNA (β-modification)	13.80	N_2-NO_2	0.889	0.650
C4MNA (α-modification)	13.62	N_1-NO_2	0.902	0.662
3NPNA	12.98	$N-NO_2$	0.841	0.624
		C_2-NO_2	0.608	0.409
EDNA	13.76	$N-NO_2$	0.880	0.676
TNA	12.90	C_6-NO_2	0.673	0.461
TNB	13.64	C_5-NO_2	0.575	0.391
TATNB	11.98	C_1-NO_2	0.820	0.579
PETN[a]	—	—	—	0.645

[a] nitric acid ester.

IV. The influence of the gaseous medium on the initiation of fast exothermic decomposition reactions

If it is assumed that the occurrence of mechanochemical reactions is in some way related to the appearance of a gas discharge in the developing crack, one may expect that the composition and pressure of the gaseous medium are capable of influencing significantly the initiation of reactions involving the fast exothermic decomposition of organic molecular crystals subjected to mechanical influences.

The influence of air and pure oxygen and nitrogen pressures (in the range $10^{-3}-10^{-5}$ Pa) as well as the pressures of argon and helium (with different concentrations of air in the latter as an impurity) on the probability of the initiation of the decomposition of C3MNA, C4MNA, PETN, TNPA, and BP [benzoylhydroperoxide?] has been investigated.[33,35,73–75] The tests were carried out under the conditions of pulsed stresses (over a period of $\sim 10^{-3}$ s) and pulsed relaxation of stresses (over a period of $\sim 10^{-4}$ s). The experimental results showed that changes in the initiation probability W are not observed in the air pressure range 10^2-10^5 Pa (Fig. 8), an appreciable decrease in W was noted in the air pressure range 0.1–1 Pa, while at a pressure of 10^{-2} Pa the probability W was close to zero. This behaviour is qualitatively the same for all the substances investigated, although it is less

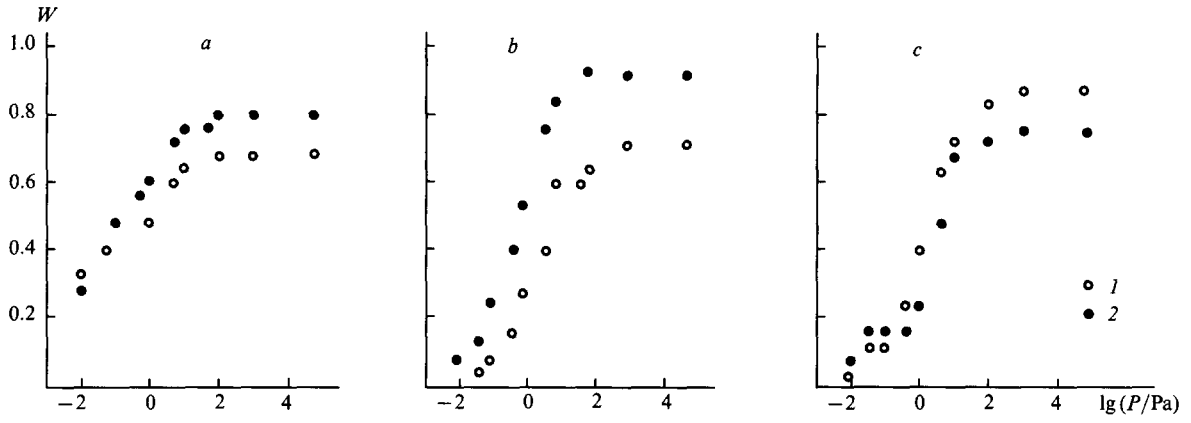


Figure 8. Dependence of the probability of initiation of the rapid exothermic decomposition of BP (*a*), C3MNA (*b*), and C4MNA (*c*) on air pressure[35,75] for a pulsed application of a stress (*1*) and for a pulsed removal of a stress (*2*).

marked in BP. For both types of influences (pulsed stresses and pulsed removal of stresses), the dependences of the probability of initiation of the decomposition on air pressure are identical.

