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Autowave modes of polymerization and other reactions in solid frozen matrixes near of absolute zero and their role in mechanisms of fast chemical transformations of substance in Universe

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SUMMARY: Almost two decades ago there were discovered new autowave selfpropagation phenomena in the cryo-chemical reactions at investigating of chemical solid phase transformations near absolute zero of temperatures. Such an autowave regime is observed for different classes of chemical reactions (polymerisation, copolymerisation and also hydrocarbon halogenation, hydro-halogenation etc). The chemical transformations studied at the such low temperatures 4–77 K proceeded with so great rates that they can be compared only with the fastest high-temperature combustion reactions known in chemistry. It allows to advance a principally new autowave conception of the matter chemical activity in solid state. The essentially non-Arrenius conception is based on the assumption that a mechanical energy accumulated in solid matrix can be transformated to the chemical forms.

Almost two decades ago there were discovered new autowave selfpropagation phenomena in the cryo-chemical reactions at investigating of chemical solid phase transformations near absolute zero of temperatures (see the reviews [1-4)]). Such an autowave regime is observed for different classes of chemical reactions: polymerisation, copolymerisation, hydrocarbon halogenation, hydro-halogenation etc. The chemical transformations studied at the such low temperatures 4 – 77 K proceeded with so great rates that they can be compared only with the fastest in chemistry high-temperature combustion reactions. It demanded to advance a principally new autowave conception of the matter chemical activity in solid state. The essentially non-Arrenius conception is based on the assumption that a mechanical energy

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accumulated in solid matrix can be transformated to the chemical forms under its brittle autodispersion. On local brittle fracture of a solid sample of reactants a chemical reaction starts on a newly formed surfaces. Temperature or density gradients arising during the reaction lead to further layer-by-layer dispersion of the solid sample. Due to this positive feedback an autowave of chemical conversion spreads over the sample. Studies have demonstrated the wide occurrence of autowave phenomena in cryochemical reactions of solids and the identity of their physical mechanisms in a wide range of chemical systems. Autowave cryo-polymerization processes are main subject of the paper.

Autowave polymerization of acetaldehyde. The propagation of the polymerisation front in solid radiolysed acetaldehyde at the relatively high temperatures 117–147 K (close to the melting point of the monomer ≈150 K) had been observed long before our investigations and had been recorded by thermograph measurements and photography 5). The authors of ref. 5) explained the occurrence of such a wave on the basis of the classical thermal mechanism of combustion. Having restricted their treatment to one thermal conductivity equation and having made a number of assumptions, the authors obtained an extremely short time for the addition of one monomer unit to the polymer chain ($\tau \approx$ 10-8 s) i.e. unreally short time. The problem of the legitimacy of the application the classical theory of combustion to the description of the polymerization front was arisen in this connection in the work 6).

Acetaldehyde. The development of ideas about mechano-chemical autowave processes made it necessary to return to the analysis of the characteristics of the given reaction at a new qualitative level. This system is of special interest about two factors. Firsts, the observation of the autowave regime in the polymerization of acetaldehyde would provide the first example of a cryochemical wave in a one-component system. Secondly, the heat of polymerization of acetaldehyde is an order of magnitude less then in the systems studied previously.

The principal ideas concerning the mechanochemical feedback in an autowave process were confirmed in the study of this system. An autowave polymerization regimes occurred in polycrystalline acetaldehyde already at 4,2–77 K both in massive (cylindrical) and thin-film specimens and its principal characteristics were investigated 7). The wave was excited in response to the local brittle fracture of frozen acetaldehyde. When the autowave passed through the specimen in the helium bath, the maximum temperature in the front was significantly lower than the melting point of the monomer (150 K). This system provides an example of an autowave process occurring exclusively in the solid phase. According to the ideas being developed, the chemical reaction front consists of a mechanical dispersion zone moving in the solid reactant.

The rate of propagation of the autowave depends on the dose of the preliminary γ-irradiation. As in the system studied previously there is a critical dose necessary for the attainment of the autowave regime. The size of this dose increases with decrease in the thermostat temperature. It could be postulated that the increase in the rate of propagation of the wave with increasing dose is caused by the increase in the concentration of stabilized active centres accumulated in the system during the preliminary radiolysis. However, the increase in the concentration of active centres during the radiolysis at 77 K of polycrystalline acetaldehyde takes place linearly only up to a dose of ≈50 kGy and then slows down. After the attainment of ≈700 kGy, the accumulation of centres ceases altogether. On the other hand, the rate of propagation of the wave in this range continues to increase in proportion to the dose.

The problem of achieving the wave process in the vitreous acetaldehyde matrix is of grate interest. Even on rapid cooling, pure acetaldehyde cannot be converted into the vitreous state 6) and its polymerization in the vitreous state had not therefore been studied previously. Kichigina et al.8) investigated a vitreous solid solution of acetaldehyde in butyl chloride, in which local brittle fracture induced an autowave polymerization regime. It was found that the critical dose of the γ-irradiation, above which the autowave propagation of the process in the vitreous solution can be attained, is only 60 kGy, while in crystalline acetaldehyde it exceeds 300 kGy.

Autowave polymerization of cyclopentadien. When describing the above autowave processes the nature of active centres arising in brittle fracture of the system was not defined concretely. As the cryochemical autowaves were mainly observed for typically radical chain reactions, it was of interest to create an autowave regime for a typically ionic chain reaction.

