Nonlinear traveling wave mechanisms of fast solid-phase cryochemical reactions

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Theoretical and experimental investigations of the traveling wave mechanisms of fast solid-phase cryochemical reactions carried out over a period of three decades are summarized. Applications of the concepts of "non-Arrhenius combustion" and "gasless detonation" to studies of cosmochemical processes near 0 K, explosive-like decays of metastable phases in solid-state physics, and new ideas about the nature of earthquakes are considered.

Key words: nonlinear traveling wave mechanisms of cryochemical reactions and phase transformations in cryochemistry, cosmochemistry, geotectonics, and solid-state physics.

Autowave regimes of cryochemical reactions in frozen matrices (mechanisms of fast chemical evolution of matter in Universe)

Nearly three decades have passed since the discovery of autowave regimes (traveling waves) of abnormally fast cryochemical reactions in solid systems of frozen reactants preliminarily exposed to radiolysis or photoirradiation.[1,2] Experiments showed that a local brittle fracture of a sufficiently long solid sample initiates a chemical reaction which propagates throughout the sample in a layer-by-layer manner (formally, analogously to the combustion front). A hypothesis was formulated, according to which a driving force of the phenomenon is the mechanochemical factor. In other words, the temperature or density gradients produced in the reaction front induce a layer-by-layer dispersion of the solid sample, which is accompanied by the formation of the active surface of freshly formed cracks that ensures a self-sustaining frontal regime of the reaction. A concept was proposed of nonlinear positive feedback between the solid-phase reaction and the brittle fracture of the frozen matrix which governs the autowave regime of the cryochemical reaction. The idea of autowave self-sustaining tribochemical mechanism was formulated.

It was established that traveling waves of solid-phase reactions at ultralow temperatures are characterized by linear velocities from a few to a few tens of centimeters per second, commeasurable with the velocities of the fastest high-temperature combustion reactions (a few centimeters per second for combustion of solid propellants). Experiments with a large number of systems confirmed that the autowave mechanism of solid-phase cryochemical reactions is a distinctive feature of a non-Arrhenius process rather than an exotic peculiarity. To date, the investigated reactions with the autowave mechanism in frozen matrices of reactants include the chlorination and hydrobromination of carbohydrates, as well as polymerization and copolymerization of various monomers.[1—4] In some cases (in particular, cryochemical chlorination of ethylene, propylene, and vinyl chloride[5]), realization of the autowave mechanism did not require pre-activation of the frozen sample by irradiation.

The first and simplest mathematical model for the description of cryochemical reactions in the autowave regime represented an equation[6] similar to the classical combustion equation except that the traditionally used nonlinear term in the form of Arrhenius law (*i.e.*, exponential dependence of the reaction rate on temperature) was replaced by a trigger function of the temperature derivative. It is assumed that cold "ignition" in the frozen sample occurs as the critical value of the temperature gradient is attained. The mechanical factor was introduced into the equation by including the critical temperature gradient as a parameter; this leads to a local breakdown of the reactant matrix accompanied by simultaneous activation ("ignition" of the reaction). The velocities of the traveling wave front obtained from analytical solution of the proposed equation appeared to be close to the experimentally observed values (10—20 cm s^{-1}). Also, an analysis of the model showed that the autowave process becomes impossible (degenerate) upon reinforcement of the matrix

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above some threshold value of the critical temperature gradient.

To validate the model proposed, a large cycle of experimental studies was carried out. The influence of the reinforcement of the reactant matrix on the velocity of the traveling wave front under uniform compression of a frozen sample was studied.[7] Indeed, in accordance with theory, reinforcement of the sample was accompanied by a decrease in the velocity of the traveling wave front. At a pressure of $6 \cdot 10^8$ Pa, it was 2.5—3 times lower than the velocity of the front in the uncompressed sample. Under particular compressions (threshold degrees of reinforcement), attempts to initiate the wave process failed. The influence of the thermal factor was studied for thin-film samples immersed into liquid nitrogen without thermal isolation (*i.e.*, under conditions of most intense heat exchange).[5] A needlestick injury easily initiated the autowave reaction. To elucidate how important brittle fracture is for the development of the autowave process, the role of the dynamics of mechanical loading of the initiator was studied.[8] A slow (~10^3 Pa s^{-1}) loading of the initiator head (plastic deformation of the initial sample) did not lead to the formation of a traveling wave, whereas the needlestick injury at which a pressure of about 10^8 Pa is produced within 0.1 s, initiated a cryochemical reaction in the autowave regime with ease. The experimentally observed features of non-thermal "ignition" of the autowave cryochemical reaction (initiation of the reaction by local fracture of the solid reactant matrix) were considered theoretically.[9] The known model[6] was refined,[10] namely, the mechanical factor was described in a more rigorous manner and it was shown that in cryochemical systems, the velocities of the traveling wave front can be much higher (of the order of a few meters per second) than in traditional systems with classical thermal combustion.