When the experiments were carried out in pure oxygen and nitrogen, it was observed that W in oxygen depends to a considerable degree on the gas pressure in the range $1-10^3$ Pa and that the pressure range is higher in oxygen than in nitrogen (Fig. 9). Tests in argon and helium with air partial pressures in the range $10^{-1}-10^3$ Pa showed that the probability of the initiation of the fast exothermic decomposition of organic molecular crystals is appreciably lower than under an air, oxygen, or nitrogen atmosphere. The concentration of air exerts a marked influence on the mechanochemical decomposition of the test substances. It has been noted that, for equal pressures of atmospheric oxygen, the probabilities W were appreciably lower when, after evacuation, the chamber was filled with an inert gas up to a total pressure of 10^5 Pa. Argon suppressed the initiation process more than helium.

The creation of a vacuum in the system used to subject specimens to various influences (gas rarefaction less than 1 Pa) is a common procedure designed to prevent gas-discharge processes.[76] In terms of this aspect, the experimental results of our investigations[33,35,73-75] constitute evidence indicating that the gas discharge in the developing crack is an important step in the initiation of fast reactions involving the exothermic decomposition of organic substances subjected to mechanical influences. It has been stated[73] that it is incorrect to compare the experimental results of tests of the given substances in gaseous media with Paschen's curve, since Paschen's law is valid only for a discharge in a constant electric field at gas pressures exceeding 10 Pa and for a distance between the electrodes greater than 10^{-3} m.[8,77] The electric discharges in the developing crack arise in the gas flow in a highly nonuniform electric field with 'pulsed' switching on for very short distances between the walls of the crack (micrometres and fractions of a micrometre). Paschen's curve establishes the relation only between the threshold breakdown potential and the product of the gas pressure and the interelectrode distance but yields no information whatever about the nature and intensity of the gas-discharge process.[8,77]

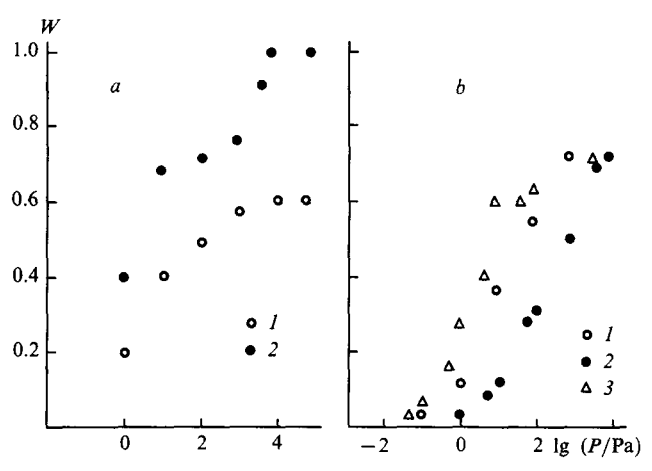


Figure 9. The influence of the nature of the gaseous medium on the probability of the initiation of the fast exothermic decomposition of C3MNA:[74] (*a*) pressure of pure nitrogen (*1*) and pure oxygen (*2*); (*b*) influence of the partial pressure of the air impurity in helium (*1*) and argon (*3*) [the data in vacuo (*2*) are given for comparison].

V. Initiation of fast reactions occurring as an explosion

In order to analyse the relation between the mechanochemical processes and the mechanical emission phenomena and in order to determine the role of the latter in the processes leading to the initiation of fast exothermic reactions, it is necessary to examine the existing concepts concerning the initiation of mechanochemical reactions in organic solids.

The thermal theories of the initiation of fast exothermic reactions have until recently gained the greatest currency in our country in relation to typical organic explosives. In our view, the following conclusions must be regarded as the greatest achievement of the thermal theories applied to typical explosives.

1. The essential preliminary step in the initiation of the decomposition reactions is fragmentation (cohesive or adhesive).

2. The initiation of a chemical reaction when the system is subjected to a mechanical influence is regarded as a multicentre process.

