

Energy density effects in the formation of organic residues in frozen methane by MeV ions

R.I. Kaiser^a, J. Lauterwein^b, P. Müller^c and K. Roessler^a

^a *Institut für Nuklearchemie, Forschungszentrum Jülich, D-5170 Jülich, Germany*

^b *Organisch Chemisches Institut, Universität Münster, D-4400 Münster, Germany*

^c *Institut für Festkörperphysik, Universität Jena, O-6900 Jena, Germany*

Carbonaceous residues were formed by irradiation of thin layers of frozen methane at 10 to 15 K by 17 MeV protons and $^3\text{He}^{2+}$ ions and successive warming to ambient temperature. Analysis was performed by optical microscopy, scanning electron microscopy (SEM), Rutherford backscattering spectroscopy (RBS), elastic recoil detection analysis (ERDA), infrared spectroscopy (IR) in transmission, hydrogen nuclear magnetic resonance ($^1\text{H-NMR}$), high performance liquid chromatography (HPLC) and gas chromatography–mass spectrometry (GC–MS). Long chain aliphatic and olefinic hydrocarbons constituted the main products. The formation of aromatic and polycyclic compounds, PAHs and amorphous carbon increased with the energy deposited in one collision cascade.

The linear energy transfer with respect to CH_4 , $L_T(\text{CH}_4)$, was varied in the systems p//Ar/CH_4 (12:1), p//CH_4 and $^3\text{He}^{2+}\text{//CH}_4$ from 160 to 10810 $\text{eV}\mu\text{m}^{-1}$, respectively. A threshold L_T for the formation of PAHs and related structures seems to range between 2 and 10 $\text{keV}\mu\text{m}^{-1}$. The experiments give evidence for a fast multicenter combination of intermediate radicals formed by the secondary suprathermal carbon atoms from knock on processes in one collision cascade. The experiments were aimed to simulate the effects of cosmic rays on primordial frozen matter. The results underline the role of heavier ion irradiation (He, etc.) in the prebiotic buildup of complex organic matter in space.

1. Introduction

Solid hydrocarbons from frozen CH_4 to polystyrene show formation of complex organic products when irradiated with energetic ions [1–10]. Hydrogen elimination, generation of unsaturated and cyclic structures and carbonization increases with radiation dose. It was, however, questionable whether the complex compounds were due to overall energy deposition or due to specific effects within the collision cascade, i.e. depending on a certain density of energy deposition [8,9]. It had been shown recently that in frozen CH_4 enclosed in metal cuvettes at 77 K, $^3\text{He}^{2+}$ -ion bombardment induced the formation of polycyclic aromatic hydrocarbons (PAHs) [11,12]. CH_4 served as a deliberately model substance for complexation of organic matter starting from a primitive, primordial molecule. The formation of PAHs may be due to a multicenter reaction of secondary energetic carbon atoms and their intermediate products such as methylcarbene with the surrounding radicals [11–15]. This prompted a new study in frozen methane at 15 K using 17 MeV cyclotron ions in order to investigate possible mechanisms for the formation of defined classes of organic species and their dependence on increasing irradiation dose ($D^* = 0.07$ to 16.8 eV per carbon atom) and energy density, expressed by the linear energy transfer with respect to CH_4 , $L_T(\text{CH}_4) = 161$ to 10810

$\text{eV}\mu\text{m}^{-1}$. In the course of the irradiations it was distinguished between open targets (condensates on (111) Si wafer) which represent icy surfaces and CH_4 in metal cuvettes which represent the bulk of icy bodies, e.g. in the interior of comets [10–12]. The analyses of gases emanating during irradiation are reported in a parallel paper [16], those of the organic residues in this work.

2. Experimental

The gas condensation system and irradiation apparatus were described in refs. [15,16] in detail. Argon and methane gases were research grade (Ar: 99.999%; CH_4 99.9995%; Messer Griesheim). 9.7 μm layers of CH_4/Ar (1:12) and 11.1 μm of CH_4 were condensed at 10–15 K and 2×10^{-5} mbar with a condensation rate of 145 $\mu\text{mole h}^{-1}$ on a (111) Si wafer attached to an aluminium cold finger. The ices were irradiated by 250 nA cm^{-2} ion beams (fluence some 10^{15} cm^{-2}) of 17.6 MeV protons and 16.9 MeV $^3\text{He}^{2+}$ ions of the CV 28 compact cyclotron of Forschungszentrum Jülich. After irradiation the cold finger was allowed to reach ambient temperature with heating rates of 0.1 to 0.5 K min^{-1} . The irradiated targets and the linear energy transfer values are summarized in table 1.

