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FEATURE ARTICLE

Nontraditional Pathways of Extraterrestrial Formation of Prebiotic Matter

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Mechanisms of solid-phase reactions were investigated experimentally and theoretically during recent decades that can have direct connections to the formation of organic substances in space and their delivery to Earth and to the problems of prebiotic evolution. Among such 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, and mechanochemical explosions and autowave propagation of chemical reactions due to the positive feedback between the fragile destruction of solids and reactions at freshly formed surfaces.

Introduction

Roughly 40 000 tons of extraterrestrial organic (virtually prebiotic) matter—initially in the form of interplanetary and interstellar dust—is accreted now annually on Earth.[1,2] This means that if the rate of such accretion during the lifetime of Earth's solid crust (4 billion years) would be constant, then the thickness of the organic layer of extraterrestrial origin at the surface of our planet would correspond to ca. 1 ton m^{-2}. However, the comparison of the accumulation of ^{3}He solar ions released into interplanetary dust between 0.2 and 0.7 million years ago[3,4] suggests that we are currently in an era of increased (by factor of 6−10) dust flux, and therefore the above mentioned average thickness of delivered organic layer can strongly decrease. Therefore the total amount of extraterrestrial organics accumulated at the land of the Earth (ca. 1.5×10^{18} cm^2) can be considerably lower, a few trillion tons.

Nevertheless, it would still mean that the organic matter on our planet has its main origins in interplanetary, or perhaps interstellar, space.[5]

General characteristics of interplanetary (IPD) and interstellar (ISD) dust are described in detail in numerous surveys (see, for example, refs 6−8), and therefore it is scarcely needed to repeat them here. The IPD particles have been proposed as the proper vehicles for carrying potential organic matter to primordial Earth's surface.[9] The most common IPD particles are collected from the stratosphere; they are fine-grained (10 μm to 1 mm) black materials, porous and fluffy, similar to carbonaceous chondrites, i.e. primitive meteorites. IPD particles contain rather complex organic molecules, e.g. polycyclic aromatic hydrocarbons (composed of two or more six-carbon rings) and their alkylated (hydrocarbon-chain-containing) derivatives. A typical feature of IPD particles is their large enrichment of deuterium and ^{15}N relative to terrestrial values.

Since the IPD particles accreted on Earth must first enter the atmosphere with rather high velocity (above 11.2 km/s), their kinetic energies are capable of melting or vaporizing the incoming particles if the energies are converted to internal heat. Estimations of temperatures of IPD particles of different sizes are given in ref 7; typical 10 μm particles are not heated above 600 °C.

Although there is a strong link between IPD and ISD—both populated the early Earth with compounds that could play important roles in the origin of life on our planet—the distinctions between their properties are really drastic. As is well-known, the most abundant element in the universe is hydrogen. The cosmic abundance of helium (relative to hydrogen) is 0.09, followed by oxygen (7×10^{-4}), carbon (3×10^{-4}), nitrogen (9×10^{-5}), magnesium, silicon, and iron ($\sim 10^{-4}$ altogether).

Among several scores of interstellar molecules detected by radio and optical spectroscopy, the most widespread apart from H_2 are CO ($\sim 10^{-4}$), NH_3, HCN, and HNC ($\sim 10^{-6}$). There is no doubt that water, methane, and ethane are also well represented in interstellar space, and one should also mention formaldehyde ($\sim 10^{-8}$), whose low-temperature polymerization was directly observed in the laboratory[10] and served as a first evidence of quantum molecular tunneling.

The total ISD amounts to only about 1.0% of the mass of interstellar gas and $\sim 10^{-4}$ the whole galactic mass ($M_{\text{stars}} \approx 10^{11}$ M$_\odot$, $M_{\text{gas}} \approx 10^9$ M$_\odot$, $M_{\text{ISD}} \approx 10^7$ M$_\odot$). Dust grains are generally assumed to consist of central "cores" ($r \gtrsim 10^{-6}$ cm) of silicates or graphite surrounded by mantles of "dirty ice" ($r \approx 10^{-5}$ cm) formed by a mixture of the above mentioned frozen substances.

The average number of hydrogen atoms per dust grain is 10^{12}. There are distinguished diffuse ($n_{\text{H}} \approx 10-10^3$ cm^{-3}) and dense or dark ($n_{\text{H,H}_2} \approx 10^3-10^7$ cm^{-3}) clouds: the former are transparent to UV radiation which causes ionization of atoms and dissociation of molecules, while dense clouds are opaque to UV radiation. Therefore, photodissociation does not proceed in the depths of dark clouds, and a much wider variety of complex, polyatomic molecules are present here. This is why dark clouds are also referred to as molecular clouds. What is the temperature of the ISD grains in these clouds? Such low values as 10 K are ruled out by recent direct observations, and a "typical temperature" of 18−19 K seems to be a proper choice.

