Non-traditional pathways of solid-phase astrochemical reactions

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Abstract: There are considered mechanisms of solid-phase reactions which were investigated experimentally and theoretically during recent decades and can have direct connections to the formation of organic substances in space and their delivery to the Earth, to the problems of prebiotic evolution. Among such mechanisms are the molecular tunneling (hypothesis of the cold prehistory of life), polycondensation of solid monomers by shock waves (problem of the delivery of organic substances to the Earth by meteorites), thermal and thermal-wave explosions and oscillations of temperature and radical concentrations in small cold particles under the radiation exposure, mechanochemical explosions and autowave propagation of chemical reactions due to the positive feedback between fragile destruction of solids and reactions at freshly formed surfaces.

Introduction

Roughly 40000 tons of interplanetary dust is accreted now annually by the Earth[1]. It means, that at the constant rate of such accretion during the lifetime of Earth's solid crust (4 Bln. years) the average thickness of layer of extraterrestrial origin at the land of our planet would be ca. 1 ton/m^{2}. Organic substances of different degree of complexity - up to the polycyclic aromatic hydrocarbons and their alkylated derivatives were found in interplanetary particles[2]. Thus recent observations suggest that "organic matter on our planet has its origin in interplanetary - or perhaps interstellar - space"[3]. There is a strong link between inter-planetary and interstellar dust. Both have populated the early Earth with compounds which could play important role in the origin of life at our planet[4].

Hypothesis concerning possible mechanisms of extraterrestrial formation of organic species (e.g. their formation in extremely cold - 10-20 K - interstellar clouds) are often based on the admittance of decisive role of ion - molecule interactions since they are known to proceed with zero activation energy in gas phase. However the absence of activation barrier for this class of reactions in solids can by no means considered firmly proven as their general property, and further detailed investigations are needed, particularly under the conditions which imitate the "dirty ice" mantles of interstellar dust grains. Anyway it is worthwhile to discuss other possible connections between contemporary experimental and theoretical studies of various solid-phase processes and the problems of astrochemistry and - to some extent - also exobiology.

Molecular tunneling and the hypothesis of cold prehistory of life.

Two main classes of scenarios of the origin of life on the Earth have been suggested.

First of them is so-called warm, terrestrial scenario ("standard model") of Oparin[5] and Haldane[6], while second is cold, extraterrestrial scenario which dates back to the "panspermia" hypothesis of Arrhenius[7]. After the classical experiments of Urey[8], Miller[9,10] and their followers which have demonstrated the formation of some prebiotic molecules (e.g. amino acids and nucleotide bases) in gaseous mixtures imitating early atmosphere of the Earth (H_2O, CO_2, CO, CH_4, NH_3, etc.) under the impact of various physical factors (UV-radiation, electric discharges etc.), main attention of researchers was for a long time paid exclusively to the warm scenario.

Revival of the interest to the cold scenario was to a large extent stimulated by the discovery of the low-temperature limit of the rate of chemical reactions (by the example of radiation - induced chain polymerization of formaldehyde) - in other words - the discovery of non-vanishing and temperature independent chemical reactivity even near the absolute zero explained as the manifestation of quantum mechanical molecular tunneling[11].

As it was emphasized in[11] "Near absolute zero entropy factors play no role, and all equilibria are displaced to the exothermic side, even for the formation of highly ordered systems. Therefore it would be of interest to establish the role of slow chemical reactions at low and ultralow temperatures in chemical and biological evolution (cold prehistory of life?)".

In several subsequent papers[12-14] we have analyzed in details possible mechanisms of formation of polyformaldehyde in the "dirty ice" mantles (which contain mainly frozen ammonia, HCN, HNC, water, ethane, formaldehyde etc.) of interstellar dust grains and virtual role of such grains as possible cold seeds of life. Kinetics and equilibrium of reactions in the bulk of grains were calculated as the "shuffling of the deck of cards" - multiply repeated sublimation and condensation plus polymerization and various chemical conversions. Analysis of our experimental results[11] and their comparison with estimations made for Arrhenius-type and tunneling kinetics[14] lead to the obvious conclusion that the formation of polyformaldehyde in interstellar dust could proceed only via tunneling.

For such estimation one should take into account following numerical values - the time between the absorption of subsequent UV quanta by each molecule of diffuse interstellar clouds or of surface layers of dark (dense) clouds: $\tau_{uv} \approx 100 yr$; the lifetime of clouds determined by their collisions and gravitational collapse: $\tau_{cl} \approx 10^5 - 10^7 \ yr$, and our kinetical data: time of the addition of new link to the growing polymer chain at the plateau (T≤12 K) $\tau_0 \approx 10^{-2} s.$, length of the polymer chain at such temperatures $v \approx 10^3$, activation energy of the growth of chains in Arrhenius region (up to 140 K) $E \approx 0,1 \ eV$.

