HIGH ENERGY AND RADIATION CHEMISTRY IN SPACE
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The increasing knowledge of sources of accelerated ions and atoms in space (solar or stellar winds and flares; plasma in planetary systems; turbulences; cosmic rays; shock waves; envelopes of cold carbon stars; expanding supernova remnants, etc.) has prompted recently the introduction of high energy chemistry into space science [1-3]. Fundamental theories and experimental approaches are derived from hot atom chemistry [4] and chemical effects of ion implantation [5]. Due to the inclusion of endoergic and atom-molecule-interactions, high energy chemistry provides new pathways to explain the formation of complex molecules in space, which are important for chemical and biological evolution.

Simulation experiments were performed under space conditions (low pressures, low temperature, impact with energies > 4 eV) in gaseous and solid systems relevant for extraterrestrial matter. The projectiles were in particular the biogenic elements carbon and nitrogen, produced either by nuclear recoil processes via cyclotron activation (e.g. $^{14}$N(p,$\alpha$)$^{11}$C, $^{16}$O(p,$\alpha$)13N) or ion implantation. The gas systems C/H$_2$O, H$_2$O-NH$_3$ (Fig. 1), H$_2$O-CH$_4$ (Fig. 2), H$_2$O-CH$_2$-NH$_3$, CH$_4$ and N/H$_2$O were studied and products such as: CO, CO$_2$, CH$_4$, CH$_3$O, CH$_3$NH$_2$, NH$_3$, NO, NO$_2$, C$_2$H$_2$, C$_2$H$_4$ etc. analyzed by chromatographic methods (GC). These studies are of special relevance for the interactions of the coma of comets with solar wind and demonstrate the preferential formation of CO in all systems containing water vapour.

Solid systems studied were: C/H$_2$O (7 and 77 K); C/NH$_3$ (7 and 77 K); C/H$_2$O-NH$_3$ (77 K); N/H$_2$O (7 and 77 K); N/CH$_4$ (77 K); C/CH$_4$ (77 K). The analysis of the products such as: CO$_2$, CH$_3$O, HCOOH, CH$_3$OH, CH$_3$NH$_2$, NH$_2$OH, C$_2$H$_2$, C$_2$H$_4$, aliphatic compounds, simple aromates, formaldoxime, cyanamide, formamidine, guanidine, and others is performed by both chromatography (GC, HPLC) and optical spectroscopy in situ. The results in frozen gases are of primary interest for the chemical processes in frost layers on interstellar grains, cometary nuclei and asteroids (with respect to the formation of carbonaceous crusts).

In both, gases and solids, the effect of accompanying radiation was followed over a wide range of radiation dose received. The transition from primary (hot) to radiolysis products can be determined. Mechanisms for high energy reactions are: abstraction of H, formation into CH, NH or OH bonds, front collisions, complex formation (in the solid with even with two target molecules), formation of intermediate ring systems such as cyclopropenylidene derivatives, and substitution reactions. One of the most important findings is the reactivity sequence of high energetic carbon and nitrogen atoms with elemental components of gas or ice mixtures: C/0, C$\rightarrow$H$\rightarrow$N and N/0$\rightarrow$H$\rightarrow$C. The products are much more complex in the solid state since complex intermediate structures can be stabilized by transfer of the reaction energy to neighbors. Due to the strong interaction of the nearby neighborhood, the individual products depend very much on the local composition, and cannot be extrapolated in binary and ternary systems from the behaviour in pure phases. In the diluted gaseous system, the lack of stabilization of energetic intermediates by energy transfer leads to fragmentation and elimination processes and, thus, to the formation of simple products only.
Problems to which high energy chemistry is applied at present are: chemical interactions of solar wind with the coma of comets, in particular the formation of CO; build-up of organic molecules and precursors of biomolecules by impact into inorganic frosts; formation of organic refractories and polycyclic aromatic hydrocarbons (PAH) at the surface of interstellar grains, cometary nuclei, etc.; chemistry upon high velocity impact of grains onto matter with respect to PIA/PUMA and COMA problems (analysis of cometary grains after impact).

Fig. 1: Products of $^{11}$C impact into H$_2$O-NH$_3$ gas mixture (1:1, 50 mbar, 298 K) as depending on the radiation dose.

Fig. 2: Products of $^{11}$C impact into H$_2$O-CH$_4$ gas mixture (1:1, 50 mbar, 298 K) as depending on the radiation dose.

References: