Reviews

Non-traditional pathways of extraterrestrial formation of organic compounds

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The mechanisms of solid-phase reactions that have been experimentally and theoretically studied during recent decades and can be directly related to the formation of organic substances in space and their delivery to Earth and to the problems of prebiotic evolution are considered. Among these mechanisms are molecular tunneling (hypothesis of the cold prehistory of life), polycondensation of solid monomers by shock waves (problem of the delivery of organic substances to Earth by meteorites), thermal and thermal-wave explosions, and oscillations of temperature and radical concentrations in small cold particles under 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.

Key words: solid-phase astrochemical reactions, mechanisms; organic substances, formation in space and delivery to Earth.

Introduction

About 40,000 tons of interplanetary dust is accreted annually on Earth's surface.[1] This means that if the accretion rate was constant during the lifetime of the Earth crust (4 billions years), the mass of the accretion layer (accreted interplanetary dust) would be ~1 ton · m^{-2}. Organic substances of different degrees of complexity (up to polycyclic aromatic hydrocarbons and their alkylated derivatives) were observed in interplanetary particles.[2] Thus, recent observations suggest that "organic matter on our planet has its origin in interplanetary — or perhaps interstellar — space."[3] In fact, both interplanetary and interstellar dust accreting on the early Earth could populate its surface with compounds that could play an important role in the origin of life on our planet.[4] Hypotheses concerning possible mechanisms of the extraterrestrial formation of organic compounds (*i.e.*, their formation in extremely cold (10—20 K) interstellar clouds) often assume that ion-molecular reactions occurring in the gas phase, as known, with the zero activation energy, play a decisive role. However, it cannot be considered as firmly established that the absence of the activation barrier is a general property of this type of reaction. Therefore, further detailed investigations are necessary, especially under conditions close to those realized in mantles of the so-called "dirty ice"

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covering interstellar dust grains. It is important to discuss the results of modern experimental and theoretical studies of various solid-phase processes in connection with the problems of astrochemistry and, to some extent, exobiology.

Molecular tunneling and hypothesis of cold prehistory of life

There are two main hypotheses of the origin of life on Earth.

The first of them is related to the so-called "warm," terrestrial scenario developed by Oparin[5] and Haldane[6] ("standard model"). The second hypothesis is based on the "cold," extraterrestrial scenario, *i.e.*, on the "panspermia" hypothesis of Arrhenius.[7] After the classical experiments of Urey,[8] Miller,[9,10] and their successors, which demonstrated the formation of some prebiotic molecules (*e.g.*, amino acids and nucleotide bases) in gaseous mixtures imitating the early atmosphere of Earth (H_2O, CO_2, CO, CH_4, NH_3, *etc.*) under the impact of various physical factors (UV radiation, electric discharges, *etc.*), the main attention of researchers has been given for a long time predominantly to the "warm" scenario.

Interest in the "cold" scenario was revived to a great extent due to the discovery of the low-temperature limit of the rate of chemical reactions (using the radiation-induced chain polymerization of formaldehyde as an example). In other words, the temperature-independent chemical reactivity nonvanishing even near absolute zero was discovered and explained by quantum-mechanical molecular tunneling.[11]

As shown in Ref. 11, "the entropy factors play no role near absolute zero, and all equilibria are shifted 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 extremely low temperatures in chemical and biological evolution (cold prehistory of life?)." In several works,[12—14] we analyzed in detail possible mechanisms of the formation of polyformaldehyde in the "dirty ice" mantle (containing mainly frozen ammonia, HCN, HNC, water, ethane, formaldehyde, *etc.*) and the hypothetical role of these grains as possible seeds of life in the "cold" scenario. The kinetics and equilibrium of the reactions in the grain bulk were calculated by the principle of "shuffling of the deck of cards," *i.e.*, as multiply repeated sublimation, condensation, polymerization, and different chemical transformations. The analysis of experimental results[11] and their comparison with the calculations for the Arrhenius type kinetics and tunneling kinetics[14] result in the obvious conclusion that the formation of polyformaldehyde in the interstellar dust could proceed only *via* tunneling.

For this estimation, the following values should be taken into account: time between the absorption of subsequent UV quanta by each molecule of diffuse interstellar clouds or surface layers of dark (dense) clouds (τ_{UV} ~100 years); the lifetime of the clouds determined by their collisions and gravitational collapse (τ_{cl} ~10^5—10^7 years), as well as the kinetic data: time of addition of a new unit to the growing polymer chain on the low-temperature plateau ($T \leq 12$ K) $\tau_0 \sim 10^{-2}$ s, the length of the polymer chain ν at these temperatures is *ca.* 10^3, and the activation energy of the chain growth in the Arrhenius region (up to 140 K) E is ~0.1 eV.

