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MODIFICATION OF PRIMORDIAL ICES BY COSMIC RAYS AS SIMULATED BY CYCLOTRON IRRADIATION

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ABSTRACT

Frozen CH₄ and CH₄/Ar mixtures closed into metal cuvettes and open to the vacuum were irradiated at 15 and 77 K with 10 to 20 MeV p and ³He²⁺ ions in order to simulate the effect of cosmic rays on solid organic matter in space. Ices exposed to vacuum represent surfaces of icy systems whereas closed systems stand for bulk ices. The products were analysed by MS, SEM, RBS, ERDA, ¹H-NMR, HPLC, GC-MS, NEXAFS and FT-IR. Volatile products consisted of a mixture of low molecular species, e.g. C₂H₂, C₂H₄, C₂H₆, and long linear aliphatic and olefinic compounds. The formation of polycyclic aromatic hydrocarbons (PAHs) and related species in solid CH₄ is due to a multi center reaction within one collision cascade and is governed by energy density effects with critical linear energy transfer values L_T between 2 and 10 keV μm⁻¹. Open ices exhibit preferential hydrogen release resulting in an increased carbonisation as compared to more hydrogen rich molecules protected inside large icy bodies.

INTRODUCTION

High energetic particles may modify primordial matter in space to complex compounds and even to precursor molecules for biological evolution. Solid CH₄ has frequently been chosen as a deliberately simple model substance to study the modification of hydrocarbons (Strazzulla and Johnson 1991; Roessler 1991). However, a detailed comparison of closed and open CH₄ targets and systematic studies of dose and energy density effects has not yet been executed. Thin ice condensates in the vacuum may represent surfaces of ices whereas CH₄ targets, closed into metall cuvettes, stand for the bulk.

EXPERIMENTAL

In the actual experiments, 11.1 μm layers of CH₄ and 9.7 μm of CH₄/Ar (1:12) (CH₄: 99.9995 %, Ar: 99.999 %) were condensed at 10 - 15 K on an (111) Si wafer attached to an aluminium cold finger of a bath cryostat. A second set of experiments was performed with closed targets consisting of 1 mm frozen CH₄ layers between a stainless steel backing and a Ti foil at 77 K. Both irradiation arrangements are described in detail in (Patnaik et al. 1990; Kaiser 1991). The ices were irradiated at 2*10⁻⁷ mbar with 250 nA cm⁻² beams (fluence some 10¹⁵ cm⁻²) of 17.6 MeV protons and 16.9 MeV ³He²⁺ ions of the CV 28 compact cyclotron of Forschungszentrum Jülich. Irradiation times varied from 5 to 90 min giving rise to doses between 0.07 and 16.8 eV per carbon atom. The linear energy transfer with respect to CH₄, L_T(CH₄), was increased from 161 (p//Ar/CH₄) via 1800 (p//CH₄) to 10810 eV μm⁻¹ (³He²⁺//CH₄).

RESULTS

The volatile species released from the open samples during irradiation and in the warm-up phase to 293 K were detected by a quadrupole mass spectrometer (MS). Immediately after onset of irradiation, species containing one carbon atom such as CH₂ and CH₄ appear and dominate all mass spectra. CH and CH₃ show lesser intensity. In all experiments, C₂H₄ and C₂H₂ were liberated some minutes after onset of beam. The yields of both products increased with time but were observed in lower yields than CH₂. C₂H₆ emerged later at the expense of the unsaturated species. Higher molecular-weight hydrocarbons were detected only in later stages of irradiation and in the warm-up phase in yields of approx. 1 - 2 % each. In closed cuvettes, up to 94 % of CH₄ were converted into volatiles, i.e. C₂H₂, C₂H₄, C₂H₆ and C₃H₈ (each up to 20 %) and lower yields of molecules containing up to 9 C atoms (~ 0.5 % each). Furtheron, He-irradiation of closed targets induced a formation of cycloalkanes and cycloalkenes such as cyclopropane, cyclopentane, cyclohexane and cyclohexene besides small amounts of benzene (Patnaik et al. 1990) whereas CH₄ ices

exposed to vacuum yielded mostly unsaturated species, i.e. mono- and disubstituted benzenes, 1,2-dihydro-naphthalene, 1,2,3,4-tetrahydronaphthalene and anthracene and/or phenanthrene (Kaiser et al. 1992a). The solid residues were analysed by visual inspection, optical microscopy (OM), Fourier transform infrared spectroscopy (FT-IR) in transmission at 293 K, scanning electron microscopy (SEM), Rutherford backscattering and elastic recoil detection analysis (RBS-ERDA), and near edge X-ray absorption fine structure spectroscopy (NEXAFS). In the targets exposed to vacuum CH₄ was finally converted into inhomogeneous solid residues, stable at room temperature and with a thickness of approx. 0.5 μm (Kaiser et al. 1992b). Aliphatic features dominate the IR spectra, whereas no unsaturated modes could be detected. With a method of higher sensitivity, H-C- bonds were analysed by NEXAFS, manifestating their concentration between 1 μmole and 1 nmole. FT-IR half widths increasing with irradiation time (factor 3 to 4) can be interpreted as an increase in oligomerization with dose. The segregation of different phases observed by SEM and OM substantiate these results as shown in Fig. 1a-b. It coincides with an overall H:C ratio decrease from originally 4 (CH₄) to 1.4, whereas samples in closed metal cuvettes exhibit a H:C ratio of 2. This indicates an preferential hydrogen release from open targets. The soluble fraction of the residues was dissolved in CDCl₃ (99.95 %) and ¹H-NMR, HPLC and GC-MS spectra were recorded. Concerning the open targets, up to approx. 90 % of the soluble phase consist of linear alkanes and 5 to 6 % of alkadienes, both containing up to 28 C atoms. ¹H-NMR spectra show 4-5 % of hydrogen located at olefinic carbon atoms. Eventually, about 0.1 % aromatic species were detected. Substituted benzenes were synthesized in all irradiated samples, but higher annulated rings and complex polycyclic aromatic hydrocarbons (approx. 0.1 %) such as naphthalene and pyrene were limited to ³He⁺⁺-irradiations with highest L_r(CH₄). They could not be detected in proton irradiated open and closed samples, although proton irradiation doses (1.4 - 2.8 eV per C atom) were similar to those of ³He⁺⁺-irradiations (0.1 - 15 eV per C atom), Fig.2.

DISCUSSION

The dualism of radiation dose and energy density and the definite differences in open and closed ice targets constitute ideal tools to discuss the experimental results. The correlation of the C₂ species in the mass spectra shows unequivocally that C₂H₂, C₂H₄, and C₂H₆ descend from the same precursor, i.e. excited methylcarbene [CH-CH₃]^{*} formed by insertion of hot carbon into a C-H bond of CH₄ (Stöcklin 1969). Hydrogen elimination of methylcarbene leads to ethyne. H-rearrangement yields ethene. Conspicuously, C₂H₆ is only formed at higher doses with a critical H concentration necessary to stimulate hydrogen pick-up of methylcarbene followed by deexcitation. The higher molecular species like propane were synthesized by additional radical attack and combination. The formation of a few % polycyclic aromatic hydrocarbons and partially hydrogenated analogs is governed by a critical linear energy transfer L_r(CH₄) of about 2 to 10 keV μm⁻¹ which induces a multi center reaction (Roessler et al. 1990), i.e. aggregation of individual insertion products of hot carbon secondaries in CH₄ and radicals such as CH, CH₂ and CH₃ in a single collision cascade. If L_r(CH₄) is below this critical value, the concentration of aggregating species is too low in the activated zone to lead to the formation of complex two- or three-dimensional molecules in the relaxation phase. Thus, the accumulated radiation dose seems to be of minor importance in the synthesis of PAHs as compared to the L_r(CH₄) value. Classical hot atom reactions such as insertion, abstraction and addition (Stöcklin 1969, Roessler 1991) cannot explain the synthesis of PAHs at lowest doses of 0.1 eV per C atom. Step-by-step production in overlapping cascades should contribute to a radiolytical formation only at doses exceeding some 100 eV per C atom. Thus, He-ions and heavier components of cosmic energetic particles are very effective in processing organic material. The synthesized species point to different chemical conversion of the original CH₄ in the bulk and near surfaces. Ices exposed to vacuum exhibit H₂ formation in aligned cascades and elimination from excited intermediates which can be considered as a kind of oxidation. H-outdiffusion as well as the loss of reactive intermediates is restricted in closed targets. Consequently, molecules are protected from being oxidized: saturated cyclic compounds were solely formed in closed samples. The hydrogen loss of icy surfaces results in an increasing carbonization, such as shown by the low H:C ratio of 1.4 and the formation of amorphous carbon and amorphous hydrogenated carbon in specific areas.