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There is a strong link between IPD and ISD. Both have populated the early Earth with compounds that could play important roles in the origin of life on our planet.[7]

Hypotheses concerning possible mechanisms of extraterrestrial formation of organic species (e.g. their formation in extremely cold interstellar clouds) are often based on the admittance of the decisive role of ion−molecule reactions since they are known to proceed with zero activation energy in the gas phase. However, the absence of an activation barrier in ion−molecule reactions in solids can by no means be considered firmly proven as their general property, and radiation-induced ionic polymerization of formaldehyde[10] serves here as one of the convincing examples.

With the decrease of temperature from 140 to 4 K the activation energy of the ionic growth of the polymer chain $\sim\!\sim CH^+{-}O\colon + CH_2{=}O \rightarrow \sim\!\sim CH_2{-}O{-}CH^+{-}O\colon^-$ gradually diminishes and reaches zero value (low-temperature limit of the chemical reaction rate) below ca. 12 K. However, at 140 K this activation energy is reasonably high, $E \approx 0.1$ eV, and by no means can explain the absence of temperature dependence of the rate of polymerization.

Obviously further detailed investigations are needed, particularly under the conditions that imitate the formation of "dirty ice" mantles of interstellar dust grains. Anyway it is worthwhile to discuss numerous possible connections between contemporary experimental and theoretical studies of various solid-phase processes and the problems of astrochemistry and—to some extent—also exobiology.

This article is devoted just to the extraterrestrial sources of organic matter on our planet, in other words, to different pathways of the "cold prehistory of life"[10] and to the revival of the Arrhenius concept of "panspermia".[11,12] It treats various mechanisms of extraterrestrial formation of rather complex organic substances as well as their delivery to Earth.

Molecular Tunneling and the Hypothesis of the Cold Prehistory of Life

Two main classes of scenarios of the origin of life on Earth have been suggested. First is the so-called warm, terrestrial scenario ("standard model") of Oparin[13] and Haldane.[14] After the classical experiments of Urey,[15] Miller,[16,17] and their followers, which demonstrated the formation of some prebiotic substances (e.g. amino acids and nucleotide bases) in gaseous mixtures imitating the early (according to their views, reduced) atmosphere of Earth (H_2, NH_3, CH_4, H_2O, etc.) via the so-called primeval (primordial) "soup", which contained a broad assortment of ingredients necessary to form long polymers able to self-replicate, mutate, and evolve, the attention of researchers was for a long time focused exclusively on the warm scenario.

However, later investigations led to significant changes of the views concerning the early atmosphere: a reduced primordial atmosphere is now considered unlikely, and slightly reduced or even oxidized states (N_2, CO, CO_2, H_2O, minor amounts of O_2, etc.) are treated as much more probable.[18−22]

Besides the gas-phase or liquid-phase mechanisms of the formation of prebiotic substances there were considered also various mineral heterogeneous pathways.[23−25] However now we would like to call attention to the cold scenario of the origin of life.

Revival of the interest in 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 nonvanishing and temperature independent chemical reactivity even near absolute zero, explained as the manifestation of quantum mechanical molecular tunneling.[10]

As was emphasized in ref 10, "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[6,26,27] we have analyzed in detail possible mechanisms of formation of polyformaldehyde in the "dirty ice" mantles of interstellar dust grains and the 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[10] and their comparison with the estimation made for Arrhenius-type and tunneling kinetics[6] led to the obvious conclusion that the formation of polyformaldehyde in interstellar dust could proceed only via tunneling.

For such an estimation one should take into account the 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. Also to be taken into account are our kinetical data: the time of the addition of a new link to the growing polymer chain at the plateau ($T \lesssim 12$ K) $\tau_0 \approx 10^{-2}$ s, length of the polymer chain at such temperatures $\nu \approx 10^3$, activation energy of the growth of chains in the Arrhenius region (up to 140 K) $E \approx 0.1$ eV.

The fulfillment of the demand $(\tau_0)_{Arrh}\nu \ll \tau_{uv}/\nu$ (preexponential factor for the growth of a polymer chain is taken as 10^{14} s^{-1}) necessitates $T > 30$ K; the demand $(\tau_0)_{Arrh} \ll \tau_{cl}/\nu$ corresponds to the softer inequality $T > 20$ K. Both values of minimal necessary temperature lie above the temperature of interstellar clouds ($\lesssim$20 K).