The condition $(\tau_0)_{Arr} \ll \tau_{UV}/\nu$ (the pre-exponential factor for the polymer chain growth was accepted as 10^{14} s^{-1}) can be fulfilled when the temperature is higher than 30 K. The condition $(\tau_0)_{Arr} \ll \tau_{cl}/\nu$ corresponds to a milder condition $T > 20$ K, and both values of the minimum necessary temperature are higher than the temperature of interstellar clouds (10—20 K).

Moreover, the τ_0 values for the Arrhenius type extrapolation of the reaction rate are the following: 10^{11} s for 20 K and 10^{36} s for 10 K, *i.e.*, they are many orders of magnitude higher than the experimental values.

At the same time, the use of the simplest Gamov type formula for the estimation of the tunneling rate: $(\tau_0)_{tun} = 10^{-14}\exp(\pi\sqrt{2}d\sqrt{mE}/2\hbar)$, where d is the width of the barrier and $m(CH_2O)$ = 30 a.m.u., results in the inequalities $d < 0.65$ Å (when τ_{UV} is used) or $d < 0.90$—0.95 Å (when τ_{cl} is used). These values of the tunneling distance seem to be quite reasonable and are a strong argument in favor of the tunneling mechanism of the formation of polyoxymethylene in the cosmic dust, which corresponds to the views in Refs. 11—14.

Thus, tunneling could increase considerably the number of possible low-temperature reactions in the dark clouds. For example, one of the possibilities is the tunneling polymerization on the surface of the interstellar dust grains to form a very thin (several molecular layers) polymer film on the surface of the "dirty ice" mantle.

Polycondensation reactions in the "dirty ice" mantles involving CH_2O, HCN, HNC, NH_3, and H_2O are of interest for studying chemical and prebiotic evolution. These reactions (exothermic but not chain-type) could result in the formation of amino acids, polypeptides, sugars, and nucleotide bases (purines and pyrimidines).

The "pure" molecular tunneling mechanism of these reactions is not necessary: the tunneling rate decreases sharply to vanishingly small values as the width and height of the barrier increase. However, each individual stage of the chemical transformation, which is an elementary gas-phase process such as the reaction

$$H_2C{=}O + NH_3 \rightarrow H_2C{=}NH + H_2O,$$

occurs in the solid as a sequence of many individual and collective conformational rearrangements of molecules, complexes, or whole regions of molecular crystals. The collision of the interstellar dust grain with a cosmic proton, the absorption of a UV quantum, or release of the recombination energy on the surface grain can result in the transfer of a "driving" particle, for example, an electron, which determines the number of conformational rearrangements. Since quantum effects open up possibilities for various low-temperature chemical transformations, it was of interest to calculate the equilibrium composition of cold grains of the interstellar dust. In these calculations, the entropy should not be taken into account, because they are exclusively based on the enthalpy values and the cosmic abundance of H, C, N, and O atoms. It was established that the maximum heat release corresponds to the formation of acetic acid, urea, and, of course, the products of their exothermic polycondensation.[15] Due to the gravitational instability, the differentiation of matter occurs in a dust-gas cloud, which results in the formation of a protostar. The dust-gas disk surrounding the protostar flattens and decomposes to form a cluster of individual thickenings (planetesimals), which then accumulate planets, asteroids, meteorites, and comets. Thus, organic substances formed in the dust-gas cloud can reach planets by two processes: first, during the formation of the planet; second, after the formation of the planet by the adsorption of these compounds on the surface of the planet that had already been formed from the surrounding space. The organic substances that had reached the planet by the second way served perhaps as the raw material for the formation of the "primordial soup."

The possibility of the synthesis of rather complicated molecules under the combination of cosmic cold and various types of radiation of the cosmic origin was postulated in Ref. 11. This viewpoint was also propagandized actively by Wickramasinghe and Hoyle,[16—18] whose publications, however, were widely disputed.

