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OVER THE POSSIBLE ROLE OF METAL ATOM CLUSTERS IN COSMOCHEMISTRY AND IN THE ORIGIN OF LIFE

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ABSTRACT

We present here the hypothesis of a possible relationship between metal atom clusters and the formation of organic molecules in the interstellar medium and on small bodies as a possible pathway to the origin of such molecules.

Two distinct stages are discussed: a) the possible formation and presence of atom clusters in space and on the primitive Earth, and b) the synthesis of interstellar and terrestrial prebiotic organic molecules, a process in which metal clusters could be the active catalysts.

The confirmation of these suggestions might be very important in order to explain the presence of extra-terrestrial organic molecules in the interstellar medium, small bodies and planetary systems, and therefore would have great relevance in cosmochemistry and in the current theories about the origins of life.

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INTRODUCTION

During the past years a large number of interstellar organic molecules have been observed by means of visible, ultraviolet, infrared and radioastronomical techniques (see Appendix, Table of Interstellar Ions and Molecules). Most of these species can be categorized as organic or carbon containing [1]; many of these molecules are important intermediates in prebiotic reactions, paticularly hydrogen cyanide, cyanoacetylene and formaldehyde [2]. These organic molecules may have been synthetized on interstellar dust grains, small bodies and planets.

Mechanisms for the synthesis of such organic molecules in the interstellar medium have been postulated based upon the available chemical data, and compared with observational results [3,4,5,6]. Experimental work has also been carried out on this subject [7,8,9].

In order to explain the synthesis of interstellar organic molecules we present here the hypothesis of the relationship between the existence of atom clusters in the interstellar medium, species which consist of tiny aggregates comprising from two to several hundred atoms that exist in a solid state, and their possible catalytic role in the formation of relatively complex organic molecules in space and other cosmic environments.

The following stages will be discussed in this paper:

— the possible formation and presence of metal atom clusters in space,
— the synthesis of interstellar organic molecules with metal clusters as catalysts,
— the formation and presence of clusters on the primitive Earth, and
— the possible role of clusters in the prebiotic chemistry on the primigenial Earth.

ATOM CLUSTERS

The word cluster has been applied to aggregates of atoms as well as to compounds comprising a core of atoms arranged in a definite geometric pattern surrounded by a number of ligands. Among the first type we should distinguish the microclusters, comprising from two to several hundred atoms [10], and large clusters, in which geometry is not a ruling factor anymore; among the second type we find the relatively new organometallic clusters, prepared mainly in the last two decades, which consist of a central array of several metal atoms (not necessarily all identical) linked to each other and to the ligands in the periphery (commonly CO).

We shall use the word "microcluster" for relatively small naked clusters, that is, up to a hundred atoms and without ligands, and "cluster compounds" for those surrounded by a coordinated ligand sphere.

The study of clusters is very interesting because they are polyfunctional species; all metal-metal and metal-ligand bonds are potential sites of reaction. Selective reactions are unlikely to be achieved without the use of protecting groups [11]; for example, transition metal cluster compounds offer the prospect of a new class of selective catalysts by virtue of the proximity of multiple reaction sites on the faces or edges of the cluster [12].

MATTER IN THE INTERSTELLAR MEDIUM

The distribution of matter in the interstellar medium is extremely tenuous, accounting for about 10% of the material in our Galaxy; this matter comprises gas and dust and accumulates in clouds, these being therefore not homogeneous; it is currently assumed that about 1% of the cloud material is dust [13].

Two types of interstellar clouds are usually distinguished, according to their physical properties and chemical constitution:

a. diffuse clouds, characterized by high temperatures (ca. 100 K) and low density (1-100 particle.cm-3),
b. dark clouds, characterized by low temperatures (ca. 10K) and high density (100-107 particle.cm-3).

In the latter type we find, among the gases, hydrogen molecules (from the combination of hydrogen atoms), and more complex molecules as well, which can exist here because of the lower temperatures and the opaqueness of these clouds to starlight. Therefore, dark clouds have been the main source of the majority of the interstellar molecules discovered up to now [13]. Interestingly, in the truly remarkable wide range of molecular species detected, carbon monoxide, CO, is the most abundant, though still taking up less than 10% of the available carbon [14].