Since a monomer, such as cyclopentadiene, polymerise only by anionic mechanism, it has been chosen to study the peculiarities of the autowave regimes of the cryochemical reactions of this kind. Earlier it has been shown that a post-radiation cyclopentadiene polymerization vitrified in a butyl chloride matrix occurs by a cationic mechanism and is observed in the temperature range of system vitrification,Tg≈97 K [9)]. These very results served as a base for the search of autowave regimes in this system [10)]. It should be noted that the "explosive" reaction of cyclopentadiene polymerization is registered in the films produced by freezing them from a molecular beam of a monomer and catalyst TiCl4, after a puncture of the film with a needle at 77 K [11)].

A solution of cyclopentadiene in butyl chloride on fast cooling down to 77 K passes to a glassy state. A local brittle fracture of a radiolyzed sample immersed in liquid nitrogen initiates a polymerization reaction propagating across a sample as an autowave. The polymerization wave velocity and the form of the temperature wave profile depend strongly on the dose of preirradiation. With an increase and the temperature wave profile become even sharper.The polymerization wave velocity grows linearly with an increase in the preirradiation dose up to 1200 kGy. This character of the dependence of the wave propagation velocity is obviously not connected with the dynamics of accumulation of the active centres with cationic nature as their accumulation stops at much lower doses.The molecular mass and yield of polycyclopentadiene produced in the autowave regime are higher then those in the termoactvated postpolymerization.

Autowave cryo-copolymerization of acetaldehyde with HCN [12, 13)]. When cooled to 77 K, the HCN-acetaldehyde mixture containing 25 mol% of HCN exhibits a transition to the dlassy state. Devitryfication (transition to a super cooled liquid) is observed at a temperature of 90 K, crystallization occurs at 110-115 K, and melting takes place at 140 K. Local brittle fracture of a sample preirradiated at 77 K results in the foamation of an autowave of copolymerization of aldehyde with HCN. The copolymerization wave front rapidly propagates down-ward along the entire sample. This is easy to observe visually by changes in the sample color. After passage of the copolymerization wave at 77 K, the sample was heated to room temperature and the yield of the polymer was determined. With increasing irradiation dose, the yield of copolymer increases and reaches an ultimate value of 45-50%. The copolymer prepared in autowave regime is colorless and completely soluble in methylethylketon. The molecular mass of the copolymer decreases virtually exponentially with increasing preirradiation dose. At the same time, the nitrogen concentration in the copolymer increases with the dose.

The autowave regime of copolymerization described above differs principally from the usual liquid-phase process: the initation rate of reaction rapidly ($\tau \sim 0{,}1$ s) reaches its maximum at the reaction front and then only decreases (the active centers accumulated in radiolysis are only consumed in the process). Apparently, this is feature that accounts for the experimentally observed characteristics of copolymerization. Note that no insoluble polymer fractions were formed under the conditions of autowave copolymerization, whereas these fractions were formed in the thermally activated regime implemented for other acetaldehyde / HCN ratios.

The developed autowave concepts must also account for the processes involving the "cold" evolution of matter in the Universe, i.e. formation of increasingly complicated molecules of elements under the conditions of interstellar dust. Beginning from its birth in the "Big Bang" during physical evolution the substance of the Universe could pass through a series of cycles of strong heating. The end of any of those cycles might be a starting point of further chemical evolution of the substance in the Universe. It is natural to think that during the cycle of heating the substance existed and evolved only in the form of chemical elements. Further cosmic processes led to its approximately fast cooling down to temperatures near absolute zero. Formation of molecules from elements and their further complication could take place only during such cooling. Molecular gases – hydrogen, oxygen, nitrogen, carbon oxide – were formed. If these gases were frozen out on the grains of interstellar dust or on cold planets, then, based on classical notions, their further existence became very problematical, even in spite of cosmic time scale. At the same time, a number of external planets and their satellites had oceans of solid ammonia and methane. Only presented above autowave concept may explain this mistery.

One can imagine the process of formation of compounds, such as ammonia and methane, out of a frozen mixture of elements from the surface of cold planets and their satellites in the following way. Those cosmic objects had sharp daily changes of temperatures. The thermal stresses arising in the solid crust of the planet were an instrument of its continuous destruction. Such multi fold brittle fracture of a frozen mixture of elements that were previously made active by solar radiation might result in chemical binding of elements in autowave modes. The same might be true also for interstellar clouds – gigantic suspensions of dust grains in the gas.

Highly probable is also the next stage of chemical evolution, when solid ammonia and hydrocarbons that were continuously dispersed in a "solar mill" might transform into amines. Formation of long polymeric chains at brittle fracture under the conditions of cosmic cold and autowave dynamics is believed to be experimentally proved on examples of polymerization of formaldehyde and acetaldehyde.

Autowaves are governed neither by diffusion of matter or heat (as in combustion processes) nor by a trevelling shock wave (as in gaseous detonation). Instead, they result from a coupling between phase transformation and the stress field, and may be classified as gasless detonation autowaves in solids. It was propose a simple model to describe these regimes 14). The model rests on the classical equations of elastic deformations in an one-dimensional solid bar, with the extra assumption that the phase (chemical) transformation induces a change of the sound velocity. The transformations areassumed to occur through a chain branched mechanism, which stats when the mechanical stress exceeds a given threshold. Our investigation shows that supersonic autowaves exist in this model. In the absence of diffusion (dissipation factor, losses), a continum of travelling wave solutions is found. In the presence of diffusion, a stead state supersonic wave solution is found, along with a slower wave controlled by diffusion.

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