Starting from the assertion that formaldehyde undergoes polymerization in the interstellar space to form polyoxymethylene and even polysaccharides, the authors soon advanced a hypothesis of "living interstellar clouds"[19] and even an extraterrestrial origin of some viruses,[20] for example, the virus of the influenza invading Earth in 1919. These speculations met with various reasonable objections. Nevertheless, the presence of polyoxymethylene in space has been recently supported by the comparison of the results of studying the coma of the Halley comet by a heavy ion analyzer aboard the "Giotto" spacecraft[21—23] with the data of the laboratory mass and IR spectra of formaldehyde polymerized on the surface of silicate grains under proton irradiation at 20 K. Molecular tunneling was mentioned in Refs. 21—23 as the most probable mechanism.

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

The absence of these attempts is disappointing, especially as in 1860 dissymmetry discoverer Louis Pasteur was firmly convinced: "Homochirality is the demarcation line between the living and nonliving matter." Nowadays it seems evident that only the coexistence of these two (and only these two) properties mentioned can serve as Ariadne's thread in the labyrinth of hypotheses of the origin of life.

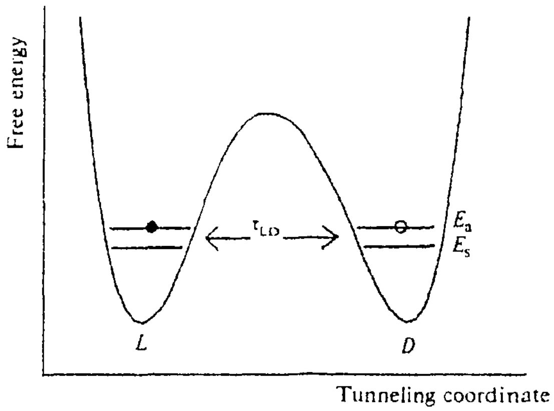

Fig. 1. Tunneling between L- and D-states of a chiral molecule: τ_{LD} is the average lifetime of the chiral state.

Relations between the chirality, origin of life, and evolution are too various to be considered within the scope of one article. Therefore, we only refer to some of our previous works[24—26] (now under further development) and consider briefly the relations between tunneling and chirality.

According to the well-known Hund's paradox,[27] in a system of two potential wells (and this very type includes the molecules with asymmetric *C atoms, which can exist in the form of L- and D-enantiomers, *i.e.*, can be localized in L- or D-wells (see Fig. 1)), none of two wave functions, ψ_L or ψ_D, describes the eigenvalue of the system. Tunneling results in spontaneous L $\rightleftharpoons$ D transformations, *i.e.*, the system oscillates and is delocalized between the potential L- and D-wells. The L- and D-states have a definite chirality, but not a definite parity. Two eigenvalues with definite parity (but not with definite chirality) are described by the symmetric (ψ_s) or antisymmetric (ψ_{as}) combination of wave functions ψ_L and ψ_D. There is a characteristic difference between the energies of two states: $\Delta E_{as} = E_a - E_s$, and the characteristic frequency of tunneling oscillations L $\rightleftharpoons$ D is the following: $\omega_{LD} = \tau_{LD}^{-1} = \Delta E_{as}/2\pi\hbar$.* Under these conditions, there is no sense in speaking about the definite sign of chirality of optically active molecules, *i.e.*, about the property inherent in bioorganic molecules.

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* Stationary states of the nonlinear Schrödinger equation[28,29] should not be eigenfunctions of the operators corresponding to the symmetry group of the potential. When the nonlinear parameter approaches ΔE_{as}, a rather sharp transition from the definite parity to definite chirality occurs, *i.e.*, permanent localization in one of the wells takes place.

In fact, when a molecule primarily exists in the L-state, it will be in the D-state over time τ_{LD}. Therefore, over the time interval $t \gg \tau_{LD}$, the probabilities that the molecule exists in the L- and D-states are the same and equal to 1/2, *i.e.*, racemization occurs during time $t \gg \tau_{LD}$. Racemization processes make it possible to preserve the mirror symmetry, which is a necessary stage of prebiotic (or protobiotic) evolution and has a tendency to reduce a system to the racemic state. Therefore, deracemization could occur only in the case of processes capable of efficiently countering the racemization tendency.

These counterracemization factors appear indeed in the "cold" scenario. It was shown[30—33] that if chiral molecules interact with an optically inactive medium consisting of a strongly cooled low-density gas, where only binary collisions are significant, the stabilization of chirality of isomeric molecules would be possible over a time longer than that of tunneling oscillations τ_{LD}. Due to the interaction of the isomer with the medium molecules, the chiral particle behaves as a damped rather than a free oscillator.