3. The initiation microcentres are localised in the fragmentation zone. These theories are based on the idea that local heating centres (the so called 'hot spots' arise in the solid subjected to mechanical influences). After the attainment of critical parameters (size, temperature, induction period), the surrounding condensed phase is ignited from these 'hot spots'. Next the decomposition reactions proceeds in the form of accelerating combustion and deformation.[78-86] Various mechanisms for the generation of 'hot spots' have been proposed — viscous heating during the rapid flow of the solid under pressure, adiabatic compression of gaseous inclusions, dry friction of the solid impurities. However, they did not receive subsequently a satisfactory experimental and theoretical confirmation. Among the thermal theories, the initiation theory indicating that brittle fragmentation of the organic substance in the condensed phase causes the formation of the heat centre received the greatest

recognition.[78,81,83–86] The following simplifications and assumptions were used in this theory: a solid crystalline substance is regarded as a continuous isotropic medium with certain generalised characteristics, to which the laws of the theory of the resistance of materials are applicable; the decomposition of the substance in the 'hot spot' is merely a solid-phase chemical reaction; the chemical reactions of the 'hot spots' obey the Arrhenius law of kinetics.

Thus the thermal theories do not consider the fragmentation of organic crystals at the atomic-molecular level and do not take into account the fact that, during the application of stresses to specimens, their mechanical properties may vary within fairly wide limits depending on the defectiveness of the crystals, the chemical purity, the crystalline modifications, the crystal habit, etc. The electrophysical phenomena and the physicochemical transformations of the organic substances accompanying the fragmentation of the crystals remain outside the scope of the thermal theories.

Plastic deformation is a preparatory stage in the formation of cracks along local zones (slip bands).[87,88] All these features render the laws of the classical theory of the resistance of materials relatively unsuitable in the present situation.

In our view, the thermal theories do not take into account the primary initiation of chemical reactions proper, i.e. the question of the way in which the mechanical influence on the organic crystal causes chemical changes and reactions. Furthermore, they do not provide a satisfactory basis for the appearance of high-temperature heating centres on fragmentation of solids, although they do describe qualitatively the process involving the propagation of reactions in the thermal regime (combustion, transition to detonation).

The theory of 'short-lived active centres', arising on the freshly formed decomposition surface of the solid, has been proposed.[49,89] It identifies the relaxation processes with the spontaneous destruction of these centres (radicals, broken bonds) in vacuo and with the destruction as a result of interaction with molecules of the surrounding gas in a chemically reactive medium. The theory of 'active centres' describes quite satisfactorily the mechanochemical processes occurring in homopolar crystals, where the rupture of covalent bonds is an obligatory consequence of the mechanical fragmentation.

It is necessary to turn attention to the fact that in this model an important role is assigned to the gaseous medium and its composition and pressures determine to a large extent the course of the chemical reaction on the fresh disintegration surface. However, this model does not consider the possibility of the activation of the gaseous medium itself during the appearance and development of cracks, whereupon the emission of electrons and radiation in various parts of the spectrum and a gas discharge with formation of excited molecules, ions, and atoms are observed.

Benderskii and coworkers[90–94] used the model of the self-activated solid matrix for low-temperature chemical processes. Self-activation occurs as a result of the chemical reaction and the operation of mechanical stresses in frozen reactants. The theoretical ideas concerning the phenomenon of the low-temperature detonation of mixtures of chlorine and hydrocarbons subjected to preliminary irradiation are described in these communications. It is suggested that the mechanical energy accumulating in the solid creates directly conditions for the acceleration of chemical processes, reducing the activation energy. This model of the occurrence of fast low-temperature reactions in a solid is based on the classical kinetic Arrhenius theory. However, it has been established[95] experimentally that the application of a stress to the specimen under the conditions of compression from all sides up to a pressure of 0.6 Pa hinders the cryochemical reactions in the solid matrix subjected to preliminary activation by photo- and gamma-irradiation, which is inconsistent with the concept of the direct influence of mechanical energy of the deformed specimen on the chemical process.