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

Meanwhile the use of the simplest Gamov-type formula for the estimation of the tunneling rate, $(\tau_0)_{tunn} = 10^{-14} \exp(\pi\sqrt{2}d\sqrt{mE}/2\hbar)$, where d is the width of the barrier and $m(CH_2O) = 28$ amu, leads to the inequalities $d < 0.65$ Å (when τ_{uv} is used) or $d < 0.90{-}0.95$ Å (when τ_{cl} is used). Such values of the distance of tunneling seem to be quite reasonable and give a strong argument in favor of the tunneling mechanism for the formation of polyoxymethylene in cosmic dust, in accordance with the views expressed in refs 6, 10, 26, and 27.

Thus, tunneling could significantly increase the number of possible low-temperature reactions in dark clouds. One case would be, for example, 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_2O, 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 purimidines); 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 widths and masses. However, each single step of chemical conversion which represents an elementary gas-phase process (such as the reaction $H_2O{=}C + NH_3 \rightarrow H_2C{=}NH + H_2O$) 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 the release of recombination energy at the grain surface, can induce the transfer of the “driving” particle, such as an 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; they 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 the formation of acetic acid, urea, and certainly also the products of their exothermic polycondensation.[28] As gravitational instability develops in the dark dust–gas cloud, a differentiation of matter occurs, and a protostar forms. Planetesimals accrete from the dust–gas disc forming around the star and enlarge to planets together with the formation of meteorites and comets. Consequently, the organic compounds that had formed in the dust–gas cloud can reach the planet by two processes: first, during the accretion of the planet; 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 that 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 various radiations of cosmic origin postulated in ref 10 was independently actively propagandized by Wickramasinghe and Hoyle,[29–33] whose publications were however widely disputed.[34–40] Starting with the claims that formaldehyde undergoes polymerization in interstellar space with the formation of polyoxymethylene and even of polysaccharides, these authors soon came to the hypothesis of “living interstellar clouds”[32] and even of the extraterrestrial origin of some viruses[33] invading Earth, e.g. the influenza virus in 1919. These speculations met various reasonable objections. Meanwhile, the presence of polyoxymethylene in space found recently supports (also not undisputable) the comparison of data obtained for the coma of comet Halley by heavy-ion analyzers aboard the Giotto spacecraft[41–43] and laboratory mass spectra and IR absorption spectra of formaldehyde polymerized at the surface of silicate grains under irradiation by protons at ca. 20 K. Molecular tunneling was mentioned in refs 41–43 as the most likely mechanism.

However, neither the warm terrestrial nor the cold extraterrestrial scenarios of the formation of complex organic molecules and prebiotic evolution—at least in the early stages of their 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 the bioorganic would (L-enantiomers of aminoacids in all proteins and D-enantiomers of sugars in RNA and DNA).

The absence of such attempts was particularly disappointing in contrast with the firm conviction expressed already in 1860 by the discoverer of dissymmetry, Louis Pasteur: “Homochirality is the demarcation line between living and non-living matter”.

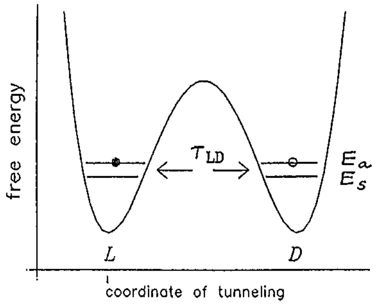

Figure 1. Tunneling between L and D states of chiral molecules. τ_{LD} is the average lifetime of the chiral state.

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 chirality, 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 recent publications[44–48] and briefly touch on connections between tunneling and chirality.

In accordance with the well-known Hund’s paradox[49] 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. can be located in L or D wells (see Figure 1)—neither of two wave functions, Ψ_L or Ψ_D, represents the system’s eigenstate. Tunneling leads to spontaneous $L \rightleftarrows D$ conversions; that is, 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, $\Psi_s = (1/\sqrt{2})(\Psi_L + \Psi_D)$, or antisymmetric, $\Psi_a = (1/\sqrt{2})(\Psi_L - \Psi_D)$, combinations of Ψ_L and Ψ_D. There is a certain difference between the energies of the two states E_a and E_s: $\Delta E_{as} = E_a - E_s$. The characteristic frequency of tunneling $L \rightleftarrows D$ oscillations equals $\omega_{LD} = \tau_{LD}{}^{-1} = \Delta E_{as}/2\pi\hbar$. (Stationary states of a nonlinear Schrödinger equation[50,51] need not be eigenfunctions of the operators corresponding to the symmetry group of the potential. When the nonlinearity parameter approaches ΔE_{as}, a rather sharp transition from definite parity to definite chirality takes place, i.e. permanent localization in one of the wells.) Under such conditions it is senseless to speak about a certain sign of chirality of optically active molecules, i.e. about the property that is intrinsic to 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 $t \gg \tau_{LD}$ 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; that is, the system of isomers racemizes itself over a time $t \gg \tau_{LD}$. Racemization processes prevent a breaking of mirror symmetry—a 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 effectively countering the tendency toward racemization.