Therefore, although the racemization occurs in the optically inactive medium, the time scale of this process increases sharply as compared to racemization time of isolated particles.

The fact that the chirality of a molecule is stabilized at low temperatures by the interaction with the medium is an attractive aspect of the "cold" scenario. However, it should be kept in mind that the problem of deracemization of the medium as a whole arises. In particular, each isomeric molecule is initially in a state with definite chirality, *i.e.*, in the L- or D-state; however, a set of these molecules probably is not a racemic mixture. Therefore, it is important to analyze the problem of stabilization of the optical activity of an ensemble of molecules incorporated in solid low-temperature matrices taking into account the contributions of relaxation processes of different types, *i.e.*, not only tunneling of particles (nondiagonal transitions), but also the transitions between each of two wells being the two-well potential (diagonal transitions).

This analysis shows[34] that at very low temperatures, time τ_s of the L $\rightleftharpoons$ D transitions in solids is considerably greater than time τ_{LD} of "free" tunneling oscillations and, moreover, near absolute zero τ_s increases as the temperature increases (Fig. 2). The most efficient suppression of racemization in molecular ensembles is observed at ~10—20 K, *i.e.*, under just those conditions typical of the "dirty ice" mantles covering interstellar dust grains.

Delivery of organic compounds to Earth. Shock-wave-induced polymerization and polycondensation

The thesis on the interplanetary or interstellar origin of organic substances on our planet needs, of course, detailed elaboration, especially concerning their main sources. There is a very popular point of view (see, *e.g.*, Refs. 35—39) that life on Earth was originated by a rain of comets, carbonaceous asteroids, and meteorites that contributed a large amount of organic matter to the primitive Earth.

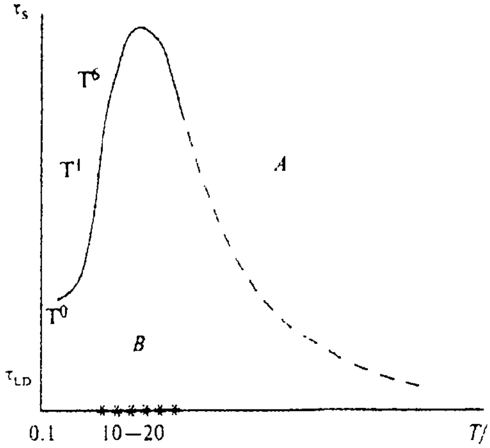

Fig. 2. Stabilization of chirality in low-temperature solids ($\tau_s \gg \tau_{LD}$. *A*, Arrhenius region; *B*, three-phonon relaxation; τ_s, chirality lifetime.

Recently, the idea even has been advanced that "the 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 Earth almost devoid of carbon, water, and all volatile and labile elements."[40] One of the most important questions arising in connection with this assertion is the following: whether prebiotic species can be brought intact to Earth.

According to Ref. 41, these "soft-landed" species can be rather small fragments that are gently retarded by the atmosphere. They are mainly meteorites of 10^{-12}—10^{-6} g. From this viewpoint of the origin of life, the problem of the delivery of intact amino acids to Earth is of special interest.

Large amounts of apparently extraterrestrial amino acids were found in the rocks at the Cretaceous/Tertiary boundary in Denmark,[42] and a hypothesis on the mechanism of their preservation was developed.[43]

The most intriguing data were obtained for the so-called Murchison meteorite that fell in Australia in 1969 and belongs to carbonaceous chondrites typically containing 2—3 wt.% carbon mainly in the form of organic substances. At least 74 amino acids were identified in the extract of this meteorite, and some amino acids characteristic of living species were among them. It was also established that some of these amino acids were not racemic (L-enantiomeric excess).[44] However, the question remains unsolved of whether this deviation from homochirality is caused by the terrestrial contamination or diagenetic reactions in space.

The review by Engel and coworkers[45] on the stereoisomeric and isotopic (^{13}C) composition of the amino acids in the Murchison meteorite offer decisive arguments. It was reported that L-enantiomeric excesses for alanine (D/L = 0.85±0.03) and glutamic acid (D/L = 0.54) were accompanied by the ^{13}C enrichment (up to 30‰) typical of extraterrestrial organic substances. The authors concluded that optically active (or, most likely, deracemized) compounds were present in the early Solar system. This conclusion evoked great interest and was commented upon in Refs. 36 and 47. As emphasized in Ref. 47, the results in Ref. 45 confirm the viewpoint[24,25] that the chiral purity of the future Earth biosphere was achieved at the stage of prebiotic evolution, and it was a necessary condition for the subsequent development of the self-replication function. Moreover, if the partially deracemized state of the amino acids mentioned in Ref. 45 is an intermediate stage of the transition to the chirally pure state, these results indicate the time scale required for distortion of mirror symmetry.