The fulfillment of the demand $(\tau_0)_{Arrh.} \ v << \tau_{uv}/v$ (preexponential factor for the growth of polymer chain is taken as $10^{14} \ s^{-1}$) necessitates $T > 30$ K, the demand $(\tau_0)_{Arrh.} \ v << \tau_{cl}/v$ corresponds to

softer inequality T > 20 K. Both values of minimal necessary temperature lie above the temperature of interstellar clouds (10-20 K).

Moreover the values of τ_0 for Arrhenius-type extrapolation of reaction rate are: 10^{11} s. for 20 K and 10^{36} s for 10 K i.e. they exceed by many orders of magnitude the experimental values.

Meanwhile the use of simplest Gamov-type formula for the estimation of tunneling rate:

$$(\tau_0)_{\text{tunn.}} = 10^{-14} \exp \left(\frac{\pi\sqrt{2}d\sqrt{mE}}{2\hbar} \right)$$ where d is the width of the barrier and m ($CH_2 O$) = 28 a.m.

leads to the inequalities: $d < 0,65$ $\overset{\circ}{A}$ (when τ_{uv} is used) or $d < 0,90 - 0,95$ $\overset{\circ}{A}$ (when τ_{cl} is used). Such values of the distance of tunneling seem to be quite reasonable and give strong argument in favor of tunneling mechanism of the formation of polyoxymethylene in cosmic dust - in accordance with the views expressed in [11-14].

Thus, tunneling could significantly increase the number of possible low-temperature reactions in dark clouds.

One case would be e.g. the possibility of tunneling polymerization at the surface of dust grains with the formation of a very thin (several molecular layers) polymer film around the inner region of dirty ice.

For chemical and prebiotic evolution, the reactions of polycondensation in dirty ice mantles with the participation of $CH_2 O$, HCN, HNC, NH_3 and H_2O are of interest. Such reactions could lead to the formation of amino acids, polypeptides, sugars and nucleotide bases (purines and pyrimidines), they are exothermic, but not chain-type.

There are no reasons why there should be a "pure" molecular tunneling mechanism of such reactions - the rate of tunneling falls steeply to a vanishingly small limit with increasing barrier width and masses. However, each single step of chemical conversion which represents an elementary gas phase process (such as the reaction $H_2C = O + NH_3 \rightarrow H_2C = NH + H_2O$), proceeds in the solid as a sequence of many individual or collective conformational rearrangements of molecules, complexes or indeed whole regions of molecular crystals. The collision of a dust grain with a cosmic proton or ultraviolet quantum, or release of recombination energy at the grain surface can induce the transfer of the "driving" particle, such as electron which determines the number of conformational rearrangements. As long as quantum effects open the possibilities of various low temperature chemical conversions it seemed to be of interest to calculate the equilibrium composition of cold interstellar dust grains. In fact, there was no need to take into account the entropy in such calculations, there were based exclusively on enthalpies and the cosmic abundance of H, C, N and O atoms. The maximum release of heat was found to correspond to formation of acetic acid, urea and certainly also the products of the exothermic polycondensation[15] .As gravitational instability develops in the dust-gas cloud, a differentiation of matter occurs and protostar forms. Planetesimals accrete from the dust-gas disk forming around the star, and enlarge to planets together with the informations of meteorites and comets. Consequently the organic

compounds which had formed in the dust-gas cloud can reach the planet by two processes: first during the accretion of the planet, and second after the planet had formed through the adsorption of these compounds on the surface of the planet from the surrounding space. The organic compounds which reached the planet in this fashion might then have served as the raw materials for the formation of the "primordial soup".

The possibility of synthesizing rather complex molecules under the combination of space cold and the various radiations of cosmic origin postulated in [11] was independently actively propagandized by Wickramasinghe and Hoyle[16-18] whose publications were however widely disputed.

Starting with the claims that formaldehyde undergoes polymerization in interstellar space with the formation of polyoxyethylene and even of polysaccharides these authors soon came to the hypothesis of "living interstellar clouds"[19] and even of the extraterrestrial origin of some viruses[20] invading the Earth e.g. the virus of influenza in 1919. These speculations met various reasonable objections. Meanwhile the presence of polyoxymethylene in space found recently support in the comparison of data obtained for the coma of comet Halley by heavy-ion analyzers aboard the Giotto spacecraft[21-23], laboratory mass spectra and IR absorption spectra of formaldehyde polymerized at the surface of silicate grains under irradiation by protons at 20 K. Molecular tunneling was mentioned in [21-23] as most likely mechanism.

