Abiogenesis and Photostimulated Heterogeneous Reactions in the Interstellar Medium and in the Primitive Earth's Atmosphere.
Relevance to the Genesis of Life

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Studies of micrometeoritic particles captured by Earth at different geological times and discovered in Antarctica have deduced that many organic substances necessary for the *Origin of Life* on Earth are synthesized in Interstellar Space and are subsequently transported to Earth by meteorites, comets, and cosmic dust (1). Over 120 types of molecules have been identified in interstellar dust clouds in the last three decades. Most organic molecules contain more than 10 carbon atoms. Phosphorous-containing molecules {e.g. PN}, CN, HCHO, cyano-ethylene and others are the molecular precursors of biologically important substances (2). Evidently, a cosmic dust particle provides a logical reactor surface on which to synthesize organic species in open Interstellar Space. The same holds for the dust particles in the primitive Earth's atmosphere. Solar and cosmic electromagnetic UV/visible radiations are excellent sources of free energy needed to drive the abiogenic synthetic process to produce organic molecules (3). Such processes find equivalence in heterogeneous photochemical reactions that belong to a class of processes in heterogeneous photocatalysis (4).

In its most simplistic format, heterogeneous photocatalysis can be described briefly and simply as

$$\mathrm{A} + \boldsymbol{Cat} + \mathrm{light} \rightarrow \mathrm{B} + \boldsymbol{Cat} \qquad [1]$$

where A and B are chemical reagents and products, respectively, in the gaseous or liquid phase, and ***Cat*** denotes the solid photocatalyst. Thus, heterogeneous photocatalysis represents the generalization of thermal heterogeneous catalysis (acceleration of a process with conservation of the catalyst ***Cat***) and photochemistry (involvement of free energy in the catalytic process). When the catalytic cycle in [1] is not complete (i.e. when ***Cat*** is not restored), the process is best referred to as a heterogeneous photochemical stoichiometric reaction.

It is now well established that solids of different nature (e.g., metal oxides, halides, sulfides, and complex natural minerals) can serve as effective photocatalysts. Different types of reactions, including radical reactions that lead to formation of multi-carbon compounds (e.g. formation of ethane, propane and ethylene from methane), take place at the surface of solid photocatalyst particles under illumination. Quantum yields are typically around 0.1 and reach unity in some systems. The heterogeneous photoreactions take place in a wide range of temperatures (from ~77 K to ca. 500 K) and in a wide range of gas pressures that includes the zero pressure limit. In the latter case, reactions occur between reagents pre-adsorbed on solid surfaces at sufficiently low temperatures. Accordingly, we infer that appropriate conditions exist to synthesize organic species in Interstellar Space on the surface of dust particles (as they were on primitive Earth).

Some peculiar features of heterogeneous photocatalytic systems, namely (i) the considerable red shift of the spectral range of a given photoreaction compared with one in homogeneous phase and (ii) the effect of spectral selectivity of photocatalysts (5), favor the synthesis of organic substrates under the above-mentioned natural conditions. The first feature utilizes a considerably larger fraction of Solar Energy than is otherwise possible in homogeneous photochemical reactions. The second feature influences the dependence of the relative chemical yields of different products of a given reaction on the wavelength of the actinic radiation. In particular, the products of complete and partial oxidation of methane and other hydrocarbons result principally from the photoexcitation of metal-oxide photocatalysts in the ***fundamental*** (i.e. ***intrinsic***) absorption bands (strong absorption of UV and of blue light). More complex organic compounds are formed under irradiation of the catalysts in the ***extrinsic*** absorption bands (weak to moderate absorption of red light). The latter peculiarity of gas/solid dust cloud-like heterogeneous systems makes them similar to what takes place in the (modern) Earth's atmosphere in which the ozone layer protects the Biosphere from destruction by UVC radiation (i.e. ultraviolet radiation below 290 nm).

Solid particles of the photocatalyst can store energy of irradiation through formation of trapped photoelectrons and photoholes at the surface and in the bulk of the solid, as well as through promotion of surface chemical reactions under additional thermal or long wavelength photoexcitation (6). Such particles also serve to adsorb molecules and radicals (at sufficiently low temperatures). Indeed, both atmospheric and cosmic dust particles are suitable vehicles that permit different stages of heterogeneous photoreactions (pre-adsorption of reagents, photoexcitation of catalyst, chemical transformation on the particle surface, and desorption of reaction products) to be separated in time and space at different locations of the interstellar medium (7). This likely occurred also in the primitive Earth's atmosphere.

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