As for the problem of the possibility of formation of amino acids on Earth due to strong shock action, the data on polymerization and condensation of several organic compounds induced by shock waves (SW) should be considered. The comprehensive description of polymerization and modification of polymers under shock compression recently has been presented in detail by Gustov.[48] An important step in studying the shock compression of the condensed phase was made by Ryabinin,[49] who invented special recovery capsules for preservation of explosion products. The schemes of these recovery capsules used in our experiments (cylindrical and flat variants) are shown in Fig. 3.

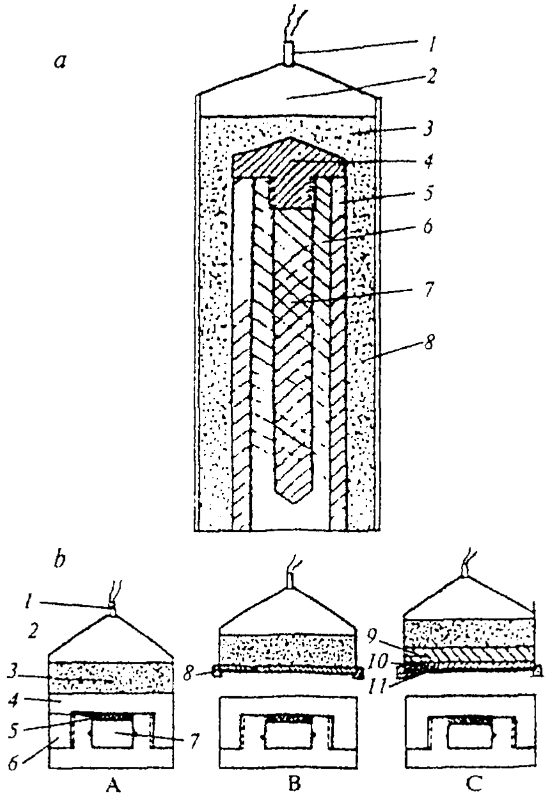

Fig. 3. Schemes of recovery capsules.
a, *cylindrical capsule*: *1*, detonator; *2*, generator of planar detonation wave; *3*, explosive; *4*, metallic stopper; *5*, external body of capsule; *6*, internal body of capsule; *7*, sample; *8*, cup.
b, *flat capsule*: A, contact assembly consisting of detonator (*1*), generator of planar detonation wave (*2*), explosive (*3*), covering of capsule (*4*), sample (*5*), capsule body (*6*), metallic stopper (*7*);
B, flying planar assembly containing additionally carrier (metallic plate) (*8*);
C, quasi-isoentropic assembly containing additionally a set of carriers with reduced density and detonation rate [*e.g.*, Al, poly(methyl methacrylate)] (*9*, *10*, *11*).

Our studies of SW-induced conversions of solids, begun in the mid-sixties, were devoted to organic compounds. It was found that destruction processes do not occur under rather drastic conditions (pressure, temperature, deformation velocity), but *contra versa* molecular association takes place.[50] When eight monomers of different types (trioxane, acrylamide, potassium acrylate, salicylaldehyde, diphenylbutadiene, tolan, and stilbene) were polymerized, the threshold amplitudes of the planar SW-induced polymerization varied from 2 to 30 GPa, and the yields of polymers varied from traces (in the case of stilbene) to 60% (for acrylamide at the pressure above 10 GPa).[51–52]

The next step of our studies was the investigation of SW-induced cross-linking of several rubbers,[53] for example, polybutadiene.

However, the observation of SW-induced polycondensation of amino acids was most interesting from the viewpoint of the delivery of prebiotic and protobiotic substances to Earth. Shock loading of glycine or D,L-tyrosine mixed with the same (by weight) amount of silica gel as a dehydrating agent resulted in the formation of polypeptides.[54] The SW-induced polycondensation of L-α-alanine was studied in more detail.[55] The samples were prepared by molding a mixture of dried alanine with silica gel. The SW-treatment of the samples was performed for 5—7 μs with the amplitudes P = 12.35 and 50 GPa at the initial temperature of 20 °C in steel flat capsules. Then the capsules cooled with liquid nitrogen were opened, and the samples were pulverized and placed in 20% acetic acid. The amino acid composition of the soluble fraction was studied by TLC, amino acid analysis, preparative paper chromatography, and mass spectrometry. The content of amino acids was determined before and after hydrolysis. An increase in the content after hydrolysis in all experiments at 35 and 50 GPa testified that polypeptides were formed under the shock wave impact in the samples studied. The mass spectral analysis showed that cyclic and/or linear polypeptides formed contained more than four amino acid residues. In later experiments,[56] the formation of amino acids from ammonium salts of carboxylic acids upon their dynamic compression was observed.