Ideas concerning the nature of the spontaneously developing high-speed autowave regimes of cryochemical reactions have been put forward.[95–100] It is suggested that, after a solid specimen subjected to preliminary irradiation is exposed to a mechanical influence, a narrow zone with a well developed network of freshly formed cracks arises and spreads. Chemical reactions creating conditions for the subsequent intense crack formation in the neighbouring zone of the matrix take place on the surface of these cracks or in its vicinity. As a result of the movement of the zone with a well developed network of fresh cracks through the solid specimen, the seemingly layer-by-layer dispersion of the substance in the travelling field of mechanical stresses takes place. The proposed model includes a sequence of feedback-controlled processes accompanied by the transformation of mechanical energy into chemical energy, i.e. the chemical reaction leads to a further brittle fragmentation of the specimen due to the density or temperature gradients giving rise to the stresses fragmenting the specimen.†

A proportion of the energy of the exothermic process, as it were, accumulates in the matrix in the form of mechanical deformations, while the unreacted portion of the specimen passes at the same instant to a nonequilibrium stressed state. The mechanical energy is then transformed into chemical energy via the brittle fragmentation stage, i.e. reactions on the fragmentation surfaces and in their vicinity are initiated. Preliminary irradiation creates two types of 'active centres' — both physical and chemical in the frozen matrix. The physical centres are local 'perturbations' of the mechanical stresses (associated with the appearance in the crystal lattice of decomposition products which entail an increase in the concentration of crystal defects) and also the centres for the initiation of new phases. The chemical 'active centres' are radicals or fragments of the initial molecules. In the proposed model,[95] the high-speed cryochemical reactions are formally similar to detonation in its classical hydrodynamic sense, although the physical nature of these two phenomena is undoubtedly different. In the irradiated matrix comprising the frozen reactants, the mechanical fragmentation is a kind of trigger which induces the appearance and development of the autowave regime in the chemical reaction.

Solid-phase chemical reactions without the formation of gaseous products over a period shorter than 10^{-7} s (on Bridgman anvils at high pressures with shear deformation), accompanied by the appearance and propagation of a powerful detonation wave, have been described.[101] Explosive decomposition and synthesis have been observed on Bridgman anvils in the study of the monoaxial compression of various substances.[102–104] These chemical reactions are accounted for by the direct transformation of the accumulated mechanical energy into chemical energy without heating.

The theory of the 'magma-plasma' ('tribo-plasma'), in which the fragmentation zone in the solid is represented as the centre of a special plasma has been proposed to account for the set of mechanoemission phenomena from the standpoint of a single general model.[6,9,10] The existence of the plasma state has been confirmed by the broad spectrum of the electron and electromagnetic emissions characteristic of the state. In the region of such high-energy states, there is a possibility of various chemical reactions which cannot be achieved during normal heating.

In relation to substances capable of rapid exothermic decomposition when acted upon by mechanical influences, we proposed a plasmochemical concept,[74] in which it is possible to differentiate two most important aspects. The first is the activation of fresh surface as a result of the fragmentation of the solid and the second is the activation of the gaseous medium in the vicinity of the fresh surface under the influence of mechanoemission phenomena.

† The autowave mechanism of the self-activation of the cryopolymerisation process has been described in a review.[99]

The brittle fragmentation of crystalline bodies, occurring in the form of crack formation, is a result of a complex interaction of the crystal lattice defects, in the first place dislocations.[87] The excited fresh surface with a high concentration of crystal lattice defects has a mosaic electric field microrelief.[15] The electrons emitted from the new surface fall on the opposite wall of the crack during its development and can induce various kinds of radiation damage, the degradation of molecules with formation of fragments and radicals, ionisation, the excitation of the molecules of the organic substance, and the appearance of secondary emissions.[1] The secondary electromagnetic and electron emissions are also capable of inducing further radiation processes in the substance. The activation of the gas phase as a result of ionisation, dissociation and excitation of atoms and molecules, reactions involving the sticking of electrons, etc. under the influence of electrons and electromagnetic waves leads to the formation of species with a high reactivity.[8,105]

The activated gaseous plasma may interact with the fresh surface, which should lead to a further decomposition of the molecules of the organic phase and to various chemical reactions on the walls of the crack. Since the decomposition of the molecules of the organic substances investigated is accompanied by the evolution of energy, this process develops and leads to the formation of a certain critical centre, in the region of which further chemical decomposition may be described within the framework of the thermal theory.[82]

Relaxation phenomena with different mechanisms must necessarily occur at all stages in the development of the process under consideration. In the gaseous plasma, the active species interact with other molecules and atoms, which leads to the transfer of the charge, excitation energy, vibrational energies, etc.[8,105] During the formation of the critical thermal centre, there is a possibility of thermal relaxation due to thermal conduction and convection.