However neither the terrestrial, warm nor the extraterrestrial, cold scenarios of the formation of complex organic molecules and prebiotic evolution - at least the early stages of the development - included any attempts to combine the explanation for the existence of two main properties of living species - the functional property of the ability for self-replication and the structural property of chiral purity, homochirality of bioorganic world (L - enantiomers of amino acids in all proteins and D - enantiomers of sugars in RNA and DNA).

The absence of such attempts was particularly disappointing in contrast to firm conviction expressed already in 1860 by the discoverer of dissymmetry Louis Pasteur - "Homochirality is demarcation line between living and non-living matter". Now it seems obvious that just the coexistence of these two (and only these two) above properties may serve as Ariadne's thread in the labyrinth of hypotheses of the origin of life.

Relations between chiralitiy, origin of life and evolution are too diverse to be discussed within the framework of this article - let us only refer to some of our previous publications [24-26] (now under further development and extension) and briefly touch connections between tunneling and chirality.

In accordance with the well known Hund 's paradox [27] in the system of two identical potential wells - and just of that kind are the systems with asymmetric C atoms which can exist in L - and D - forms (left and right enantiomers) i .e. be located in L - or D wells (see fig.1)- neither of two wave functions - Ψ_L or Ψ_D represents the system's eigenstate. Tunneling leads to spontaneous L $\rightleftarrows$ D conversions, i.e. the system is oscillating, is delocalized between L and D potential wells.

L and D states would have a definite chirality but not a definite parity. Two eigenstates of definite

parity (but not definite chirality) are described by either symmetric $\Psi_S = \frac{1}{\sqrt{2}}(\Psi_L + \Psi_D)$ or anti -
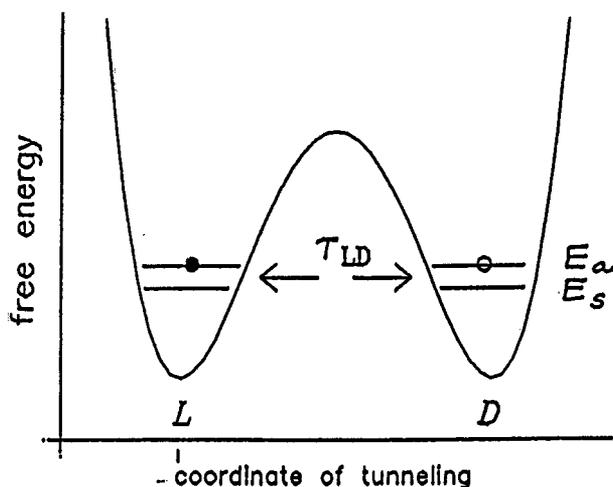

Fig. 1. Tunnelling between L and D states of chiral molecule: τ_{LD} is the average lifetime of chiral state.

symmetric $\Psi_S = \frac{1}{\sqrt{2}}(\Psi_L - \Psi_D)$ combinations of Ψ_L and Ψ_D. There is certain difference between the

energies of two states - E_a and E_s : $\Delta E_{as} = E_a - E_s$, and the characteristic frequency of tunneling

$L \rightleftarrows D$ oscillations equals $\omega_{LD} = 1/\tau_{LD} = \Delta E_{as}/2\pi\hbar$ (*). Under such conditions it is senseless to

speak about certain sign of chirality of optically active molecules, i.e. about the property which is

intrinsic for the bioorganic molecules.

Indeed, if the molecule is initially in, say, the L - state then after a time τ_{LD} it will be in the D-state.

Consequently, over a time $t >> \tau_{LD}$ the probability for finding a molecule in the L - state, will be the

same as that for finding it in the D - state, 1/2, i.e. the system of isomers racemized itself over a time

$t >> \tau_{LD}$. Racemization processes prevent a breaking of mirror symmetry - necessary stage of

prebiotic (or protobiotic) evolution - tending to restore the system to a racemic state. Consequently,

a deracemization could have occurred only if there exist the processes capable of effective

countering the tendency toward racemization.

Such counterracemization factors appear indeed in a cold scenario. It has been shown[30-33] that if

chiral molecules interact with an optically inactive medium consisting of a strongly cooled gas of

low density, where only binary collisions are significant, stabilization of the chirality of isomer

molecules would be possible over times much longer than the tunneling oscillation time

τ_{LD}. The interractions of the isomer with the molecules of the medium have the consequence that

the chiral particle behaves as a damped rather than free oscullator.

(*) Stationary states of a nonlinear Schrödinger equation[28,29] need not be eigenfunctions of the

operators corresponding to the symmetry group of the potencial. When the nonlinearity parameter

approaches ΔE_{as} it takes place rather sharp transition from definite parity to definite chirality, i.e.

permanent localization in one of the wells.

Consequently, although racemization does occur, the time scale for the process increases sharply compared with the racemization time for an isolated particle.