Thus, all data obtained in the laboratory experiments described above can be considered an argument in favor of the fact that amino acids and products of their polycondensation were delivered to our planet from space by extraterrestrial carriers.

Thermal regime of cold solid particles containing trapped active centers

Among different pathways of the extraterrestrial formation of complex organic molecules, there is the possibility of explosions of interstellar dust grains containing high concentrations of free radicals accumulated due to the action of various cosmic radiations (mainly UV). Several calculations and laboratory experiments devoted to these explosions were performed by Greenberg.[57–59]

Two mechanisms of thermal explosions of chemical systems were widely discussed in the literature: the genuine thermal explosion described by the classical theory of Semenov[60,61] and Frank-Kamenetskii[62,63] and the so-called "thermal-wave" (or "thermal-chain") explosions.[64–66]

It is known that the conditions of appearance of thermal explosions are determined by the ratio of heating rates of the system due to the exothermic (and accelerated with the temperature increase) chemical reaction and the heat removal through the walls of the system.

The origin of thermal-wave explosions is quite different. The recombination point of the radical pair serves as a center of divergence of the spherical thermal wave. This wave throws other radicals from traps occupied by them, and these radicals recombine and generate new thermal waves. Thus, peculiar energy chains of the radical recombination appear, which under normal conditions prevent the accumulation of the radicals in concentrations higher than tenths per cent independently of the intensity of the radiation that generates these radicals.

Thermal-wave explosions can play a noticeable role only in sufficiently large particles with $l > \sqrt{\chi\tau_r}$, where χ (cm^2 s^{-1}) is the thermal diffusivity coefficient and τ_r is the characteristic time of radical recombination that is determined by their diffusion.[67,68] Thermal explosions should predominate in smaller samples, for example, in cosmic dust grains.

It is quite evident that only the steady-state, but not overcritical (necessary for explosion) concentration of radicals can be attained under the stationary irradiation of samples. The passage through the critical concentration level results in "soft" outburning of overcritical excess of the radicals and returning to the steady-state level of their concentration, *i.e.*, peculiar oscillations appear. The initiation of thermal explosions requires a change in the thermophysical properties of the system, *i.e.*, a strong thermal pulse or a sharp decrease in the heat conductivity. The first of these variants was realized in Greenberg's experiments[57–59] simulating an explosion of irradiated grains under laboratory conditions by powerful heat pulses. The second variant was demonstrated[66] for the recombination of nitrogen atoms precipitated on the helium lining in helium at the temperatures below the temperature of the transition of helium to the superfluid state, *i.e.*, below the λ-point.

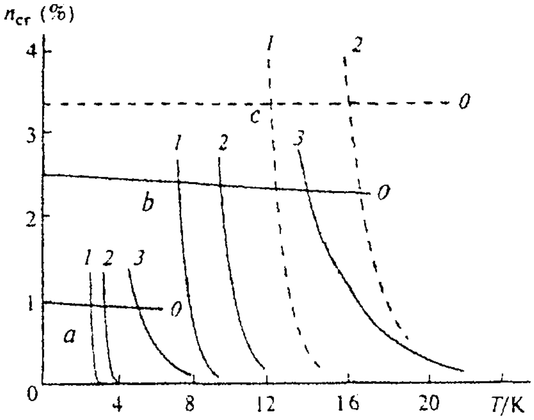

Fig. 4. Temperature dependence of limiting concentrations of atoms in nitrogen matrices calculated for thermal-wave (*0*) and thermal (*1, 2, 3*) mechanisms of explosions. Effective activation energies of recombination (cal mol^{-1}): *a*, 200; *b*, 600; *c*, 1000. Sizes of the system (cm): 1 (*1*), 10^{-2} (*2*), 10^{-4} (*3*).

Under these conditions, the concentration of the nitrogen atoms exceeded 1.6%, and the majority of the atoms accumulated recombined during heating just at the λ-point (T_λ = 2.19 K).