A scheme reflecting the general features of the high speed reactions occurring when solids are subjected to mechanical influences has been put forward.[35] This scheme is applicable to the reactions occurring on Bridgman anvils, in a roller apparatus with pulsed application and removal of stresses, and also to a low-temperature explosion, etc. Plastic deformation (induced by mechanical forces), combined with a high pressure leads to the formation of a fresh surface with a high concentration of crystal defects. Under the influence of various types of emission, accompanying this process, there is a possibility of the appearance on the surface and in the near-surface layer of the substance of local zones with a postcritical density of active species. Such active species may be radicals, ions, point defects, etc. The initiation of reactions in these local zones leads subsequently to their propagation throughout the bulk of the specimen, i.e. the microregion of the explosive reaction arises from the microcentres. The propagation of the reaction through the substance is determined by factors such as its chemical nature and its structural characteristics and takes place in a thermal regime[82] or in the form of an autowave process.[95]

VI. Conclusion

In our view, high-speed chemical reactions in a solid matrix (in particular, during the initiation of the explosion) proceed in three stages, which differ fundamentally in their physicochemical nature.

The first stage is the appearance of active species under the influence of a set of mechanoemission phenomena. The application of the rules of radiation chemistry and photochemistry, taking into account the pulsed regime in the process involving the decomposition of organic molecular crystals or other substances, is valid in this case.

The second stage involves the interaction of active species with 'inactive' atoms and molecules, where the energy is supplied not in the form of heat but via electron, ion, and photon impacts and via interaction with electronically excited atoms and molecules (plasma) with imposition of electric fields generated on the fresh fragmentation surface.

The third stage involves the propagation of the decomposition reactions of organic substances throughout the bulk phase.

A thermodynamically nonequilibrium system, containing highly reactive species (electrons, ions, radicals, etc.) and arising when solids are subjected to a mechanical influence, promotes a course of the processes which is significantly different from that in the usual thermochemistry.[106-108] The characteristic features of these processes are as follows:[106-108] high local bulk-phase and surface energy densities; non-equilibrium conditions (non-Maxwell and non-Boltzmann distribution with respect to the energy of translational motion and the population of the quantum levels for the species comprising the system); the mutual approach and overlap of the characteristic times for the physical phenomena and chemical processes; the leading role in the chemical processes of electrons, ions, excited molecules, and radicals, which do not play a significant role in traditional kinetics; the multipath nature of the processes in the reacting system.

The traditional kinetic energy of chemical reactions and the theory of rate processes are inapplicable in this case. The translational, rotational, and vibrational energies of the molecules and atoms may differ greatly and the system components may have different temperatures. There is actually a possibility of the case where the concept of "temperature" is altogether inapplicable to high-speed chemical reactions. Classical chemical kinetics do not apply in this case and the expression for the chemical reaction rate constants loses its significance.[108]

The fraction of the substance participating in the second stage of the initiation of the explosion depends on the overall area of the fragmentation surface in the specimen. Under the conditions of the intense formation of cracks and rapid dispersion, a considerable proportion of the substance participates in chemical reactions the kinetics of which differ from 'Arrhenius' kinetics. This also explains the unusual, atypical products of the mechanical and chemical reactions which have been frequently observed experimentally.

The third stage in the initiation of the explosion is the propagation of the decomposition reactions throughout the bulk of the substance. Depending on the conditions, this stage can proceed in a thermal regime and can be described satisfactorily by Arrhenius kinetics or it can proceed in the form of an autowave process of the kind observed in low-temperature explosions.[95-100]

For a long time, investigators avoided mentioning certain reliable experimental data in considering various models, since such data had no acceptable explanation. For example, investigators carrying out experiments on the initiation of the explosion in typical explosives know that particles of solid impurities significantly increase the probability of the initiation of the decomposition process (sensitivity) when the system is subjected to mechanical influences. Metallic surfaces in contact with the specimen act slowly when the extent of their treatment is reduced, i.e. with increase in microroughness.[35,109] The current initiation theories cannot explain satisfactorily these seemingly simple phenomena. The concept of the three-stage development of the explosive decomposition of organic substances proposed by the present author readily accounts for the relations indicated. The particles of solid impurities and the microrugosities on flat solid surfaces are factors intensifying the crack formation process, which stimulates in its turn an appreciable increase in the area of the fragmentation surface in the specimen and the occurrence of chemical reactions in the zone of such cracks in the second stage of the initiation of the explosion.