The very fact that the chirality of a molecule is stabilized at low temperatures by the interaction with the medium is, understandably, an attractive aspect of a cold scenario but one should also keep in mind that the problem of the deracemization of the medium as a whole arises here. Specifically, each of the isomer molecules is initially in a state with a definite chirality, i.e. in either the L - state or the D - state. The ensemble of such molecules however is probably in a racemic state. Therefore, it is quite important to analyse the problem of the stabilization of the optical activity of the ensemble of molecules incorporated in solid low-temperature matrices taking into account the contributions of various types of relaxation processes, i.e. not only the tunneling of particles (non-diagonal transitions) but also the transitions inside each of two wells of two-well potential (diagonal transitions).

Such analysis shows[34] that at very low temperature the time τ_S of L $\rightleftarrows$ D transitions in solids strongly exceeds the time τ_{LD} of "free" tunneling oscillations and moreover τ_S rises in the vicinity of absolute zero with the increase of temperature (Fig.2) and the most effective suppression of racemizing processes in molecular ensembles should be observed at T $\approx$ 10-20 K i.e. just under the conditions typical for dirty-ice mantles or interstellar dust grains.
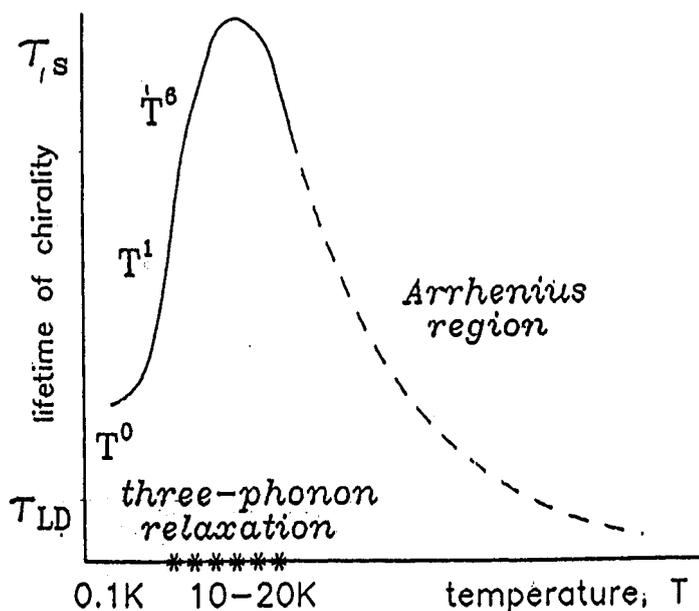

Fig. 2. Stabilization of chirality in low temperature solids ($\tau_S \gg \tau_{LD}$).

Delivery of organics to the Earth. Shock-wave induced polymerization and polycondensation.

The thesis on the interplanetary or interstellar origin of organics on our planet needs of course detailed elaboration - in particular concerning main sources of this organics. Quite popular is the view that life at the Earth was nurtured by a rain of comets that just comets, carbonaceous asteroids and meteorites contributed large amounts of organic matter to the primitive Earth (e.g.[35-39]).

Recently it was even expressed the view[40] that "total amount of carbon in our carbonates and the total amount of water in our oceans were brought about by a late bombardment of comets on an Earth almost devoid of carbon, of water and of all volatile and labile elements". Within the framework of such view one of most important questions is whether some impactors can bring prebiotic species intact to the Earth. According to[41] only fragments small enough to be gently decelerated by the atmosphere - principally meteors of 10^{-12} - 10^{-6} g. - can serve as such "soft - landed" impactors. From the point of view of the origin of life it is of course of particular interest the problem of delivery to the Earth of intact amino acids.

Large amounts of apparently extraterrestrial amino acids were found recently in rocks at the Cretaceous/ Tertiary (K/T) boundary in Denmark[42] and the hypothesis of the mechanism of their preservation was put forward in[43] .

Most intriguing data were obtained by the studies of so-called Murchison meteorite which fell in Australia in 1969 and belongs to the number of carbonaceous chondrites that typically contain 2 - 3% carbon by weight, mostly in the form of organic materials. At least 74 amino acids have been identified in Murchison extract, among them several amino acids that are common in living systems. Some of these amino acids were found to be not racemic (L - enantiomeric excess)[44] however it remained open the question whether this deviation from homochirality could be caused by terrestrial contamination or by diagenetic reactions occurring in space.

Subsequent combined study by Engel et al.[45] on the stereoisomeric and isotopic (^{13}C) composition of amino acids in the Murchison meteorite gave arguments of decisive importance. They reported L - enantiomeric excesses for alanine (D/L = 0,85 ± 0,03) and glutamic acid (D/L = 0,54) accompanied by a ^{13}C enrichment typical of extraterrestrial organic materials (up to 30⁰/₀₀) and concluded that optically active (or rather deracemized) compounds were present in the early Solar system. This conclusion attracted wide interest and was commented - inter alia - in[46,47] . As it was emphasized in[47] , results of[45] support the view [24,25] that the chiral purity of the future Earth's biosphere was achieved at the stage of prebiotic evolution and was a necessary condition for the subsequent development of self-replication.