Studies on the regularities of "ignition" of cryochemical reactions by local mechanical fracture of samples revealed a strong effect of the "ignition" technique on the dynamics of the development of the autowave process.[11,12] The velocity of propagation of the brittle-fracture-initiated reaction wave throughout the frozen sample in the tube appeared to be different for initiation at the bottom of the tube and at the top of the sample, being much higher in the former case. The velocities of propagation of the polymerization wave front differ by a factor of two for the cyclopentadiene—butyl chloride system (6 *vs.* 3 cm s^{-1}, respectively) and by two orders of magnitude for chlorination of butyl chloride. An explanation for this phenomenon is based on the changes in the mechanism of dispersion of the solid matrix within the traveling wave front.[11,12] If the wave is initiated at the bottom of the tube, "mechanical unloading" of the sample is difficult by a permanent solid plug composed of unreacted reactants. This ensures a better utilization of the energy accumulated during radiolysis for realization of chemical acts of transformation at the instant of brittle fracture and accelerates the wave propagation. Self-dispersion of the sample upon initiation of the transformation wave from the free surface proceeds solely by the thermal mechanism (induction of abrupt temperature gradients in the traveling wave front followed by rupture of the sample). But if the process is initiated at the bottom of the tube, one deals with a shock-wave mechanism of dispersion of matter within the wave front due to the density difference between the initial reactant and the reacted substance. This mechanism is essentially close to the detonation mechanism, more exactly, to the "gasless detonation" mechanism.

For this reason the velocity of the thermal wave initiated at the top is much lower than that of the "detonation" wave initiated at the bottom of the tube. In particular, a study of low-temperature chlorination of butyl chloride revealed high velocities of traveling waves (~10 m s^{-1}) under shock-wave ("detonation"-like) initiation which differ by more than two orders of magnitude from the wave front velocities observed upon thermal initiation (~8 cm s^{-1}).[11] The variety of regimes of autowave solid-phase cryochemical reactions predetermines the possibility for spontaneous transitions between these regimes to occur in the course of a reaction. Physically, this phenomenon is analogous to the self-acceleration of the reaction front from the thermal propagation of flame to the detonation regime (this phenomenon is sometimes called "deflagration") known in the classical physics of combustion and explosion.[13] In cryochemical experiments, a jumpwise slow-to-fast (thermal-to-detonation) transition was observed in a study of acetaldehyde copolymerization with hydrogen cyanide.[14]

Based on the concept of real intense autowave solid-phase cryochemical reactions, a hypothesis was proposed[1,12,15,16] according to which it is these mechanisms that offer an explanation for the phenomenon of fast chemical evolution of matter in cold Universe. This concept gives an answer to the centuries-old mystery why cold planets of the Solar system, such as Pluto are covered with a ammonia/methane crust. On the Earth, these compounds are formed only at very high temperatures and pressures in the presence of catalysts. The acetaldehyde—hydrogen cyanide polymerization system[14] is of particular interest in connection with the possibility of formation of macromolecules in space at low temperatures under irradiation. Moreover, reactions of simple organic compounds detected in space (in particular, the reaction of acetaldehyde with hydrogen cyanide) can be considered basic to prebiological chemical evolution of matter because they result in proteins and other large molecules in the cold Universe.

Based on the research potential accumulated during the studies of autowave cryochemical processes, a possibility of designing original space technologies can be considered. In particular, specific features of traveling wave regimes of solid-phase cryopolymerization of filled acetaldehyde monomer were investigated.[17] The results obtained in studies of the model systems acetaldehyde—alumina, acetaldehyde—fiber glass, *etc.* are basic to the elaboration of synthetic routes to polymeric composite materials in space at low and ultralow temperatures in the traveling wave regime using the energy of cosmic and solar radiations for activation of the frozen monomer matrix.

Application of the concept of "gasless detonation" to the description of explosion-like decomposition mechanisms of metastable phases in solid-state physics

The problem of stability of metastable states (first of all, amorphous phases) is important for solid-state physics and materials science of solids. In this connection, research on "explosion-like crystallization" of amorphous semiconductor materials and on fracture of tempered glasses, as well as search for stabilization methods of amorphous ("glassy") states of metals and alloys, are important for both basic and applied science.[18—20] Nevertheless, the nature of instability of these solid metastable systems as well as the mechanisms and dynamics of their decomposition are still to be clarified and deserve thorough studies.

We believe that the concept of "gasless detonation" developed in our studies of autowave solid-phase cryochemical reactions can be considered as a methodological base for the interpretation of mechanisms and for the description of the decomposition dynamics of metastable phases in solid-state physics. Again, this theory is based on the assumption of positive feedback between the mechanical fracture of a metastable solid matrix and the phase transformation occurring at freshly formed cleavages. Namely, the shock due to the density difference between the initial and final phases breaks the neighboring layer of the sample and ensures the self-sustaining regime of frontal propagation of the decomposition of the initial metastable state. By analogy with the classical detonation process, the velocity of propagation of "gasless detonation" waves in solids should be of the order of the speed of sound in a solid matrix (a few kilometers per second).