Such counterracemization factors appear indeed in a cold scenario. It has been shown[52–55] 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 interactions of the isomer with the molecules of the medium have the consequence that the chiral particle behaves as a damped rather than free oscillator. Consequently, although racemization does occur, the time scale for the process

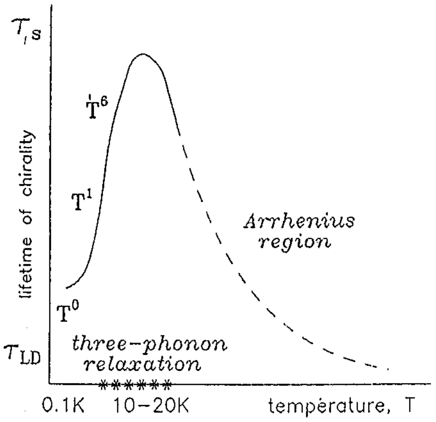

Figure 2. Stabilization of chirality in low-temperature solids ($\tau_s \gg \tau_{LD}$).

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 apparently in a racemic state. Therefore, it is quite important to analyze 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 (nondiagonal transitions) but also the transitions inside each of the two wells of the two-well potential (diagonal transitions).

Such analysis shows[56,57] that at very low temperatures 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 (Figure 2); and the most effective suppression of racemizing processes in molecular ensembles should be observed at $T \lesssim$ 20 K, i.e. just under the conditions typical for dirty ice mantles or interstellar dust grains.

Delivery of Organics to 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 is the view that life on Earth was nurtured by a rain of comets, that only comets, carbonaceous asteroids, and meteorites contributed large amounts of organic matter to the primitive Earth (e.g. refs 9 and 58–61).

Recently the view[62] was even expressed 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 an Earth almost devoid of carbon, of water and of all volatile and labile elements". Within the framework of such a view one of the most important questions is whether some impactors can bring prebiotic species intact to Earth. According to ref 63, 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 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,[64] and the hypothesis of the mechanism of their preservation was put forward in ref 65.

Most intriguing data were obtained by studies of the so-called Murchison meteorite, which fell in Australia in 1969 and belongs to a 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);[66] however, the question remained open whether this deviation from homochirality could be caused by terrestrial contamination or by diagenetic reactions occurring in space.

A subsequent combined study by Engel et al.[67] 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 30‰) and concluded that optically active (or rather, deracemized) compounds were present in the early solar system. This conclusion attracted wide interest and was commented on—inter alia—in refs 68 and 69. As was emphasized in ref 69, results of ref 67 support the view[44,45] 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 the partially deracemized state of amino acids observed in ref 67 represents an intermediate stage in the transition to a chirally pure state, the results can provide an indication of the time scale required for the mirror symmetry-breaking process.

Finally, in regard to the question of whether extraterrestrial amino acids can be delivered to Earth by a large impactor, it would be worthwhile to turn to the data on shock wave (SW) induced polymerization and polycondensation. A comprehensive survey of polymerization and modification of polymers under shock compression was presented recently by Gustov,[70] and it is almost complete.

Our studies of SW-induced conversions of solids started in the mid-1960s and were devoted to organic compounds. It was found that under rather rigorous conditions (pressure, temperature, deformation) there occur not the destruction processes but the molecular association.[71]

Eight monomers of different types were polymerized (trioxane, acrylamide, potassium acrylate, methylacrylamide, tolan, salicylaldehyde, stilbene, diphenylbutadiene), threshold amplitudes of plane SW-induced polymerization varied from 2 to 30 GPa, and yields of polymers ranged from traces (stilbene) to 60% (acrylamide above 10 GPa).[72,73]

The next step of our studies was the observation of SW-induced cross-linking for a number of rubbers,[74] e.g. polybutadiene.