Moreover, if partially deracemized state of amino acids observed in[45] represents an intermediate stage in the transition to a chirally pure state the results can provide an indication of the timescale required for the mirror symmetry - breaking process.

Finally, in regard to the question of whether extraterrestrial amino acids can be delivered to the Earth by a large impactor it would be worthwhile to turn to the data on shock wave (SW) induced polymerization and polycondensation.

Comprehesive survey of polymerization and modification of polymers under shock compression was presented recently by Gustov[48] . An important step in the investigation of shock compression of condensed phase was made by Ryabinin[49] who invented special recovery capsules for preservation of the substances after the explosion.

Schemes of such recovery capsules used also in our experiments (cylindrical and plane variants) are shown at the Fig.3.
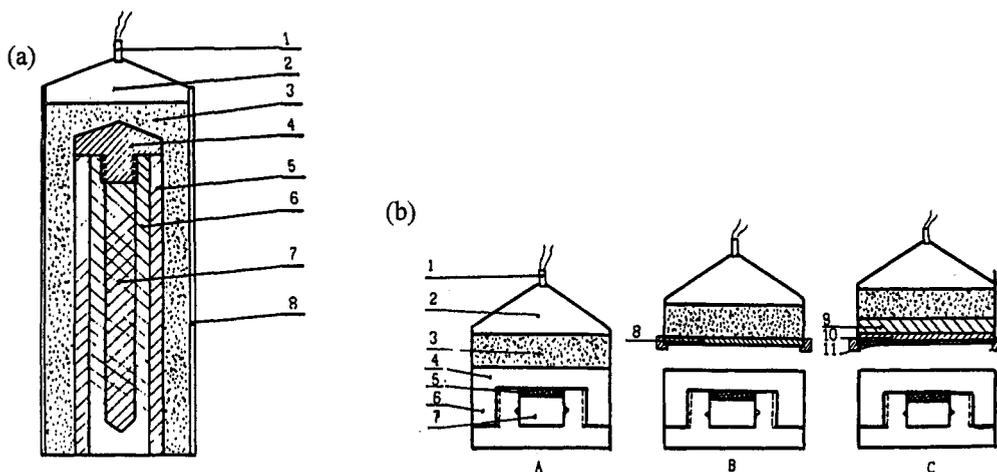

Fig. 3. Schemes of recovery capsules. (a) Cylindrical capsule. 1 - Detonator, 2 - Generator of plane detonation wave, 3 - Explosive, 4 - Metal stopper, 5 - External body of a capsule, 6 - Internal body of capsule, 7 - Sample, 8 - Cup. (b) Plane capsule. A - Contact assembly consists of: 1 - Detonator, 2 - Generator of plane detonation wave, 3 - Explosive, 4 - Cover of a capsule, 5 - Sample, 6 - Body of capsule, 7 - Metal stopper; B - Flying plate assembly contains in addition, 8 - Impactor (metal plate); C - Quasiisoentropic assembly contains in addition 9, 10, 11 - set of impactors with reduced density and detonation velocity (e.g. Al, polymethylmethacrilate).

Our studies of SW - induced conversions of solids started in the mid-sixties and were devoted to organic compounds. It was found that under rather rigorous conditions (pressure, temperature, deformation velocity) there occur not the destruction processes but the molecular association[50] .

There are polymerized eight monomers of different types (trioxane, acrylamide, potassium acrylate, methylacrylamide, tolan, salicylaldehyde, stilbene, diphenylbutadiene), threshold amplitudes of plane SW induced polymerization varied from 2 to 30GPa, yields of polymers - from traces (stilbene) to 60% (acrylamide above 10 Gpa)[51,52] .

Next step of our studies was the observation of SW induced cross-linking for a number of rubbers[53] , e.g. of polybutadiene.

However most interesting for the problem of delivery of prebiotic and protobiotic substances to the Earth became the observations of SW induced polycondensation of amino acids. Shock loading of glycine or D, L - tyrosine mixed with the same (by weigjt) amount of dehydrating agent - silica gel led to polypeptide formation[54] . More detailed were the studies of polycondensation of α- L - alanine under the action of shock waves[55] . Samples were prepared by pressing a mixture of dried alanine with silica gel. Treatment of the samples by shock waves lasting 5-7 μs with amplitudes $P = 12,35$ and 50 GPa at an initial temperature 20 °C was conducted in steel plane capsules. After the explosion experiments the capsules were opened while cooling with liquid nitrogen on a lathe. The extracted samples were pulverized and placed in 20% acetic acid. The soluble fraction was investigated by thin-layer chromatography and mass spectrometric analysis. The content of the amino acid was determined before and after hydrolysis, and the increase of this content due to

hydrolysis in all the experiments at 35 and 50 GPa characterized the formation of polypeptides in the studied samples under the SW impact. Mass spectrometric analysis demonstrated that the formed cyclic and/or linear polypeptides contained more than four amino acid residues.