The linear energy transfer is the limiting factor in formation of complex molecules in space (Fig. 3). At the relatively long irradiation times at low fluxes in space, the annealing of defects and reactive species may decrease the necessary concentration for build-up of larger units.

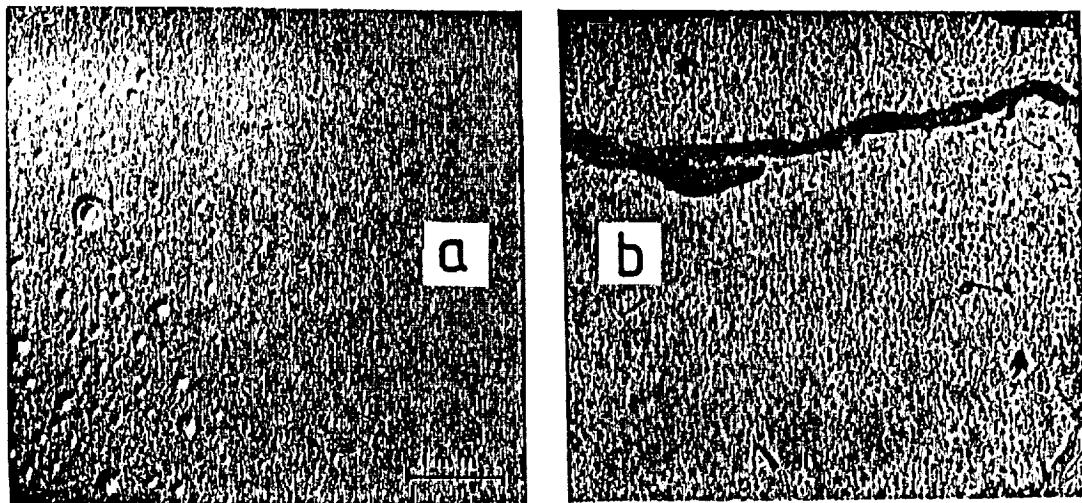
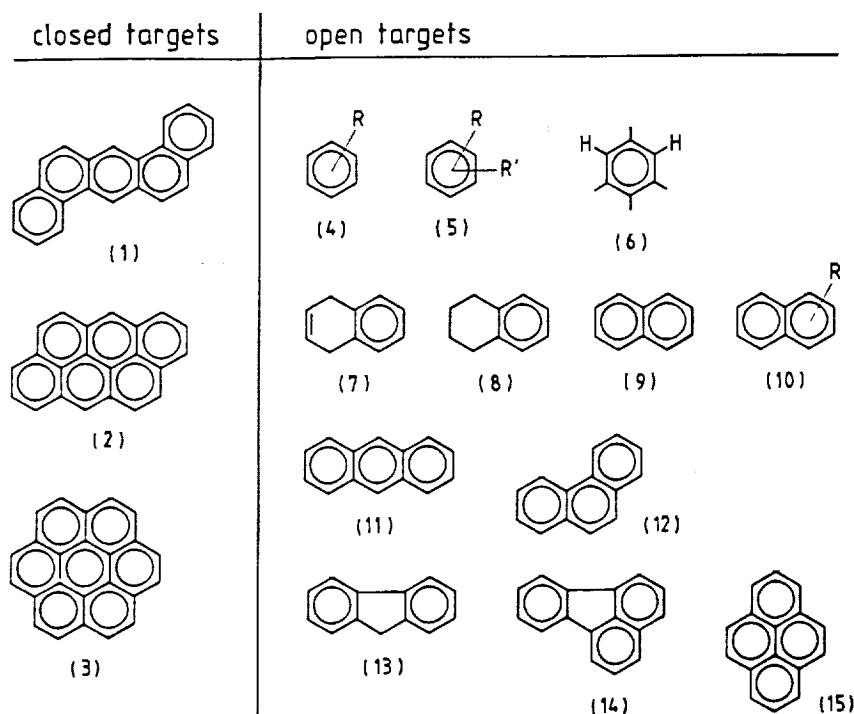


Fig.1a-b : Microscopy of residues on Si wafer. a) p//Ar/CH₄, D* = 0.07 eV/C, L_T(CH₄) = 161 eV μm⁻¹; b) ³He⁺⁺//CH₄, D* = 16.87 eV/C, L_T(CH₄) = 10810 eV μm⁻¹.

Fig.2 : Polycyclic aromatic hydrocarbons formed in open targets and in metall cuvettes (1:dibenzo[a,b]anthracene, 2:dibenzo[def,mno]chrysene, 3:coronene, 4-6:mono-, di and tetrasubstituted benzenes, 7:1,2-dihydronaphthaline, 8:1,2,3,4-tetrahydronaphthaline, 9:naphthaline, 10:alkylnaphthaline, 11:anthracene, 12:phenanthrene, 13:fluorene, 14:fluoranthene, 15:pyrene).



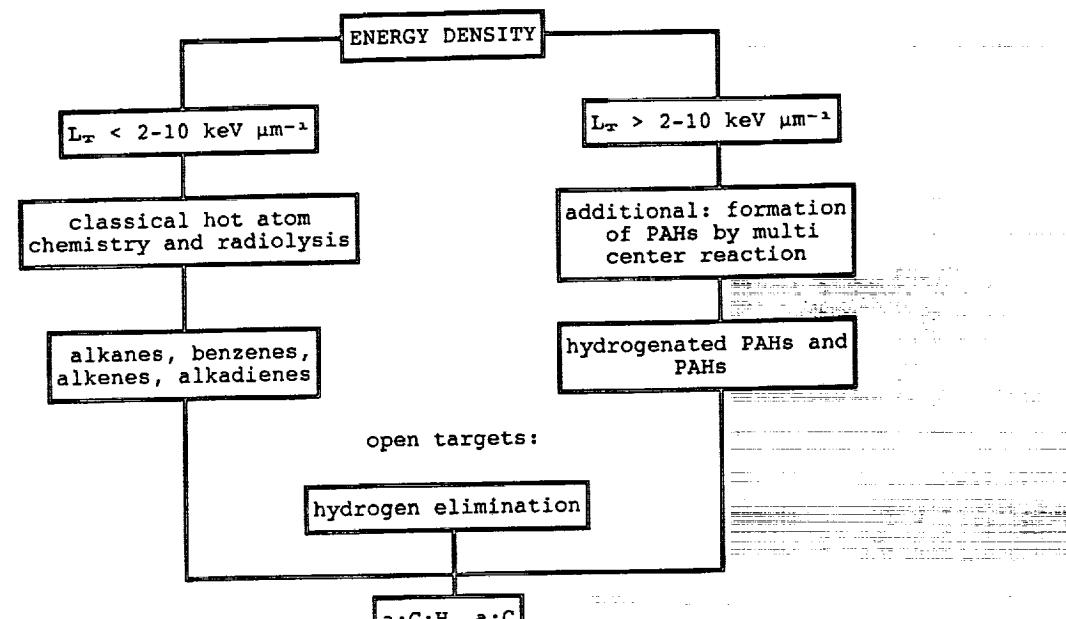


Fig.3 : Mechanisms of modification of pure CH_4 and synthesized species under MeV particle irradiation.

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