The solids in a cloud constitute the interstellar dust grains, tiny frozen particles formed by the heavier elements generated by thermonuclear fusion in stars and supernovas. The most abundant of these elements are oxygen, carbon and nitrogen (known collectively as the organics), followed by neon (which is totally inert), iron, silicon and magnesium [15]. The interstellar grains are formed chiefly by these six condensable elements, along with the hydrogen they capture.

At this point we would like to stress the following observation: silicon and magnesium, and especially their oxides, are amongst the best catalytic support systems known in terrestrial chemistry; iron, as the metal or in the form of clusters and organometallic compounds, is one of the most catalytically active elements known for the formation of complex organic molecules out of simple ones, like hydrogen, CO, HCN and others (i.e. the Fischer-Tropsch process). Therefore, these six condensable elements and hydrogen represent a complete chemical processing plant of "advanced" catalytic technology!

Unfortunately, the study of interstellar grains is hampered by the inaccessibility of the material; no specimens in their pristine state have been gathered for laboratory examination, and the only direct source of information is the electromagnetic radiation from stars after it has passed through regions of the sky which contain interstellar grains [15]. Cosmic dust and micrometeorites depositing on the Earth (notably in Antarctica [16]) have passed through an oxidyzing atmosphere at high temperatures, so that any metal present as such would inmediately react to yield the corresponding oxide. Particles collected in the stratosphere are subject to the same denaturing conditions; interestingly, however, these particles do contain a relatively large amount of iron-nickel sulfides [17]; others contain, besides iron and nickel, also copper, chromium, zinc, titanium and other metals [18], thus confirming that interplanetary dust contains a significant amount of some transition metals.

Lately, another method of study has provided valuable insight in this matter: laboratory experiments simulating the interaction of gases, solids and radiation in interstellar space [15]. From both these methods of study it has emerged that interstellar grains possess a remarkable complexity: they certainly are not mere inert amorphous particles of cosmic dust, but have a distinct internal structure, with a core made up chiefly of silicates and a mantle of more volatile organics; this mantle is the site of elaborated chemical processes [15].

If the grain is present in a diffuse cloud of interstellar gas, the mantle consists of relatively non-volatile organic compounds of higher molecular weight. Grains in denser clouds are believed to be coated with volatile inorganic and organic compounds, like water, methane, ammonia, carbon monoxide and dioxide, etc., along with the higher molecular weight organics [19].

Smalley et al. [20] have suggested that a microcluster holding 60 carbon atoms in a cage of hexagons and pentagons ressembling a soccer ball (the currently much-studied buckminsterfullerene or "bucky-ball") may be the interstellar dust particle responsible for the absorption of radiation which causes a gap in the observed ultraviolet spectrum [10]. We believe that the presence of microclusters-not only those formed by carbon atoms-in the interstellar medium may be significantly widespread. We particularly suggest that metal atom clusters (microclusters and cluster compounds) may easily be formed under prevalent cosmic conditions and, moreover, that they may be playing an important calytical role in the formation of organic molecules in space.

Greenberg et al. [14,15] have stated that a grain of interstellar dust, assumed to be in the form of an elongated silicate particle of ca. 0,05 um radius, for example, can be formed in the atmosphere of cool evolved stars and then be blown out by radiation pressure into the surrounding space, ultimately to be swept up into the general gaseous matter and, being coupled to the gas atoms and ions, to begin to partake in the evolution of the clouds. Cooled to 10 K or so, these grains are the seeds on which atoms and molecules of the gas condense with molecular clouds to form mantles of organic matter, by means of photolysis by the ultraviolet radiation from distant stars [19].

Let us first assume-and we believe this to be possible-that Greenberg's model of the birth of a dust grain is essentially correct. Since all elements have been detected in the atmospheres of stars, as atoms, vapors or ions [21], it does not seem unreasonable to imagine that some of these atoms will attach themselves to the surface of the newly formed grain, and that these can eventually aggregate to build small clusters. Initially deposited metal can grow in two or three dimensions on surfaces depending on the energy of interaction between the surface and the metal [22]. Thus, we may expect that these condensed metal atoms may form microclusters on the surface or in the pores of dust grains.