In later experiments[56] it was observed the formation of amino acids from ammonium salts of carboxylic acids under dynamic compression.

Thus, the totality of data obtained in above laboratory experiments can be treated as an argument in favor of the possible delivery to our planet of amino acids and even the products of their polycondensation by extraterrestrial impactors.

Thermal regime of cold solid particles containing trapped active centers.

Among the different pathways of extraterrestrial formation of complex organic molecules there were considered the possibilities of explosions of interstellar dust grains containing high concentrations of free radicals accumulated there in the field of various space (mainly UV) radiations. Series of calculations and laboratory experiments devoted to such explosions was performed by Greenberg[57-59] .

As it is well known, two mechanisms of thermal explosions of chemical systems were widely discussed - genuine thermal explosion described by classical theory of Semenov[60,61] and Frank-Kamenetskii[62,63] and so-called "thermal-wave" (or "thermal-chain") explosions.[64-66]

Conditions of the appearance of thermal explosions are determined by the ratio of the rates of system's heating at the expense of exothermic (and accelerated with the increase of temperature) chemical reactions and the removal of heat through system's walls.

Origin of thermal-wave explosions is quite different. The point of recombination of radical pair serves as the center of diverging spherical thermal wave. Such wave throws other radicals out of traps occupied by them, these radicals in their turn recombine and generate new thermal waves. Thus there appear peculiar energetic chains of recombination of radicals which prevent under the ordinary conditions the accumulation of radicals in concentrations above few tenths of per cent independent on the intensity of radical generating radiation Thermal-wave explosions can play marked role only in considerably large samples - of the dimension $l > \sqrt{\chi t_r}$ where χ (cm^2s^{-1}) is the heat diffusivity and t_r (s) - characteristic time of recombination of radicals determined by their diffusion[67,68] . Thermal explosions should dominate in the samples of lesser dimensions, e.g. in the cosmic dust grains.

It is quite obvious that under the conditions of stationary irradiation of samples only the steady - state but not the overcritical (necessary for explosion) concentration of radicals can be reached. The passage through the critical level of concentration will lead to a "soft" outburning of overcritical excess of radicals and return to the steady - state level of their concentration, i.e. there will appear peculiar, oscillatons.
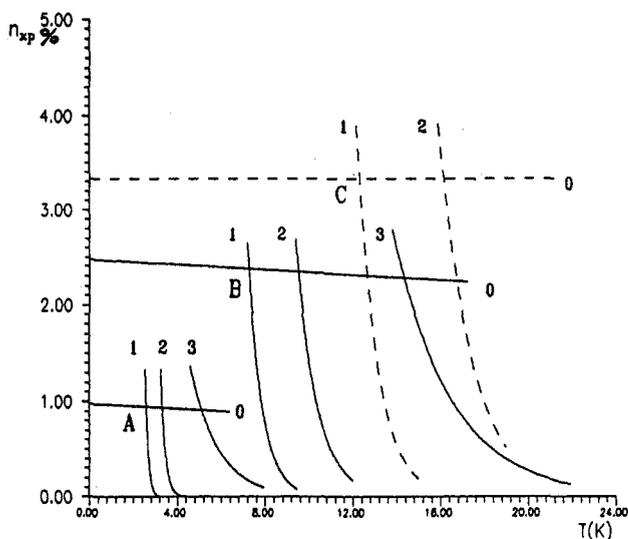
Fig. 4. Temperature dependence of limiting concentrations of nitrogen atoms in nitrogen matrix, calculated for thermal-wave (0) and thermal (1,2,3) mechanisms of explosions. Effective activation energies of recombination (cal/mol) are: A - 200, B - 600, C - 1000. Dimensions of the system (cm) are: (1) 1, (2) 10^{-2}, (3)10^{-4}.

The initiation of thermal explosions demands jumpwise change of thermophysical properties of the system, e.g. strong pulse of heating or sharp decrease of heat conductivity. First of these variants was released in experiments of Greenberg[57-59] who imitated under laboratory conditions the explosions of irradiated grains by the powerfull heat pulse. Latter case was demonstrated[66] by the example of recombination of nitrogen atoms precipitated at the helium lining at the temperature below the λ - point (T_A = 2,19 K) i.e. below the temperature of transition of helium into superfluid state.