In our view the separation of these three stages of high-speed chemical reactions, differing fundamentally in their nature and occurring when the system is subjected to mechanical influences, may help to eliminate the disagreements arising among

investigators when an attempt is made to extend laws valid for one stage to the entire set of mechanochemical reactions in the given substance.

The chemical reactions occurring when inorganic crystals are subjected to mechanical influences have their characteristic features. Thus it has been found[110] that the mechanical fragmentation of a number of sodium salts leads to the formation of gaseous products different from those produced on thermal decomposition. The differences between the gaseous products detected have been explained by the appearance in the cracks at the top of the specimens of short-lived highly excited ions and radicals, which give rise to low-molecular-weight products on recombination.

The breakdown of stoichiometry on the cleavage plane of a LiF crystal has been noted.[111] The surface undergoes metallisation after fragmentation under these conditions as a consequence of the formation of σ-centres near a dislocation step at a distance not exceeding the critical Auger ionisation radius of the dislocation electron. The acceptor σ-centres may form with the polymer [in particular with poly(vinyl chloride)] surface chemical (irreversibly bound) charge-transfer complexes.[112]

The influence of the concentration of point defects (F-centres) on the adhesion of metals (gold, silver, and copper) for a bulk density of F-centres of 2×10^{16} cm^{-3} and a surface density of $\sim 10^{13}$ cm^{-2} has been observed in LiF crystals.[113] The adhesive interaction has been explained by the formation of the Li^0–metal bond.

The appearance of defects of the type of F-centres on the fresh cleavage surface of an ionic crystal has been established.[114]

The emission of negatively charged (O^-, O^{2-}) and positively charged (Cu^{2+}) species has been observed on cleavage of superconductors.[115] The authors explain this effect by the electron–hole recombination involving the surface active centres with participation of copper ions and neutral oxygen diffusing from the bulk of the $YBa_2Cu_3O_{7-x}$ ceramic during vacuum annealing. The active centres were excited both mechanically (cleavage *in vacuo*) and by the ionisation irradiation of the specimens.

The exciton and dislocation processes occurring on mechanochemical dissociation of ionic crystals have been examined.[116]

The appearance of an excess charge on the surfaces of dielectric materials freshly formed on mechanical fragmentation is a consequence of the appearance of additional defects. As already stated, the charge density on a fresh cleavage surface of a crystal may attain values corresponding to electrical breakdown (10^8–10^9 V m^{-1}).[15] Vorob'ev et al.[117] observed the formation of extended dislocations in alkali metal halide crystals after these had been acted upon by a powerful electric field ($\sim 10^8$ V m^{-1}), which is due to the mechanical stresses already existing in the specimen and which become manifest following the application of an electric field (both pulsed and constant potentials were applied). Zuev et al.[118] demonstrated the aggregation of impurity–vacancy pairs with dislocations in a sodium chloride crystal doped with Ca^{2+} ions, the aggregation being stimulated by an electric field.

Okuyama et al.[119] investigated mass-spectrometrically the desorption of the K^+ and Na^+ ions and of cluster ions from the surfaces of potassium and sodium chloride crystals in a strong electric field.

The results of Laptenkov et al.[120] indicate the possibility, in principle, of regulating with the aid of strong electric fields the kinetics of the chemical reactions in ammonium perchlorate occurring with participation of dislocations. The effect of the electric field on the thermal decomposition of ammonium perchlorate single crystals was explained within the framework of the dislocation model of the development of reactions centres. The increase in the rate of growth of these centres following the application of an electric field may be caused by the Coulombic interaction of the external electric field and the edge-type charged dislocations, which move and multiply under the influence of the mechanical stresses in the crystal during the evolution of the gaseous ammonium perchlorate decomposition products.

The electric field causes the ageing of solid dielectric materials[121] and the initiation of ionic polymerisation processes.[122] It has been shown[123] that prolonged pulsed application of a $5 \times 10^7 - 10^8$ V m^{-1} electric field to solid polymers (polystyrene, organic glass) induces the accumulation in the material of bulk-phase charges (fields up to 1.7×10^7 V m^{-1}). At the same time, microcracks are initiated and develop, which leads to the formation of either a fragmentation zone, comparable in size to the interelectrode distance (1–2 mm), or of a tree-shaped dendrite channel.