The calculations of the temperature dependences of the limiting concentrations of atoms (n_{cr}) for thermal-wave and thermal explosions are presented in Fig. 4. The limiting concentrations of atoms stabilized at very low temperatures are determined by the stability of the system to the thermal-wave explosion. At higher temperatures ($T \geq 4$ K), the stability to the thermal explosion is decisive. In this region, contrary to the thermal-wave explosion, the n_{cr} value is an exponential function of the temperature and proportional to the square size of the sample.

The comparison of the experimental results[57–59,66] with the theoretical data[66] shows that the explosions observed were indeed of thermal rather than thermal-wave nature. The detailed analysis of the thermal regime that should be typical of interstellar dust grains under the UV irradiation of permanent intensity was performed in our very recent work.[69]

The plane of dimensionless control parameters g (proportional to the rate of the radical formation under UV irradiation, P/cm^{-3} s^{-1}) and Semenov's number S (which characterizes the ratio of the scales of the rates of heat release and dissipation of the heat energy) is presented in Fig. 5. The region of the aforementioned oscillations is shaded, and the rest of the plane corresponds to the stationary regimes. The area to the right of g_m is the region of the so-called "stationary combustion." Here the temperature of the grains is high, but the

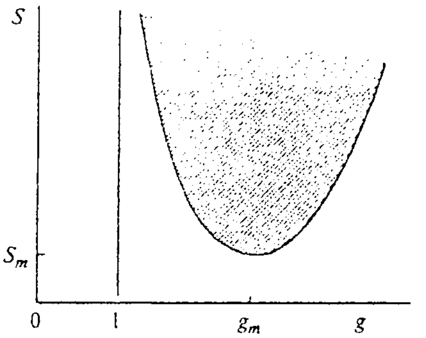

Fig. 5. Schematic illustration of different thermal regions of the behavior of interstellar dust grains under UV exposure.

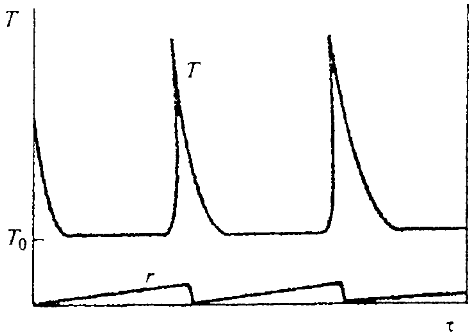

Fig. 6. Schematic illustration of oscillations of temperature (*T*) and radical concentration (*r*) in interstellar dust grains under UV exposure (T = 10—20 K).

concentration of the radicals is very small. Due to fast diffusion, the formation of the radicals is immediately followed by recombination. The photon that appeared in the recombination is absorbed, and its energy is transformed to heat and escapes into space.

Figure 6 shows the oscillations of the radical concentration in the interstellar dust grains (r/cm^{-3}) and temperature of the grains (T). The stages of accumulation of the radicals alternate with the flashes when the accumulated radicals are completely consumed. After a flash, the grain is cooled down to T_0, and the whole cycle is repeated. For the typical (of diffuse clouds and outer layers of dense clouds) rates of the radical formation under UV irradiation (g = 1 corresponds to P ~10^{11}—10^{12} cm^{-3} s^{-1}), Semenov's number S of ~10^5—10^6, and T = 10—20 K, the concentration of the radicals accumulated before the flash is equal to $(0.6-1) \cdot 10^{19}$ cm^{-3} and the time between subsequent flashes is equal to $(0.3-1) \cdot 10^7$ s. The number of the radicals recombining in a grain ~10^{-5} cm in diameter is equal to $(0.3-1) \cdot 10^4$, which corresponds to a rather weak increase in temperature (~10 K) and cannot result in the explosion and destruction of the grain.

Thus, we conclude that thermal (not to mention thermal-wave) explosions of interstellar dust grains in the static field of cosmic irradiation are rather improbable events.

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

A specific phenomenon, the explosion of the deeply cooled solid mixture of reagents (methylcyclohexane (MCH) and chlorine), was observed in 1980 at the Institute of Chemical Physics of the USSR Academy of Sciences.[70] The authors of Ref. 70 interpreted this phenomenon as a thermal explosion that occurred due to the appearance of internal thermoelastic tensions in the cooled system and the corresponding decrease in the activation energy of the reaction studied. Soon another research group[71] studied the same reaction in the glass-like system activated by ^{60}Co γ-irradiation. The rates of cooling and freezing out of the MCH—Cl_2 system were varied in the temperature range from 4.2 to 77 K, and it was observed that the reason for the initiation of the chain chlorination reaction is the formation of cracks in the monolithic samples following a fast change in temperature (see Fig. 7). The explosion-type transition, which is accelerated due to the formation of new cracks, can be defined as the heterogeneous mechanochemical explosion.