However, most interesting for the problem of delivery of prebiotic and protobiotic substances to Earth became the observations of SW-induced polycondensation of amino acids. Shock loading of glycine or D,L-tyrosine mixed with the same (by weight) amount of dehydrating agent, silica gel, led to polypeptide formation.[75] More detailed were the studies of polycondensation of α-L-alanine under the action of shock waves.[76] Their results are presented in Table 1. 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 amplitude P = 12, 35, and 50 GPa at an initial temperature of 20 °C was conducted in steel plane capsules. After the

TABLE 1: Action of Shock Waves on a Mixture of α-L-Alanine and Silica Gel (1:1)

		alanine content in soluble fraction (% of initial)	
expt no.	*P* (GPa)	before hydrolysis	after hydrolysis
I	12	14.5	14.5
II	50	0.4	3.9
III	50	10.7	37.6
IV	35	2.3	17.3
V	50	0.9	6.4
VI	50	0.9	9.0
VII	50	2.9	6.0
control experiment 100, 135, 170, 200 °C; 20 min		100	

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, amino acid analysis, preparative paper 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[77] the formation of amino acids from ammonium salts of carboxylic acids under dynamic compression was observed.

Thus, the totality of data obtained in the 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 were performed by Greenberg.[78−80]

As is well-known, two mechanisms of thermal explosions of chemical systems were widely discussed: a genuine thermal explosion described by the classical theory of Semenov[81,82] and Frank-Kamenetskii[83,84] and the so-called "thermal-wave" (or "thermal-chain") explosions.[85−87]

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

The origin of thermal-wave explosions is quite different. The point of recombination of the radical pair serves as the center of the diverging spherical thermal wave. Such a wave throws other radicals out of traps occupied by them; these radicals in turn recombine and generate new thermal waves. Thus there appear peculiar energetic chains of recombination of radicals, which prevent under ordinary conditions the accumulation of radicals in concentrations above a few tenths of a percent, independent of the intensity of radical-generating radiation. Thermal-wave explosions can play a marked role only in considerably large samples, of the dimension $l > \sqrt{\chi t_r}$, where χ (cm^2 s^{-1}) is the heat diffusivity and t_r (s) is the characteristic time of the recombination of radicals, determined by their diffusion.[88,89] Thermal explosions should dominate in the samples of lesser dimensions, e.g. in the cosmic dust grains.

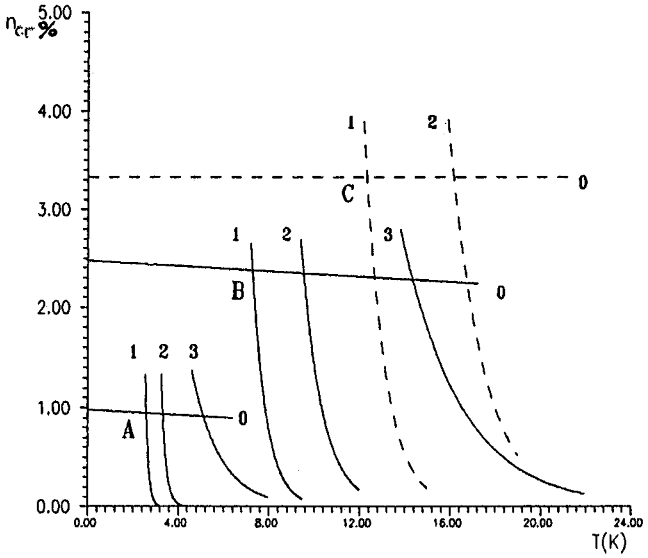

Figure 3. Temperature dependence of limiting concentrations of nitrogen atoms in nitrogen matrix, calculated for thermal-wave (0) and thermal (1, 2, 3) mechanisms of explosions. Effective activation energies of recombination (cal/mol) are (A) 200, (B) 600, (C) 1000. Dimensions of the system (cm) are (1) 1 (2) 10^{-2} (3) 10^{-4}.

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 the overcritical excess of radicals and a return to the steady-state level of their concentration; that is, there will appear peculiar oscillations.

The initiation of thermal explosions demands a jumpwise change of thermophysical properties of the system, e.g. strong pulse of heating or sharp decrease of heat conductivity. The first of these variants was realized in experiments of Greenberg,[78−80] who imitated under laboratory conditions the explosions of irradiated grains by the powerful heat pulses. The latter case was demonstrated[87] by the example of recombination of nitrogen atoms precipitated at the helium lining at temperatures below the λ-point ($T_\lambda = 2.19$ K), i.e. below the temperature of transition of helium into a superfluid state.

The concentration of N atoms under such conditions exceeded 1.6%, and most of the accumulated atoms recombined during the heating, just at the λ-point.

Computations[87] of the temperature dependence of limiting concentrations of N atoms vs temperature for thermal-wave and thermal explosions gave the results presented in Figure 3.