Polyethylene films maintained in a 2×10^7 V m^{-1} field for 5–60 h undergo the degradation of macromolecular chains.[124] The appearance of oxygen-containing groups (C=O) in polyethylene following the application of an electric field has been described.[125] Under the influence of a strong electric field, free radicals of two types are formed in polyethylene prior to electrical breakdown. They accelerate the fragmentation of the polymeric dielectric material.[126] According to Gezalov and Kerimov,[126] the appearance of radicals is a consequence of the local heating of the specimen and also of the development of ionisation processes in the polymer.

Zakrevskii and Slutsker[127] discussed the initial stages of the fragmentation of polymers under the influence of mechanical stresses and an electric field. The mechanisms of the rupture of macromolecules in these fields, including the ionisation of the macromolecules as a result of tunnelling electron transfer and subsequent decomposition of the positively charged macroions, are considered. The authors conclude that the mechanical and electric fields exert a 'cross' influence. In their view, the application of an electric field to a mechanically stressed polymer should accelerate the stage involving the tunnelling ionisation of the macromolecules, while the mechanical stress should accelerate the stage involving the fluctuation decomposition of macroions in the electric field. However, in real cases the external field employed should not influence appreciably the tunnelling effect. The mechanical strength (longevity) is reduced in the electric field, whilst the electrical strength is reduced under the influence of the mechanical stress.[127]

The study of the dynamics of the release of a charge carrier from a dipole trap (an analogue of the elementary step in a chemical reaction) in a polymer matrix under the influence of an electric field has been investigated by the Monte Carlo method.[128] The authors suggest a series of experiments to test this calculation.

The emission of negatively and positively charged species from inorganic and organic solids has been investigated[129] in the corrosion of metals and in the exposure of polymers of different nature to thermal influences ('cooling to cryogenic temperatures–heating' cycles). Krylova[129] believes that, regardless of the method of excitation, the emission of charged species is induced by the same phenomena, which are analogous to the Auger relaxation and Auger recombination processes in atomic and ionic collisions on surfaces known in emission electronics. The energy evolved in these exothermic processes is the cause of the low-temperature 'pre-threshold' emission of charged (as well as neutral) species. In other words, the rupture of chemical bonds during corrosion (electrochemical formation of metal ions) and also in the cryolysis of polymers leads to the separation of the charges formed, and their subsequent recombination is accompanied by the evolution of the energy required for the emission of the charge. This approach follows from the development of the physicochemical concept of exoemission.[40]

It has been shown[130,131] that exoemission is a sensitive method for the monitoring of the initial stages in the fragmentation of polymeric materials subjected to mechanical (and radiation) influences as well as cooling–heating cycles. It has

been established[36,132] that the electrons emitted when solids (dielectric materials, metals, and polymers) are subjected to mechanical influences are capable of inducing the dissociative ionisation of the water molecules adsorbed on the surfaces.

The studies mentioned above demonstrate unambiguously an interrelation between the mechanoemission phenomena and the mechanochemical processes. It is at least incorrect to ignore the influence of electroemission phenomena on the chemical processes and reactions occurring when solids are subjected to a mechanical influence.

The principal fluxes of electrons, ions, and other charged and high-energy species, and of electromagnetic radiation are observed during the short period of the movement of the main crack in the solid specimen ($\sim$1 μs) and it is not always possible to record them experimentally. Nevertheless they undoubtedly affect the structural changes and chemical interactions in the vicinity of the charged fresh fragmentation surface. The presence of an excess charge on the cleavage planes of solids, especially dielectric materials, should affect the chemical reactions occurring on application of mechanical stresses. (The appearance of an excess charge on the fragmentation surface of a solid has been explained by its increased defectiveness and the deviation from stoichiometry.) It appears therefore that, in considering the mechanochemical reactions in solids, it is essential to take into account also the electroemission phenomena. The question arises whether they are of decisive importance. The answer to this question should be sought in each specific case when a particular solid is subjected to a mechanical stress, taking into account the experimental conditions.

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