Second, extending Smalley's suggestion that the carbon microcluster may in itself be a particle of interstellar dust [20], we suggest that this idea be not restricted to carbon clusters, but that microclusters, homo-or heteronuclear, of all elements may exist among the particles of interstellar dust. Such clusters might be all-metallic or carbon-metallic (many examples are now known among cluster compounds in organometallic chemistry), or, in general, non- metal-metallic. Their origin would be the same as that of the dust grain, that is, they would be formed in the cooler portions of stellar atmospheres and be blown out by radiation pressure into space.

Assuming that atom clusters are formed, as suggested above, as particles of interstellar dust and/or as species on the surface or in the pores of silicate dust grains, it is reasonable to expect that many of these clusters would be metallic in nature, mainly consisting of iron atoms; some of them might be iron-carbon clusters too.

It is now well known, especially from experiments in a relatively new synthetic technique of metal vaporization and co-condensation (now being used quite often in organometallic syntheses), that "naked" metal atoms and clusters are highly reactive, even at very low temperatures of ca. 10 K or so [23], towards simple inorganic and organic molecules, yielding in some cases complex compounds as products [24]. As another example, it can be mentioned that bare cationic iron clusters produced by sputtering in an FT-ICR mass spectrometer are capable of dehydrogenating ammonia and hydrazine [25].

Interestingly, the conditions for the technique of metal vaporization are not unlike interstellar conditions: in this technique, a heat source evaporates metal in a high vacuum (10^{-6} - 10^{-8} Torr), and the metal atoms and aggregates formed are allowed to react, either in the gas phase or, more often, after co-condensation on a very cold surface, with the desired ligand molecules (often simple ones like CO, amines, hydrocarbons, etc.). In our model, the heat source would be a star, and the atoms, aggregates of them and other particles blown out by radiation pressure would later enter very cold regions of space, where condensation would occur.

ATOM CLUSTERS IN INTERSTELLAR CHEMISTRY

Throughout most of the published work on the formation of organic molecules in the interstellar medium, the gas phase chemistry based on cation-molecule reactions induced by a high energy source (cosmic rays and the ultraviolet radiation from stars) is considered as the most probable mechanism; grain-catalyzed chemistry is largely neglected due to the difficulty of evaluating just how important it may be, for, as mentioned above, the constitution of dust grains is still uncertain. Nevertheless, we believe that grain-catalyzed chemistry is definitely important, especially in dense clouds where temperature is low (ca. 10 K) and sources of high-energy photons are scarce; only cosmic rays penetrate these clouds. And still, it is in these clouds where most of the complex organic molecules have been detected (vide supra).

Carbo et al. [13] have summarized a series of chemical mechanisms which may account for the formation of species in diffuse and dense clouds through gas-phase ion-molecule reactions. Diffuse clouds are easily penetrated by starlight, and this precludes the existence of complex molecules. Consequently, these cloud's chemistry is reduced to that involving atomic or simple species like H_2, OH, CO, CH, etc. Clusters of certain metals have a great ability to absorb light (photoreceptivity), due to the extreme density of their valence electrons, their high surface-to-volume ratio (which puts many electrons near the surface) and the ease with which their electron clouds can be distorted or polarized; they can often absorb more than one photon [10]. For this reason we believe that, should metal clusters be present in diffuse clouds, starlight radiation would cause their activation and/or ionization and, in this manner, initiate chemical processes.

In dense clouds, opaque to ultraviolet radiation, photodissociation and photoionization are negligible; their only external energetic source is the cosmic rays, which are present throughout the whole Galaxy [13]. Thus, in our model, they would be responsible for the initial ionization step, forming a cluster cation; such species are highly reactive towards even very simple and inert molecules and would in this manner initiate reactions yielding complex molecules. Even ionic cluster compounds and under normal terrestrial chemistry conditions are very reactive towards simple molecules, a well known reaction is [26]:

$$Fe_4(CO)_{12}C^- + CO \longrightarrow [M]C{=}C{=}O \xrightarrow[MeOH]{} [M]C\text{-}C(O)Me^-$$

$Me = CH_3$, $[M] = Fe_4(CO)_{12}$

ATOM CLUSTERS, AS CATALYSTS, IN DUST GRAINS

J. Sinfelt [27] has explained very clearly how a catalytic process takes place; it is convenient to reproduce here some excerpts from his work.