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

Comparison of experimental data[78−80,87] with theoretical considerations[87] give evidence that the observed explosions were indeed of thermal rather than of thermal-wave nature. A detailed analysis of the thermal regime that should be characteristic of interstellar dust grains under UV exposure of constant intensity was performed in our most recent article.[90]

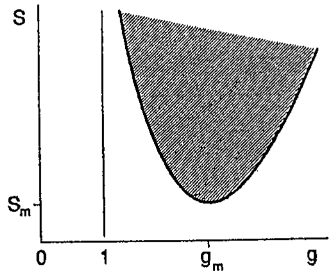

Figure 4. Plane of control parameters. Region of self-oscillations is shaded. Remainder of the plane corresponds to stationary regimes. When $g \ll 1$, each radical pair recombines before the next pair is generated by UV radiation. The opposite regime at $g \gg 1$ is similar to that of the stationary combustion. Intense generation is compensated for here by fast recombination (because of high temperature).

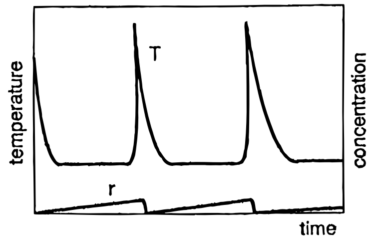

Figure 5. Schematic illustration of the oscillations of temperature (T) and radical concentration (r) in interstellar dust grains under UV exposure (T = 10−20 K).

Figure 4 represents the plane of dimensionless control parameters: g (proportional to the rate of generation of radicals by the UV radiation p, $\mathrm{cm^{-3}\ s^{-1}}$) and the Semenov number S (which characterizes the ratio of the scales for heat release and heat escape). The region of above mentioned oscillations is shaded; the rest of the plane corresponds to stationary regimes. The area to the right from g_m is the area of "stationary conbustion". The temperature of grains is high here, but the radical concentration is extremely small. Because of fast diffusion, the recombination immediately follows the radical production, and the energy of the absorbed photon transforms into heat and then escapes to space.

The case of oscillations of grains temperature T and radical concentration in grains r ($\mathrm{cm^{-3}}$) is illustrated by Figure 5. 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 $p \approx 10^{11}-10^{12}\ \mathrm{cm^{-3}\ s^{-1}}$), Semenov number $S \approx 10^5-10^6$, $T = 10-20$ K, the concentrations of radicals accumulated before the flash are $(0.3-1) \times 10^{19}\ \mathrm{cm^{-3}}$, and the duration of time between two subsequent flashes is $(6-1) \times 10^7$ s.

The number of radicals recombining in the grain of $\sim 10^{-5}$ cm diameter is $(0.3-1) \times 10^4$, which corresponds to a quite minor increase of temperature (~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 seem to be plausible events.

Mechanochemical Explosions and Autowave Propagation of Chemical Reactions in Cold Irradiated Solids

The peculiar phenomenon, explosion of a photolyzed solid mixture of reactants (methylcyclohexane (MCH) with chlorine) upon deep cooling, was observed in 1980 at the Moscow Institute of Chemical Physics.[91] The authors of ref 91 interpreted this phenomenon as the thermal explosion that occurred due to the appearance of internal thermoelastic tensions in the cooled system and corresponding decrease of activation energy of the investigated reaction. Soon afterward, another group[92] studied the same reaction in a glasslike system activated by ^{60}Co γ-radiation. The rates of cooling and defreezing of the MCH−$\mathrm{Cl_2}$ system between 4.2 K and 77 K were varied, and it was claimed that the initiation of the chain reaction of chlorination is caused by the formation of cracks in monolithic samples at the fast change of their temperature (see Figure 6). 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.

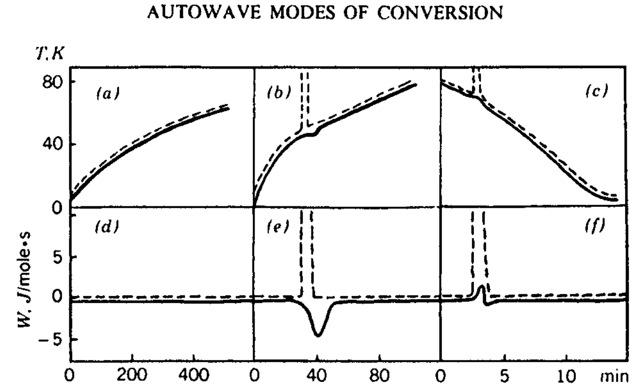

Figure 6. (a, b, c) Time dependence of the temperature of the sample ($\mathrm{Cl_2}$ + MCH, molar ratio 1:3) and (d, e, f) thermal effects: (solid lines) nonirradiated samples: (dashed lines) samples irradiated by ^{60}Co γ-rays at 77 K, dose 27 kGy.

