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Astrochemistry Involving Dust Grains

One of the fundamental questions regarding astrophysical and (exo)planet atmosphere environments and small Solar System bodies (comets, asteroids and their meteoritic remains) is the origin of detected molecular species. Chemical processes leading to the formation of molecules in space can be divided into two groups, gas phase and dust grain surface reactions. Dust grains provide a meeting place for reactants; act as a third body allowing for dissipation of excess energy released in bond formation; play a catalytic role, as a classical catalyst lowering diffusion barriers for reactants and activation barriers of reactions and by direct participation in reactions by atoms or functional groups; can bond (trap) surface species not allowing them to desorb; and may shield molecules synthesized in surface reactions from destructive fields. Surface reaction pathways lead to a greater complexity of molecular species. Experimental and computational studies have even shown that the building blocks of biological macromolecules, such as sugars, amino acids, and nucleobases, can be produced in surface reactions under astrophysically relevant conditions. These studies in combination with the detection of the aforementioned species in comets and meteorites link astrochemistry to the big scientific question - the origin of life on Earth - and motivate the search for extraterrestrial life and other habitable planets.

The physics and chemistry on the surface of laboratory analogues of cosmic dust grains were recently reviewed [1]. This review highlighted a major problem – in spite of several pioneering studies, the catalytic formation of molecules on dust grains has never been studied systematically and is not reflected by currently accepted models of cosmic chemistry. In this contribution, I will try to show, on the basis of my research, why dust grains should be involved into the astrochemistry game.

Nanometre- to micrometre-sized dust grains (at their later evolutionary stage - the building blocks of planets) are present in many cosmic environments, from cold diffuse and dense interstellar clouds, through cold/warm protostellar envelopes and planet forming disks, to comets, asteroids, and hot atmospheres of exoplanets. However, experimental and computational astrochemical research has largely focused on chemical processes in/on the molecular ices that cover the dust grains in cold and dense environments. This is due to (1) the rich chemistry in those environments, known from detections of many organic

molecular species, (2) the typical view of grains in such environments as a compact refractory dust core covered by a thick (tens or hundreds of monolayers) ice layer, and (3) the last but, probably, not least – more sophisticated tools are required for research involving dust grains.

Point (2) leads to the consideration that physical and chemical processes occurring on and in thick ices are independent of the properties of the dust surface. This view, however, does not take into account the potentially high porosity of dust grains despite of considerable supporting evidence from laboratory experiments on cosmic dust analogues, dust evolution models, and analysis of cometary and interplanetary dust particles (see [2] and references therein). High porosity means the availability of the bare dust surface even in cold and dense environments due to a much larger surface area as compared to a compact dust core, as recently demonstrated in our research [2]. Therein, it was estimated that the coverage of porous grains by water ice (the main constituent of ices in cold and dense regions) could typically be in the range from the sub-monolayer to a few monolayers. These results reinforced the proposition made in Ref. [3] that, in contradiction to the popular “onion” model, bare dust grain surface in cold astrophysical environments would be available for species other than water to adsorb onto due to the self-aggregation of H₂O molecules. Furthermore, recent years have seen the studies of pathways to molecular complexity in low-density regions of the interstellar medium with low or no ice coverage, e.g., [4-7]. Figure 1 shows a new view of cosmic dust grains mixed with ice species (considering the high porosity of dust grains) presented in [2], the main sources of their processing in astrophysical environments, and examples of the main surface processes.

Thus, dust grain surfaces should be available for chemical reactions in a wide range of environments: cold diffuse interstellar clouds, which are characterized by low density and, thus, by the absence (or very low amounts) of ices; cold dense interstellar clouds and outer parts of protostellar envelopes and protoplanetary disks due to the high porosity of the grains and self-aggregation of water molecules; warm inner parts of protostellar envelopes and protoplanetary disks and hot exoplanet atmospheres due to the temperature not allowing ices to stay on the surface and to condense; and interiors of comets and asteroids due to the physical mixing of dust and ice as considered by the majority of models. In the following, I discuss briefly the results of my experimental studies demonstrating the catalytic role of carbonaceous and siliceous dust grains (laboratory analogues of cosmic dust grains). The interested reader can find more examples in the aforementioned review paper [1]. One more important aspect of dust/molecule interaction discussed below is trapping (strong bonding) of water ice molecules on silicate grains, the phenomenon which has rather physical than chemical nature but may influence the surface chemistry.

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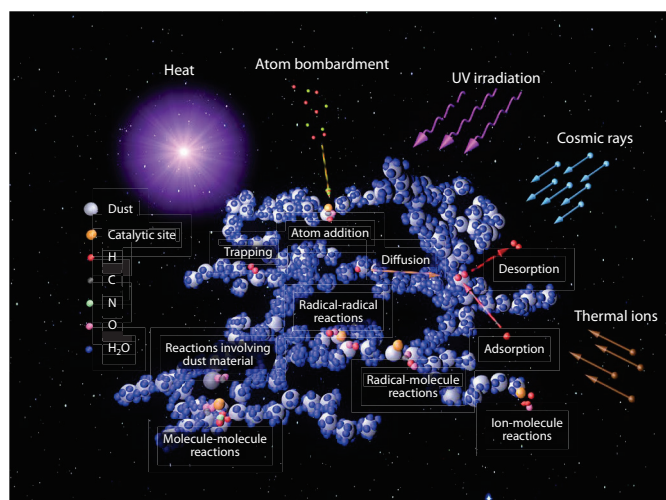


Fig. 1: Schematic illustration showing dust grains mixed with ice species, the main sources of their processing in astrophysical environments, and examples of the main surface processes. Image credit: MPIA Graphics Department, Axel M. Quetz. Background image: DSS2/STScI/ESO.

