ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 1, pp. 80–83. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © L.A. Gribov, 2007, published in Geokhimiya, 2007, No. 1, pp. 89–93.

SHORT COMMUNICATIONS

Some Principles in the Formation of Organic Matter during the Early Stages of Chemical Evolution

L. A. Gribov

*Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,
ul. Kosygina 19, Moscow, 119991 Russia*

Received January 25, 2006

DOI: 10.1134/S0016702907010077

Formulation of the problem. The origin of the diversity of organic compounds on the Earth, up to the development of processes that determine the possibility of life itself, is one of the most interesting problems in cognition of the world [1].

It is generally recognized that all vital processes proceed, so to say, in the world of molecules, which were, in turn, formed by the gradual complication of constituents of this world (molecular structures), beginning from protozoa.

It is hardly possible to trace in detail the entire evolution of the conditions leading to the formation of vitally important processes in the molecular world, but some of the most important concepts can hopefully be perceived based on the ab-initio principles, i.e., under the assumption that all processes are rooted in the fundamental natural laws, primarily, those formulated in physics.

In this paper, an attempt is made to reveal some general principles of the increasing complexity and diversity of the organic world is mode.

An important problem arising at the very beginning is why are all processes related to molecules? Which specific properties of objects of the molecular world finally provide the phenomenon of life?

An attempt to answer this question was made earlier [2–5].

First of all, attention must be given to the fact that any transformations of the objects of an ensemble are accompanied by information receiving and processing. No evolution is possible without them. In this respect, the molecular world offers unique possibilities.

It was shown that molecules can, first, “record” the input information and, second, their spontaneous or initiated transformations could be correlated with logical operations, which are anticipated by formal mathematical logics (Boolean algebra).

It was also found out that the treatment of input information could be a very complex process, up to the recognition of an image, i.e., reducing many factors to a single feature which occurs only when the whole set of the factors is present.

Crystalline objects have no aforementioned properties.

Important characteristics of the existence and evolution of the biological world are, on the one hand, determinism expressed in the emergence of a genetic code and, on the other hand, ambiguity providing adaptation to environmental changes.

From the mathematical viewpoint, the biosphere can evolve only if its constituents are able to treat information supplied as fuzzy sets. Therefore, one of the most important conclusions is that molecules are capable of processing this information to yield an invariable result.

All conclusions based on fundamental physical laws offer an unambiguous answer to the above question: why molecules?

Now we attempt to answer another important question based on the ab-initio principles: which mechanism generates the tremendous diversity of molecular objects required, at a fairly high complexity of their structures, to produce a new quality resulting in life.

To substantiate the further principal conclusions, let us briefly enunciate the key points of the modern theory (also developed by the author) of molecular processes, including chemical transformations [6, 7].

Physics of transitional states. According to the principle of short-range interactions, any chemical transformations (both mono- and bimolecular) proceed within a small volume that contains all atoms of a single molecular object (structural isomerization) or of a closely related pair (synthesis or decomposition). Any transformations of a system could be regarded as processes responsible for the transitions of the same atomic set from the initial to final states. Owing to these transitions, the initial geometrical configuration is replaced by another, which is stable with respect to isomerization reactions. A reaction of synthesis can be interpreted as the transition from the initial quasistationary state (when two nearby molecular objects “live” for a relatively long time and are, thus, described by stationary wave function) to the state of a stable united system (a new molecule).

During its decomposition reactions, the initial stationary system is transformed into a quasistationary one that is almost divided into two parts, which can later become separated in a space not limited by the free path length.

In any case, the atoms become rearranged. During structural isomerization, atoms in new positions seem to be strongly bound with one another.

Synthesis involves the substitution of the initial weak intermolecular bonds by stronger chemical bonds.

In contrast, the rearrangement of atoms during decomposition leads to the significant weakening of some chemical bonds and the appearance of a pair of weakly bound objects.

Within a single molecular system (a set of atoms within a limited volume), atoms are rearranged only during the excitation of high-amplitude vibrational movements, primarily, the highest overtones of normal vibrations. Therefore, observations obtained by the calculation of animation images of atomic shifts at normal vibrations with elevated amplitude could fairly exactly indicate which movements are able to lead to reconstructions, which simulate chemical transformations.