Analogous results were obtained for the chlorination of other saturated hydrocarbons, for hydrobromination of ethylene, and for polymerization. A summary of experimental data and a detailed description of their theoretical treatment were presented in the surveys.[93,94]

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 that contain stabilized free radicals accumulated during preceding γ-irradiation.

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

The initial mechanical or thermal fracture produces a reaction outburst and an autowave propagation of the reaction front along the sample with a rate (1−4 cm $\mathrm{s^{-1}}$) much above that of heat transfer but much below the sound velocity. A typical example of this autowave propagation is illustrated by Figure 7.

The chain reaction of chlorination, $\mathrm{C_4H_9Cl + Cl_2}$, was triggered by mechanical impact: a slight turn of the thin metallic rod frozen in 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 basis of a positive feedback between the brittle fracture and chemical conversion of the samples. Formation of cracks in a monolithic sample initiates its chemical conversion at the fresh surfaces of cracks, and the 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:

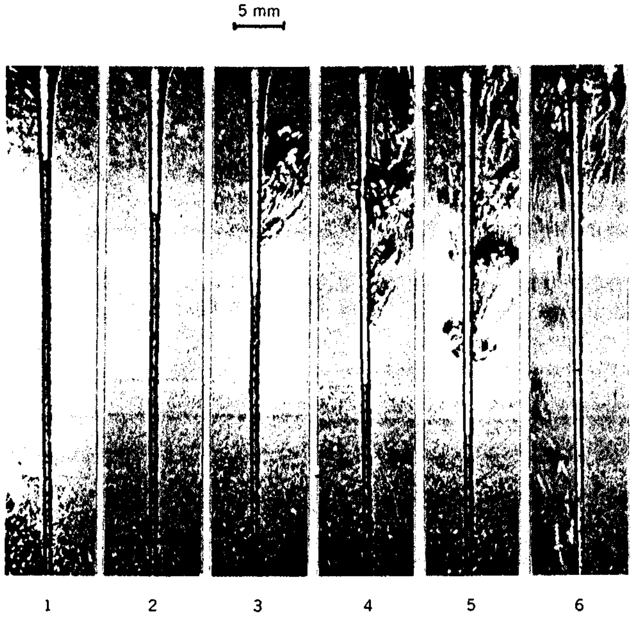

Figure 7. Cinegram of reaction front propagation ($Cl_2 + C_4H_9Cl$, molar ratio 1:3) in a capillary, diameter ~1 mm, at 4.2 K. Time intervals between frames 1 and 2, 0.14 s; 2 and 3, 0.06 s; 3 and 4, 0.14 s; 4 and 5, 5 and 6, 0.72 s. Dose of preceding ^{60}Co γ-irradiation is 45 kGy.

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

where S is the specific surface area per unit volume, $F(S)$ is the generation rate of active surfaces, 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 the form $F(S) \propto S^m$, where $m > 1$, will qualitatively correspond to the observed experimental facts.

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

$$\lambda\frac{d^2T}{dx^2} - \rho CU\frac{dT}{dx} + Qa = 0 \tag{2}$$

$$U\frac{da}{dx} = -\frac{a}{\tau} \tag{3}$$

where λ (cal cm^{-1} grad^{-1} s^{-1}) is the heat conductivity, x (cm) is the coordinate, ρ (g cm^{-3}) is the density of the solid mixture of reactants, C (cal grad^{-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 reaction heat release, a is the dimensionless concentration of reactants, and τ is the duration of the reaction (inverse rate constant).

The boundary conditions look like

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

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

$$\lambda H = \rho CU(T_r - T_0) \qquad T_r = |T|_{x=0}$$

Solution of equations 2 and 3 under the above boundary conditions leads to

$$H = \frac{T_{adiab} - T_0}{U\tau + \dfrac{\lambda}{\rho CU}} = \frac{Q\tau}{\rho C}\,\frac{1}{U\tau + \dfrac{\lambda}{\rho CU}} \tag{4}$$

The 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.[95] Brittle fracture that initiates the reaction occurs when the temperature gradient reaches its critical value H; that is, it produces the stress equal to the ultimate strength of the material.

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

Conclusion

Many different approaches were developed recently for the description of various mechanisms of solid-phase astrochemical extraterrestrial reactions in prebiotic evolution.

Particularly important turned out to be an alternative to the “warm”, “terrestrial” scenario of the origin of prebiotic life on Earth, based on the discovery of quantum molecular tunneling and the revival of the “panspermia” hypothesis of Svante Arrhenius. The famous “Hund’s paradox” formulated in 1927 and contrasting the eigenstates based on chirality and parity can be boldly defined as the first highlight of quantum chemistry. The year 1959 marked the introduction of the notion of crossover temperature—the borderline between temperature regions of classical and quantum chemical kinetics—and the prediction of a low-temperature limit of chemical reaction rate (experimentally discovered in 1973). Hundreds of original papers, surveys, and monographs devoted to the tunneling phenomena in chemical physics appeared during the last quarter of the century, and the concept of the “cold prehistory of life” became one of the most important in exobiology.