Concentration of N-atoms under such conditions exceeded 1,6% and most of accumulated atoms recombined during the heating just at the λ - point.

Computations[66] of temperature dependence of limiting concentrations of N-atoms vs. temperature for thermal-wave and thermal explosions gave the results presented at the Fig.4.

The limiting concentration of atoms (n_{cr}) stabilized at very low temperatures are determined by the stability of the system to thermal-wave explosion. At higher temperatures (T $\geq$ 4 K) stability to thermal explosion is decisive. In this region - in contrast to thermal-wave explosion - the value of n_{cr} depends very strongly (exponentially) on the temperature and quadratically on the dimensions of the sample.

Comparison of experimental data[57-59,66] with theoretical considerations[66] gave an evidence that the observed explosions were indeed of thermal rather than of thermal-wave nature. Detailed analysis of thermal regime which should be characteristic of interstellar dust grains under UV exposure of constant intensity was performed in our most recent article[69] .

Fig.5 represents the plane of dimensionless control parameters - g (proportional to the rate of generation of radicals by the UV radiation p cm^{-3} s^{-1}) and Semenov number S (which characterizes the ratio of the scales for heat release and heat escape). The region of abovementioned oscillations is shaded, the rest of the plane corresponds to stationary regimes. The area to the right from g_m is the area of - so to say - "stationary combustion". The temperature of grains is here high but the radical
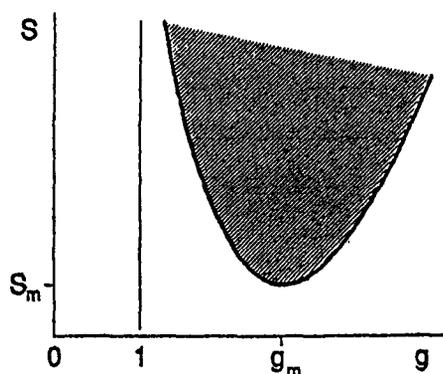
Fig. 5. Schematic illustration of various thermal regions of behavior of interstellar dust grains under the UV exposure.
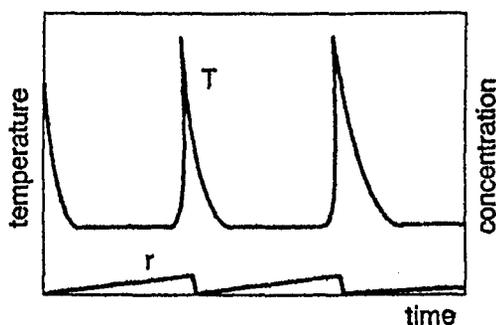
Fig. 6. Schematic illustration of the oscillations of temperature (T) and radical concentration r in interstellar dust grains under the UV exposure ($T = 10$–20 K).

concentration is extremely small. Because of fast diffusion the recombination immediately follows the radical production, the energy of absorbed photon transforms into the heat and then escapes to space.

The case of oscillations of grains temperature T and radical concentration in grains r (cm^{-3}) is illustrated by the Fig.6. Stages of accumulation of radicals at the temperature close to T_0 alternate with the flashes when the accumulated radicals are completely consumed. After the flash the grain cools down to T_0 and the whole cycle is repeated. At the typical (for diffuse clouds and outer layers of dense clouds) rates of UV generation of radicals (g = 1 corresponds to $p \approx 10^{11}$ - 10^{12} cm^{-3} s^{-1}) Semenov number S $\approx 10^5$ - 10^6, T = 10 - 20 K, the concentrations of radicals accumulated before the flash are $(0,3 - 1)\ 10^{19}$ cm^{-3}, and the duration of time between two subsequent flashes are $(0.3 - 1)10^7$ s The number of radicals recombining in the grain of $\sim 10^{-5}$ cm diameter is $(0,3 - 1)\ 10^4$ which corresponds to quite minor increase of temperature ($\sim$10 K) and cannot lead to the explosion and destruction of the grain.

Therefore we conclude that even thermal (not to mention thermal-wave) explosions of interstellar dust grains in the permanent, stationary field of space radiation don't look as plausible events.

Mechanochemical explosions and autowave propagation of chemical reactions in cold irradiated solids.