Chemical transformations themselves correspond to transitions from one stationary state to another. This corresponds to the maximum mixing between wave functions of the two subsystems, which is possible if the combined functions correspond to the energetically equivalent states of the subsystems, i.e., quantum resonance. If ψ_1 and ψ_2 are the stationary eigenfunctions of subsystems, then the common states resulting from resonance will have functions $\psi_{1,2} = \frac{1}{\sqrt{2}}(\psi_1 \pm \psi_2)$. Since the transition (tunnel) proceeds without change in energy, it can be referred to as radiation-free.

As was already mentioned above, chemical transformations can be interpreted as a change in the geometry of the same atom group. The finite movements of atoms in each state are possible only if they can be limited by the walls of the corresponding potential wells. Only in dense media, where infinite movements of microobjects are constrained by a length of free path, can the potential holes be ascribed to the first stages of decomposition or the final stage of synthesis. Note that the chemical equilibrium during decomposition can also be attained only in dense environments. Both the geometrical characteristics and the properties of the "wells" can be shown in a system of normal coordinates ($\mathbf{Q}_2$ and $\mathbf{Q}_1$ for combined states). The normal coordinates are suitable for the demonstration of both the geometrical characteristics of molecular objects (values of the equilibrium lengths of the bonds, the valence angle, and others) and the forms of the potential wells, which determine the localization area of the wave functions. The space of normal coordinates is multivariate. Each molecular transformation can be described by shifts showing the state of point objects in such a space. It is important that the normal coordinates of the second subsystem can be expressed through those of the first system using matrix proportions $\mathbf{Q}_2 = \mathbf{A}\mathbf{Q}_1 + \mathbf{b}$, where $\mathbf{Q}_1$ and $\mathbf{Q}_2$ are the corresponding matrix columns of normal coordinates, $\mathbf{A}$ is the square matrix of rotations and changes in the scales of the coordinates, and $\mathbf{b}$ is the vector (column) of shift of the minimums of potential wells of combined states and, hence, their localization areas.

The aforementioned requirement of resonance of subsystem states (levels) for the proceeding reaction is a necessary but not sufficient condition. For a reaction to take place, functions ψ_1 and ψ_2 must significantly overlap. If the shift of $\mathbf{b}$ is very large, such an overlapping will be too small for the reaction to proceed.

The possibility of structural transformation can be related to the overlapping integral of functions ψ_1 and ψ_2. This implies that the possibility of a reaction transition is proportional to a value of $\exp(-b^2)$, where b^2 is the square of the module of the normal coordinate shift. Thus, the reactions can be easily classified into rapid and slow.

It is important that slow reactions can proceed by many ways and have practically no limitations. This is very important for understanding geochemical processes, because it offers the possibility of taking into account low probable transformations.

Trend in the complication of the world of organic molecules during the early stages of its evolution. The formation of the world of organic molecules during early evolutionary stages attracts the keen attention of many researchers. A general consensus was reached concerning the transition from a spontaneous evolution driven by increasing entropy in closed systems to self-organization processes, which is possible only in open systems. In the latter case, a decrease in the entropy of one subsystem whose objects experience structural complication is accompanied by an advanced increase in the entropy of another subsystem related to the former.

However, in the context of the newly formulated conclusions about the course of chemical reactions, it seems to be useful to discuss, applying visual models, another problem. Since we refer to the formation of more complex molecular structures from a set of more simple ones, we can use the model of a closed system consisting of two interrelated subsystems. The phase space of the former contains molecules of the initial matter, while the second bears molecules formed owing to simple biomolecular synthesis. Let the molecules of the first type be denoted A and those of the second type be B. Assume that, at the initial time moment, there are only molecules of type A, and they are evenly distributed throughout the whole phase volume. Then, applying the cellular model, all cells N of this model will be occupied by molecules A. Then the extent of the degeneration of the macrostate of this subsystem will be equal to one, while the entropy (S) will be zero.