It should be emphasized here the paramount importance of the overlap of two crucial directions of astrocryochemistry and exobiology: the leading role of deep cosmic cold in the domination of tunneling and in the resistance against racemization. The extraordinary significance of chiral purity of the bioorganic world of Earth for the origin of life and prebiotic evolution is now absolutely doubtless, and the stimulating role of deep space cold in the preservation of such purity is of certain importance for the “cold prehistory of life”.

However even the combination of the problems of tunneling and chirality is still very far from completion of a wide assortment of pathways of extraterrestrial formation of prebiotic matter. Among the puzzles of enantiomeric and isotopic compositions of meteoritic substances delivered to Earth are the excesses of L-amino acids and ^{13}C in the Murchison meteorite.[66] Both these facts speak in favor of the existence of optically active (or rather, deracemized) compounds in the early solar system. If this partially deracemized state represents an intermediate stage in the transition to a chirally pure state, the results can provide an indication of the time scale required for the process of breaking of mirror symmetry in nature. According to ref 96, it could be as short as 10^6-10^7 years, whereas the whole prebiotic stage of Earth’s history lasted 200−500 million years.

In regards to the question of whether extraterrestrial amino acids can be delivered intact to Earth by a large impactor, we have demonstrated[76] that shock waves with amplitudes of as much as 50 GPa need not destroy amino acids but can instead initiate their condensation into oligopeptides. A broad range of explosive processes in solids plays an outstanding role in astrochemistry and exobiology, although many problems along this line still remain open. The similarities and distinctions between thermal and thermal-wave explosions are now certainly much more understandable than at the time of the appearance of the classical Semenov−Frank-Kamenetskii theory. It became clear—inter alia—that under the conditions of stationary irradiation of solid samples with accumulated active centers the steady-state but not the overcritical (explosive) concentration of radicals (or other active centers) can be reached. Only recently[90] it was quantitatively shown and analyzed in detail that the passage through the critical level of concentration of active centers will lead to peculiar oscillations of temperature and radical concentration in the cold interstellar dust grains under permanent UV exposure.

Thus we have considered and analyzed quite broad range of phenomena that are on the borderline between solid-phase astrochemistry and exobiology. Still many problems—although propounded in a qualitative or semiquantitative way—are awaiting further development. We saw that quite strong shock waves (35−50 GPa) don't destroy but, quite opposite, oligomerize various amino acids. However we were unable to compare our laboratory data with the masses and velocities of meteorites, asteroids, and other natural impactors. Therefore, we were deprived of the possibility of making any definite conclusion about the virtual role of various extraterrestrial impactors in the delivery of prebiotic substances to Earth.

Wide possibilities of the formation of various organic (even prebiotic) products seem to be opened by mechanochemical explosions and autowave propagation of chemical reactions discovered in our experiments.[92] However, to estimate quantitatively these possibilities, we must know the sizes of colliding dust particles, their relative velocity, the frequency of collisions, etc.

Thus, summarizing all experimental data and theoretical considerations presented in this article, we come to the following order of priority of the connections between the solid-phase astrophysical reactions and extraterrestrial formation of prebiotic matter: (1) cold prehistory of life, i.e. quantum low-temperature limit of chemical reaction rate, nonvanishing and temperature independent chemical reactivity even at the vicinity of absolute zero; (2) decrease of the racemization rate with the diminishing of temperature, particularly in the region of temperatures characteristic of the interstellar dust clouds; (3) oligomerization of amino acids with dehydrating admixtures (e.g. silicagel) by the impact of shock waves (threshold effect, $P > 35-50$ GPa); (4) Thermal and (or) thermal-wave explosions of organic samples with sufficiently large (overthreshold) concentrations of free radicals (or other active centers) due to the short powerful heat pulses or jumpwise change of thermophysical properties of the systetm (e.g. sharp decrease of heat conductivity); (5) oscillations of the radical concentration and the temperature of the small (IPD or ISD) grains as a function of periodical accumulation and consumption of active centers in the permanent field of UV (or other) radiation above and below the critical values; (6) mechanochemical explosions of irradiated glasslike solid samples and autowave propagation of the front of chemical reactions along these samples caused by the positive feedback between fragile destruction of solids and increased reactivity at the surfaces of fresh cracks.

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