The peculiar phenomenon-explosion of photolysed solid mixture of reactants (methylcyclohexane MCH with chlorine) at its deep cooling was observed in 1980 in Moscow Institute of Chemical Physics[70]. Authors of[70] interpreted this phenomenon at the thermal explosion which occurred due to the appearance of internal thermoelastic tensions in the cooled system and corresponding decrease of activation energy of the investigated reaction. Soon afterwards another group[71] has studied the same reaction in glass-like system activated by ^{60}Co γ - radiation. There were varied the rates of cooling and defreezing of MCH - Cl$_2$ system between 4,2 K and 77 K and it was claimed that the initiation of chain reaction of chlorination is caused by the formation of cracks in
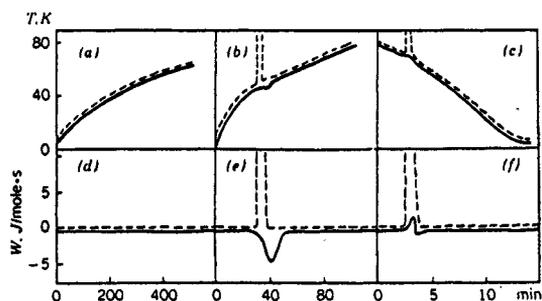
Fig. 7. (a, b, c) Time dependence of the temperature of the sample (Cl_2 + MCH, molar ratio 1:3) and (d, e, f) thermal effects; solid lines: nonirradiated samples; dashed lines: samples irradiated by ^{60}Co γ-rays at 77 K, dose 27 kGy.

monolithic samples at the fast change of their temperature (see Fig.7). New cracks which accelerate the transformation that accounts for its explosive nature appear during the process which can be defined as the heterogeneous mechanochemical explosion.

Analogous results were obtained for the chlorination of other saturated hydrocarbons, for hydrobromination of ethylene and for polymerization. Summary of experimental data and detailed description of their theoretical treatment were presented in the surveys[72,73].

Thus, it was shown that fast self-propagating chain reactions are initiated at low temperatures (down to 4,2 K) by brittle fracture of vitreous and polycrystalline samples which contain stabilized free radicals accumulated during preceding γ- irradiation.

The dependence of the reaction rate on a strength of a triggering impact and on a concentration of preaccumulated active centers was found to be of a threshold type.

The initial mechanical or thermal fracture produces reaction outburst and the autowave propagation of the reaction front along the sample with a rate (1 - 4 cm^{-1}) much above that of heat transfer but much below the sound velocity.

Chain reaction of chlorination: $C_4 H_9 Cl + Cl_2$ was triggered by mechanical impact - slight turn of thin mettalic rod frozen into an upper end of the vitreous sample scratched it and formed an initial crack.

All observed peculiarities of mechanochemical explosions of cold irradiated vitreous and polycrystalline samples and autowave propagation of the front of chain reactions found an explanation on the base of a positive feedback between the brittle fracture and chemical conversion of the samples. Formation of cracks in a monopolic sample initiates its chemical conversion at the fresh surfaces of cracks and resulting transformation penetrates into the sample's depth and produces new cracks etc.

The equation of the formation of a new surface can be written in a form analogous to that of a branched-chain process:

$$\frac{dS}{dt} = F(S) - G(S) \qquad (1)$$

where S is the specific surface area per unit volume, F(S) is the generation rate of active surface, and G(S) is the rate of their deactivation. Since G(S) must be a linear function (as for a unimolecular

process), the dependence of form $F(S) \infty S^m$ where m > 1 will qualitatively correspond to the observed experimental facts.

Equations describing the autowave process in the systems in question take a form:

$$\lambda \frac{d^2 T}{dx^2} - \rho C U \frac{dT}{dx} + Qa = 0 \qquad (2)$$

$$U \frac{da}{dx} = -\frac{a}{\tau} \qquad (3)$$

where λ (cal. cm^{-1} grad^{-1} s^{-1}) is the heat conductivity , x (cm) - the coordinate, ρ (g.cm^{-3}) -densityt of the solid mixture of reactant, C (cal. grad^{-1} g^{-1}) - specific heat , U (cm s^{-1}) -propagation velosityt of the temperature wave front, Q (cal. cm^{-3} s^{-1}) - the rate of reaction heat release, τ - the duration of reaction (inverse rate constant).

The boundary conditions look as

$$x = 0, \quad a = 1, \quad \frac{dT}{dx} = H$$

$$x = \infty, \quad a = 0, \quad \frac{dT}{dx} = 0$$

$$\lambda H = \rho C U (T_r - T_0) \quad T_r = |T_0|_{x=0}$$

Solution of equations (2), (3) under the above boundary conditions leads to:

$$H = \frac{T_{adiab} - T_0}{U\tau + \frac{\lambda}{\rho C U}} = \frac{Q\tau}{\rho C} \cdot \frac{1}{U\tau + \frac{\lambda}{\rho C U}} \qquad (4)$$

Principal difference between the autowave fracture and combustion processes is that the third term in (2) is a function of temperature gradient rather than of temperature. Brittle fracture which initiates the reaction occurs when the temperature gradient reaches its critical value H , i.e. it produces the stress equal to the ultimate strength of the material.

It seems plausible that mechanochemical explosions of solid and autowave propagation of their chemical conversions can play certain part also at the space conditions, resulting in the formation of diverse products in bodies undergoing fragile destruction at various collisions.

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