Similar results were obtained for chlorination of other saturated hydrocarbons, hydrobromination of ethylene, and polymerization. The totality of the experimental results and detailed description of their theoretical treatment are presented in the reviews.[72,73]

Thus, it was shown that fast self-propagating chain reactions are initiated at low temperatures (down to 4.2 K) by the brittle fracture of vitreous and polycrystalline samples containing stabilized free radicals accumulated during preceding γ-irradiation.

It was determined that the dependence of the reaction rate on the intensity of a trigging impact and on the concentration of preaccumulated active centers has a threshold character.

The initial mechanical or thermal fracture produces the outburst of the reaction and its autowave propagation along the sample at a rate of 1—4 cm s^{-1}, which is much faster than that of heat transfer, but considerably

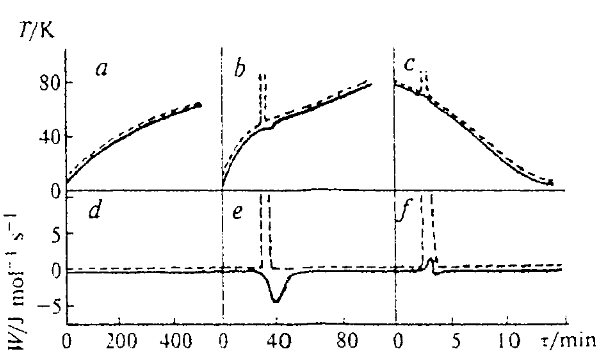

Fig. 7. Time dependence of temperature of the sample (Cl_2 + MCH, molar ratio 1 : 3) (*a, b, c*) and thermal effects (*d, e, f*). Solid lines indicate nonirradiated samples, dashed lines correspond to ^{60}Co γ-irradiated samples at 77 K, dose 27 kGy.

slower than the sound velocity. The typical examples for this autowave propagation were observed in cinegrams.

The chain chlorination reaction $C_4H_9Cl + Cl_2$ was initiated by the mechanical impact: a slight rotation of thin metallic rod frozen into the upper end of the vitreous sample in a capillary resulted in scratching the sample by the rod to form the initial crack.

All specific features observed for mechanochemical explosions of cold irradiated vitreous and polycrystalline samples and for the autowave propagation of the chain reaction front were explained on the basis of a positive feedback between the brittle fracture and chemical conversion of the samples. The formation of cracks in a monolithic sample initiates its chemical conversion on fresh surfaces of the cracks, the resulting transformation penetrates deep into the sample to produce new cracks, *etc.*

The equation of the formation of a new surface can be written in a form analogous to the 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 rate of formation of active surfaces, and $G(S)$ is the rate of their deactivation. Since $G(S)$ should be a linear function (by analogy with the monomolecular process), the dependence in the form $F(S) \propto S^m$ $(m > 1)$ will correspond qualitatively to the experimental facts observed.

The equations describing the autowave process in the system discussed take the form

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

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

where λ (cal cm^{-1} deg^{-1} s^{-1}) is the heat conductivity, x (cm) is the coordinate, ρ (g cm^{-3}) is the density of the solid mixture of reagents, C (cal deg^{-1} g^{-1}) is the specific heat, U (cm s^{-1}) is the propagation velocity of the temperature wave front, Q (cal cm^{-3} s^{-1}) is the rate of heat release, a is the dimensionless concentration of reactants, and τ is the duration of the reaction (inverse rate constant).

The boundary conditions are the following:

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

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

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

The solution of Eqs. (2) and (3) under the aforementioned boundary conditions results in the following equation:

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

The basic difference in the autowave fracture of samples and combustion process is the fact that the third term in Eq. (2) is a function of the temperature gradient rather than of temperature. When the temperature gradient reaches the critical value H, *i.e.*, stress is produced equal to the ultimate strength of the material, the brittle fracture initiating the reaction occurs.

It seems possible that mechanochemical explosions of solids and autowave propagation of their chemical conversions can play a certain role under cosmic conditions as well, resulting in the formation of various products in bodies undergoing fragile destruction in various collisions.

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