"In a typical situation in heterogeneous catalysis a fluid phase (often a gas) flows through a bed of catalyst particles. One widely employed type of catalyst consists of particles of a porous material, known as a carrier, in which submicroscopic metal clusters are embedded... The material constituting the bulk of the particles is often an oxide such as alumina or silica containing a network of pores... The metal clusters reside on the walls of the pores and therefore must be smaller than the pores".

As the gas flows through the catalyst bed, reactant molecules diffuse into the pores of the particles and are adsorbed onto the surfaces of the metal clusters. In the chemisorption, or chemical adsorption, of a reactant molecule on a metal cluster, a chemical bond forms between the molecule and a surface site... The chemisorption process forms a surface compound.

The surface compound then undergoes chemical transformations on the clusters to yield molecules of a different chemical species, which are subsequently desorbed (the process of adsorption in reverse). The product molecules then diffuse out through the network of pores into the gas stream flowing through the empty space between the particles. The desorption of a product molecule from the metal cluster releases a site for further participation in the reaction. The composition of the gas stream changes in its passage through the catalyst bed as the gas is depleted of molecules of reactant and enriched in molecules of product".

We suggest that this process may be quite analogous to that which may take place in a grain of interstellar dust containing metal clusters. The silicate would be the carrier, the cluster the catalyst, and interstellar gas the material for organic synthesis.

ATOM CLUSTERS AND ORIGINS OF LIFE

The emergence of life on Earth was the result of a long process of evolution, a process which started not from an organic source, but from the realm of the inorganic chemistry. The presence of the biochemical monomers (i.e. aminoacids, purines, pyrimidines, etc.) in the protocell and of the replicating structures (i.e. RNA and/or DNA) in the primitive organisms represents a much later stage of chemical evolution.

As in the interstellar medium, metal clusters may also have been present on the primigenial Earth, and they could have been deposited in the pores of siliceous materials (i.e. clays). Their formation could be due to the heating of material in volcanic eruptions, whence metallic material would have been vaporized in a non-oxidyzing atmosphere, but in a reducing one, thus forming atoms or aggregates of the metal. Such clusters, if embedded in siliceous material, may have been present in the atmosphere or on the surface of the Earth, and have acted as catalysts for the synthesis of complex molecules from simple ones, i.e. HCN, HCHO, etc. from H_2, CO, NH_3, etc. Reactants and products would have been in the gas phase, catalyst and carrier in the solid phase.

At least part of the products may have remained trapped in the pores of the siliceous material, and this would have protected them from destruction by ultraviolet radiation. Gradually, as the result of constant evaporation and precipitation of water, bodies of the liquid formed and the organic molecules synthetized in the atmosphere and on the surface were carried and dissolved in them. Very slowly, more and more complex molecules appeared in these waters, until microsystems were formed, comparable, in a certain way, to a protocell. Such microsystems must have possessed a permeable membrane towards ions and simple molecules, as well as internal compartments where chemical processes could have taken place.

On the other hand, the siliceous material in the solid-liquid interphase might have been dissolved and the clusters contained in it encapsulated in the microsystems. Since the membranes of these were permeable for simple molecules, catalytic processes may have occurred in the interior of the microsystems, thus enriching their internal medium, be it for the gradual replacement of their primigenial structures or as substrate for subsequent reactions; any excess was eliminated to the external medium. This stage could be described as a very primitive type of metabolism.

Depending on the type of clusters present in the microsystems, different catalytic reactions may have taken place; some microsystems contained clusters which catalyzed only simple reactions; others, perhaps contained more sophisticated clusters (i.e. organometallic clusters) and these were responsible for the formation of complex molecular systems. It was in these last that a process of continual chemical evolution took place, thus initiating a natural selection mechanism. It is in this stage of evolution where, gradually, there occurs the transition from the inorganic to the organic, from the simple to the elaborated, from the elementary to the very complex.

It is also possible that the membrane of the microsystems would have permitted the entrance of the necessary species for the formation of more clusters, identical to their predecessors, the only difference between these and the former being in their origin, the latter arising from a purely chemical process, the former from a geochemical one. If more clusters were formed in the microsystems, they might have experimented some type of fragmentation or division, giving birth to others with the same characteristics; such a process would represent a very primitive method of (inorganic) transmission of information.

CONCLUSION

The formation of atom clusters and their presence in the interstellar medium are quite possible processes considering the available evidence up to this moment; these clusters would thus be present among the material comprising dust/gas interstellar clouds, where important synthetic reactions are taking place. Some of the atom clusters will be metallic in nature, and some of these will be found on the surface and in the pores of silicate dust particles. A metal atom cluster containing chiefly the transition metal iron, in combination with a carrier material such as silica or magnesia, constitutes an extremely active heterogeneous catalytic system for reactions between such simple gas molecules as hydrogen, carbon monoxide, and others, yielding much more complex molecules. Thus, many organic compounds detected in the interstellar medium, be it in clouds or in small bodies, could be the resultat least partially or in such locations where conditions are most favourable for such processes (i.e. dark interstellar clouds) -of low-temperature, low-energy heterogeneous catalytic reactions, occurring spontaneously thanks to the combined presence of the extremely active transition metal clusters, carrier material, and simple gas molecules in large quantities.

The confirmation (or contradiction) of this hypothesis requires a large experimental effort to be undertaken; specific research techniques and experiments will have to be designed and carried out in order to gain some concrete evidence about the possible role of clusters in interstellar chemistry. We believe that metal vaporization techniques will be of great help in research of this type, and the contribution of the insights gained from organometallic chemistry will undoubtedly be of great importance towards a better understanding of cosmochemistry and the origins of life.

APPENDIX : TABLE OF INTERSTELLAR IONS AND MOLECULES**

Type	Detection
SIMPLE INORGANIC MOLECULES	
CO	UV, IR, Radio
H_2	UV, IR
CS	Radio
H_2S	Radio
SO_2	Radio
SiO	Radio
SiS	Radio
H_2O	Radio
NH_3	Radio
HCL	Radio
SiH_4*	Radio
C_2H_4*	Radio
NaCl*	Radio
AlCl*	Radio
KCl*	Radio
AlF*	Radio
OCS	Radio
HYDROCARBONS	
CH_4*	Radio
HC_2	Radio
C_4H	Radio
HC_2CH_3	Radio
HC_2H	IR
AMINES AND DERIVATES	
CH_2NH	Radio
CH_3NH_2	Radio
NH_2CHO	Radio
HNCO	Radio
ACIDS AND DERIVATES	
CH_2=C=O	Radio
HCO_2H_2	Radio
HCO_2CH_3	Radio
ALCOHOLS	
CH_3OH	Radio
C_2H_5OH	Radio
NITRILES	
HCN	Radio
HNC	Radio
NH_2CN	Radio
C_2CN	Radio
CH_2=CHCN	Radio
CH_3CN	Radio
CH_3C CCN	Radio
HC_3N	Radio
HC_5N	Radio
HC_7N	Radio
HC_9N	Radio
$HC_{11}N$	Radio
RADICALS	
CH	VIS, Radio
CN	VIS, Radio
C_2	UV,IR
OH	Radio
HCO	Radio
C_3O	Radio
SO	Radio
NS	Radio
NO	Radio
ALDEHYDES AND KETONES	
H_2CO	Radio
CH_3CHO	Radio
IONS	
CH^+	VIS
N_2H^+	Radio
HCO^+	Radio
HCS^+	Radio
MISCELLANEOUS	
PN	Radio
C_3N	Radio
C_3H_2	Radio
SiC_2	Radio
H_2CS	Radio
CH_3OCH_3	Radio
HNCS	Radio
CH_3SH	Radio

* Detected only in the envelope around IRC+10216.
** Adapted from references [1], [13], [28], [29] and [30].

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