A mathematical model[15,16] for "gasless detonation" uses a classical equation of motion to describe the propagation of a deformation excitation in one-dimensional uniform elastic solid medium.[21] Unlike the classical case, we consider a metastable medium in which phase transformation can occur. Kinetically, the formation of the new phase is described by the auto-catalytic function (diffusion term can be neglected because of small diffusion coefficients in solids). A transformation can be initiated only as a response to some critical strain in the deformation field, which breaks the solid matrix (in particular, as a response to a local mechanical excitation of a particular threshold amplitude). The speed of sound in the newly forming phase differs from the initial value because the density of the reacting medium changes. It is assumed that the speed of sound in the reaction zone is a linear function of the concentration of the new phase and it changes from its initial to the final value.

Analytical and numerical studies of the model[15,16] showed that the system of equations in question does have stable autowave solutions in the form of supersonic traveling decomposition front of the initial metastable phase. Also, the dependences of the existence regions of these solutions and the threshold values of local excitations necessary to initiate the traveling wave process on the critical parameters were established. Among them, there are the rupture strain threshold, as well as the changes in the density and in the speed of sound for the initial matrix and the reaction product.

The "gasless detonation" model should be treated as a first approximation when considering an ideal elastic active medium. Theoretical concepts should be developed taking into account the role of the shock-wave energy dissipation to heat and in acts of plastic deformation of the solid matrix.

A remarkable example of "gasless detonation" is provided by the explosion of Batavia´s tears (so-called "Prince Rupert´s drops"). This phenomenon was discovered by alchemists many centuries ago but remained a mystery until recently. The dynamics of this exotic phenomenon was studied[22] by high-speed chronophotography. It was established that (i) explosion is initiated by a local rupture of the drop and occurs in the traveling-wave regime with a velocity of 1—3 km s^{-1} and (ii) a glass dust is formed behind the wave front. Special experiments revealed no traces of gaseous components during the explosion. Thus, in this case all indications are typical of "gasless detonation".

The fine structure of oscillograms of the explosion-like decomposition of heavy metal azides belonging to classical detonating agents was studied.[23] An analysis of the dynamic pattern of explosion revealed that the final step of detonation decomposition of the particle to nitrogen and metal is preceded by a phase transformation (with no evolution of gaseous components) which propagates at a supersonic velocity. The existence of the "gasless detonation" step in the detonation of solid explosives was for the first time claimed as early as in 1994.[23]

These examples are remarkable. But clearly, it is expansion of experimental facilities that is crucially important to validate the formulated concept. This requires specific equipment for recording of very fast traveling wave processes of decomposition of metastable solid systems propagating at supersonic velocities.

Explosive regimes of polymorphous transformations of metastable phases in Earth´s crust — a new approach to elucidation of mechanisms and to description of the dynamics of geotectonic phenomena and earthquakes

Problems of polymorphism and polymorphous transformations of rocks in Earth crust are intrinsic and basic to geochemistry and geophysics. Taking into account specific features of the chemical and physical processes of formation of Earth crust, one can assume that the formation of metastable phase states in Earth rocks is quite probable during the evolution of Earth crust. Indeed, numerous metastable phases were found in rocks. Based on these assumptions, we propose a hypothesis, according to which the mechanism of and theoretical model[15,16] for explosion-like decompositions of metastable solid phases (see above) can be used to describe the initiation and dynamics of propagation of geotectonic phenomena and earthquakes. In the case of earthquakes, the applicability of this model is confirmed by the conclusions drawn in the geophysical studies[24,25] whose authors used the concept of phase transitions (polymorphous transformations) to explain particular aspects of earthquakes.

Clearly, the theory[15,16] gives no direct answers to how to predict or prevent earthquakes. However, the mechanisms of initiation and propagation of geotectonic phenomena disclosed by this theory are of paramount importance for general geophysics of these processes.

Of course, direct experimental validation of this concept is difficult because of the scale and disastrous effects of geotectonic phenomena. One should search for relevant "laboratory-scale models for earthquakes". Here we again look at the explosion of Prince Rupert´s drops[22] (see above) and consider it as the simplest laboratory model for an earthquake (silicate glass drops are chemically very close to many rocks because silica is one of the most abundant constituents of the Earth crust matter). The development of these investigations and transition to studies on the decomposition dynamics of amorphous silica in two-dimensional film samples should be considered as experimental facilities for subsequent refinement of theoretical foundations of earthquake physics.

To conclude the review of our investigations on the traveling wave mechanisms of very fast chemical reactions and phase transformations in solids, mention may be made that we succeeded to propose novel approaches to understanding the nature of processes occurring in such seemingly far branches of chemistry and physics, as cosmochemistry, physics of phase transformations, geotectonics, and earthquake physics within the framework of the a unified concept of "non-Arrhenius" combustion and "gasless detonation".

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