Let one reaction of synthesis take place $A + A = B$. Then, two "holes" are formed in the set of particles A in the same space, and "one" appears in the similar space of B molecules. The extent of degeneration for the subsystem with particles A will increase from unit to $\frac{N_1!}{2(N_1-2)!}$. Assuming $N = 100$, the extent of macrostate degeneration $G_1 = 4950$. The extent of degeneration for a subsystem with particles B, whose maximum number is $N_2 = \frac{N_1}{2} = 50$, also increases from 1 to 50. In all cases, the total entropy $S = S_1 + S_2 \sim \mathrm{In} G_1 + \mathrm{In} G_2$ will increase. The entropy will increase until the maximum of the extent of degradation is attained $G_{1\max} = \frac{N_1!}{[(N_1/2)!]^2}$ and $G_{2\max} = \frac{N_2!}{[(N_2/2)!]^2}$.

The question then arises as to whether the synthesis $A + A = B$ can proceed spontaneously, without external effect for real molecular objects. Evidently, if A is a molecule consisting of atoms H and C, only reaction $A + A = B + H_2$ is possible. As is known, the hydrogen content in the Earth's atmosphere is negligible. Hence, hydrogen released during this synthesis can be ignored. Furthermore, it has a zero (10^{-8}) vibrational entropy (see below).

It is pertinent here to recall the conclusion formulated above that all conceivable reactions can be subdivided into rapid, which are characterized by limiting rules, and slow, onto which these rules exert no significant effect. This indicates that, first, at slow chemical reactions, the reactions of the second type could be predominant during slow geochemical processes, giving a wider diversity of products. The latter condition is required for the further choice to reveal a new quality: determinism.

Let us consider the physics of this process using an illustrative example of a simple model.

Assume that the initial subsystem completely consists of CH_4 molecules. Then, $CH_4 + CH_4 = C_2H_6 + H_2$. This reaction is highly improbable but is known to proceed at temperatures that are, although high, still insufficient to decompose CH_4 molecules. The process also requires a high-density environment, i.e., a high pressure. The accumulation of ethane molecules should be terminated when the limiting values of the degradation $G_{1\max}$ and $G_{2\max}$ are attained, after which the total entropy starts to decrease, forbidding the further evolution of processes in isolated systems.

Let us now take into consideration the vibrational component of the set of CH_4 and C_2H_6 molecules. For gas moles, they equal, respectively, 0.355 and 2.8656 J/(K mol). It is seen that an increase in the entropy during C_2H_6 formation will be four times higher than its decrease during the decomposition of two CH_4 molecules.

Such a drastic change in the vibrational entropy (internal) can be readily understood, given the appearance of the C–C bond formed by heavy atoms in the C_2H_6 molecule, which leads to the appearance of normal vibration with a significantly lower frequency compared to the lowest frequency in a methane molecule.

Remember that the vibrational entropy is calculated by the formula

$$S = -R\sum_i g_i \ln\left[1 - \exp\left(-\frac{hc}{kT}w_i\right)\right] + R\frac{hc}{kT}\sum_i \frac{g_i w_i \exp(-hc/kTw_i)}{1 - \exp(-hc/kTw_i)}.$$

Here w_i is the frequency of vibrations (cm^{-1}); g_i is the extent of degradation (occupancy) of level; R, k, h, and c are the gas and other constants (generally accepted abbreviations). An increase in total entropy (including the vibrational one) will shift the equilibrium towards a greater number of more complex molecules C_2H_6, because the source material (CH_4) is still not completely exhausted.

Imagine that the process is more complex and involves the following reactions:

$$CH_4 + C_2H_6 = C_3H_8 + H_2,$$
$$CH_4 + C_3H_8 = C_4H_{10} + H_2,$$
$$CH_4 + C_4H_{10} = C_5H_{12} + H_2,$$
$$CH_4 + C_5H_{12} = C_6H_{14} + H_2,$$

and so on. With the transition from the reaction of ethane formation from a pair of methane molecules to other reactions listed above, the values of the relative changes in the vibrational entropy will be as follows: 4.028, 3.2, 1.88, 1.57, 1.37. It is seen that the vibrational energy decreases with increasing complexity of the formed molecules. In the extreme case, the entropy ratio for two adjacent steps decreases and tends to one. This means that the "entropic limit" in the consideration of the vibrational constituent will shift toward a greater number of molecules more complex than CH_4 and C_2H_6 and will not completely disappear, preventing complete exhaustion of initial "building" material (the set of CH_4 molecules).