Dust grains as a classical catalyst

The previous research of the catalytic formation of molecules on dust grain analogues was focused on simple molecules, such as H_2 and H_2O (see Ref. [1] for a review). In our research, we studied the pure thermal reaction $\text{CO}_2 + 2\text{NH}_3 \rightarrow \text{NH}_4^+\text{NH}_2\text{COO}^-$ leading to the formation of ammonium carbamate. This organic molecule is potentially important for prebiotic chemistry as it is a possible precursor of urea, and urea, in turn, can be a precursor of pyrimidine, which is required for the synthesis of nucleobases in RNA molecules. The studies discussed below provided the first demonstration of the catalytic role of dust in low-temperature surface formation of complex organics.

In our first study, it was demonstrated that surface catalysis on amorphous silicate and carbon grains accelerates the kinetics of the reaction at a temperature of 80 K by a factor of up to 3 compared to the reaction occurring on a standard, chemically inert substrate [8]. In the follow up study [9], the temperature range of the experiments was extended down to 50 K and the catalytic role of the dust grain surface was related to a reduction of the reaction barrier. The reaction activation energy, obtained by fitting the temperature dependencies of the reaction rate coefficients with the Arrhenius law, was found to be about three times lower on grains compared to the corresponding ice layer on the chemically inert substrate.

Dust grains participating in reactions

Energetic processing of carbon surfaces covered by water ice at low temperatures has a long story started by Mennella et al. in 2004 [10] and continued by other groups (see Ref. [1] for a review). All those studies demonstrated the formation of CO and CO_2 molecules, with the carbon surfaces as the source of C. In our study [11], we extended the temperature range of such experiments up to 150 K and presented the first direct evidence of the efficient formation of CO_2 on amorphous carbon

grains covered by water ice at high temperatures (beyond the desorption temperature of CO_2 ice). Thus, the known low-temperature formation route of CO_2 remains valid as long as H_2O is present on carbon grains. The high-temperature chemical pathway to CO_2 may lead to the chemical erosion of carbonaceous grains in planet-forming disks, providing an alternative explanation of the loss of solid carbon in the innermost disk regions that resulted in the formation of carbon-poor Earth and other terrestrial planets in the Solar System.

A new route of the formation of organic molecules through grain surface processes was experimentally investigated. We studied the bombardment of bare carbon grains by O and H atoms at low temperatures [4]. The results show that such a bombardment leads to the formation of CO molecules, with further hydrogenation of CO leading to the formation of solid formaldehyde (H_2CO), and thus to increasing molecular complexity in the absence of an ice layer as compared to the previous research on carbon/ H_2O interfaces. Formaldehyde is a direct precursor of methanol, which is generally taken to be a starting point towards more complex organic molecules. Grain surface processes could explain the origin of organic molecules, such as CH_3OH , HC_5N and CH_3CN , detected in diffuse and translucent clouds [12, 13], where dust grains have no or a minor ice coating.

Trapping of water molecules

Water is the main constituent of ices in cold and dense astrophysical environments, accounting for more than 60% of the ices (e.g., [14]). The typical assumption says that solid-state water exists, as molecular ice, only in such environments (dense interstellar clouds, protostellar envelopes and planet-forming disks beyond the water snowline). However, the influence of the dust on surface processes forces us to consider interactions between the dust surface and atomic and molecular species on it more carefully. It was shown, first by models (e.g., [15]) and then by laboratory experiments on silicate-grains/water-ice mixtures performed by our group [16–19] that water molecules can be trapped (strongly bound) on silicate grains far beyond the desorption temperature of H_2O ice. Our experiments demonstrated the physical nature of the trapping (physisorption rather than chemisorption) and that the trapping efficiency is strongly dependent on the properties and composition of the surface [19].

The trapping (strong bonding) of H_2O molecules on silicates allow us to assume the presence of solid-state water in environments where we did not expect it before, e.g., in diffuse interstellar clouds, in planet-forming disks inside the snowline, and in the atmospheres of exoplanets. First evidence of the presence of solid-state water in diffuse clouds was provided by our group [18]. We also detected trapped water in extraterrestrial particles (cometary particles returned by the Stardust mission, interplanetary dust particles, and meteorites) [20]. The detection of trapped water inside the snowline in planet-forming disks is the primary goal of our JWST Cycle 1 project “Solid-state water inside the snowline in planet-forming disks: exploring the origin of water on terrestrial planets”. The data were recently obtained and are presently being analyzed.

Summary and Outlook

To understand the real picture of the physico-chemical evolution of space, it is necessary to involve chemically active dust grain surfaces into experimental and modelling astrochemical studies. Such research may and, I am sure, will clarify the origin of organic species detected in astrophysical environments, comets, asteroids, and meteorites. Understanding of the physics and chemistry involving dust grain surfaces will provide molecular targets and technical requirements for future astronomical observations and space missions to comets and asteroids and may shed light on the big scientific questions, such as the origin of life on Earth and formation of habitable planets.

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