The example considered above may seem to be oversimplified . However, we should not forget that the formation of the organic world was driven by the synthesis of more complex structures from the simplest molecular objects. In any event, the formation of the carbon "skeletons" of molecules must lead to the appearance of low-frequency normal vibrations, which significantly increase the contribution of the vibrational constituent to the total entropy of the ensemble.

An increase in the entropy can also be facilitated by structural isomerization (the numbers of isomers of even small molecules reach hundreds of thousands) and the decomposition of complex compounds into constituents, for example, paraffins with shorter molecular chains and olefins with double bonds: $C_9H_{19} \longrightarrow C_5H_{11} + C_4H_8$. Such reactions increase the diversity of the system, and hence, the total extent of degradation in a set of subsystems. It is very important that the decomposition reaction considered above does not require any additional external volume. Although the variations in the total entropy cannot be calculated with regard for the diversity of the arising structures, fundamental considerations suggest that a spontaneous process should terminate upon attaining chemical equilibrium, i.e., the Boltzmann distribution of the occupancy of levels (in all subsystems potentially arising in the system). This corresponds to the maximum value of the total entropy but not to the maximally organized structure. One can assume that all building material from CH_4 molecules was incorporated into a long paraffin chain. As was shown above, beginning at a certain level, an increase in the length of such a chain will not cause an increase in the vibrational entropy. The ordering entropy (related to the filling of the cells of the phase volume) will tend to zero. This indicates that the appearance of extremely highly organized structures in a closed system is impossible, because their formation consumes the bulk of the initial building material, which is not replenished.

The examples described above suggest that no energy is spent on the reactions of synthesis, isomerization, and decomposition. This seems to involve a contradiction, because the possibility of the aforementioned reactions is controlled by external effects, which are not considered here. This contradiction can be reconciled when we consider all of the above conclusions concerning the course of chemical reactions, which were obtained in the theory of chemical transformations. According to the aforesaid, for example, the reaction $CH_4 + CH_4 = C_2H_6 + H_2$ is always possible, and it makes sense only to discuss its probability. At low temperatures, the rate of this reaction can be negligible, leading to the generally accepted conclusions about its impossibility without external effect (an increase in the ambient temperature). If this probability (and, hence, rates) is very small, then common chemical sense suggests this reaction is forbidden. However, this does not necessarily mean that the concentrations of the reaction product cannot significantly increase over thousands of years. Such periods are not long for geochemical processes.

Thus, the considerations presented above show that the initial complication stage of the molecular world can also occur in closed systems without disturbance of the second principle of thermodynamics and the law of increasing entropy.

Progressive complications in a closed system are terminated upon the significant exhaustion of the initial building material (simplest molecules). Further complication of objects is possible already only in open systems, i.e., at active interaction with the environment. If the formation of structurally complex molecular objects is referred to as self-organization, this process is possible only after the first accumulation stage of large molecules, which can be referred to as thermodynamic or entropic.

The problems of the main factors that control the possibility of self-organization will be discussed in further publications.

REFERENCES

1. E. M. Galimov, *Phenomenon of Life: Between Equilibrium and Non-Linearity. Origin and Principles of Evolution* (Editorial URSS, Moscow, 2001) [in Russian].
2. L. A. Gribov, "On the Problems of Directed Transmission of Signals and Energy in the Molecular Systems," Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 213–219 (2002).
3. L. A. Gribov, "Molecules as Information Receiving–Processing Systems," Vestn. RAN **72** (7), 611–617 (2002).
4. L. A. Gribov, "Principles of Information Receiving and Processing by Molecular Systems," Zh. Fiz. Khimii **78** (1), 123–132 (2004).
5. L. A. Gribov, "Some General Relations and Tendencies in the Recognition of Images by Complex Molecular Systems," Zh. Fiz. Khim. **78** (2), 295–299 (2004).
6. L. A. Gribov, *From the Theory of Spectra to the Theory of Chemical Transformations* (Editorial URSS, Moscow, 2001) [in Russian].
7. L. A. Gribov and V. I. Baranov, *Theory and Methods of Calibration of Molecular Processes* (URSS, Moscow, 2006) [in Russian].