Table 1
Cyclotron ions, targets and energy densities (L_T) of the experiments

Projectile	Target	$d[\mu\text{m}]$	$L_T(\text{CH}_4)$, [$\text{eV}\mu\text{m}^{-1}$]
Open target			
17.6 MeV p	Ar/ CH_4 12:1	8.6 Ar 1.1 CH_4	161
17.6 MeV p	CH_4	11.1	1800
16.9 MeV $^3\text{He}^{2+}$	CH_4	11.1	10810
Closed target			
17.4 MeV p	CH_4	10^3	1755
18 MeV $^3\text{He}^{2+}$	CH_4	10^3	9200

The solid residues were analysed in situ by visual inspection, optical microscopy, IR in transmission (293 K), SEM and RBS-ERDA. The soluble phase was dissolved in CDCl_3 (99.95%, Aldrich), and $^1\text{H-NMR}$ (1 dim; H-H-shift correlated 2 D NMR (COSY)). HPLC and GC-MS spectra were recorded. The insoluble fraction on the Si wafer was analysed by IR in transmission at room temperature.

In situ and on-line determination of chemical modifications in closed targets were impossible. Consequently, their analyses were restricted to $^1\text{H-NMR}$, HPLC and GC-MS.

3. Results

MeV ion irradiation with $D^* = 0.07$ to 16.8 eV per carbon atom converted the original CH_4 into an inho-

mogeneous solid residue with a thickness of 0.5 ± 0.2 μm , stable at room temperature. The IR spectra exhibit the dominance of typical aliphatic features such as $\nu_{\text{as}}(\text{C-H}) \text{sp}^3 \text{CH}_3 = 2955\text{--}2963 \text{ cm}^{-1}$, $\nu_{\text{as}}(\text{C-H}) \text{sp}^3 \text{CH}_2 = 2926\text{--}2928 \text{ cm}^{-1}$, $\nu_{\text{s}}(\text{C-H}) \text{sp}^3 \text{CH}_3 = 2870\text{--}2875 \text{ cm}^{-1}$, $\nu_{\text{s}}(\text{C-H}) \text{sp}^3 \text{CH}_2 = 2853\text{--}2855 \text{ cm}^{-1}$ and their corresponding $\delta_{\text{as}}(\text{CH}_3) = 1450\text{--}1452 \text{ cm}^{-1}$, $\delta_{\text{s}}(\text{CH}_3) = 1370\text{--}1371 \text{ cm}^{-1}$, $\delta(\text{CH}_2) = 1460\text{--}1465 \text{ cm}^{-1}$ and $\tau(-(\text{CH}_2)_n\text{-chain}) = 722 \text{ cm}^{-1}$ and $\delta(\text{C-C}, -(\text{CH}_2)_n\text{-chain}) = 1298 \text{ cm}^{-1}$. No olefinic, acetylenic or aromatic vibration modes were detected beyond a limit of about 1 μmole . With increasing irradiation dose the half widths of IR features became larger by a factor of 3 to 4. This and the decreasing transmittance of the base line can be interpreted in terms of an increase in aggregation.

This oligomerization coincides with a segregation of different phases, observed by optical microscopy and SEM. Fig. 1a for the lowest irradiation dose by 17.6 MeV protons on Ar/ CH_4 exhibits a low variety of structures and only some small bubble like formations, whereas the irradiation at maximum dose and energy density results in an extreme inhomogeneous distribution of relative carbon intensity from 100% (black areas) to about 10% (gray) and 1% (white) and clear segregation of these three phases (fig. 1b and fig. 2).

The soluble fraction consists of about 90% linear alkanes, 5 to 6% linear alkadienes, both with ≤ 28 C atoms. The $^1\text{H-NMR}$ spectra show 4–5% unsaturated compounds as a first hint of hydrogen elimination (fig. 3); the position of organic sidegroups –R and aromatic structures Ar (= aryl) were calculated from H-increments and H–H-coupling constants.

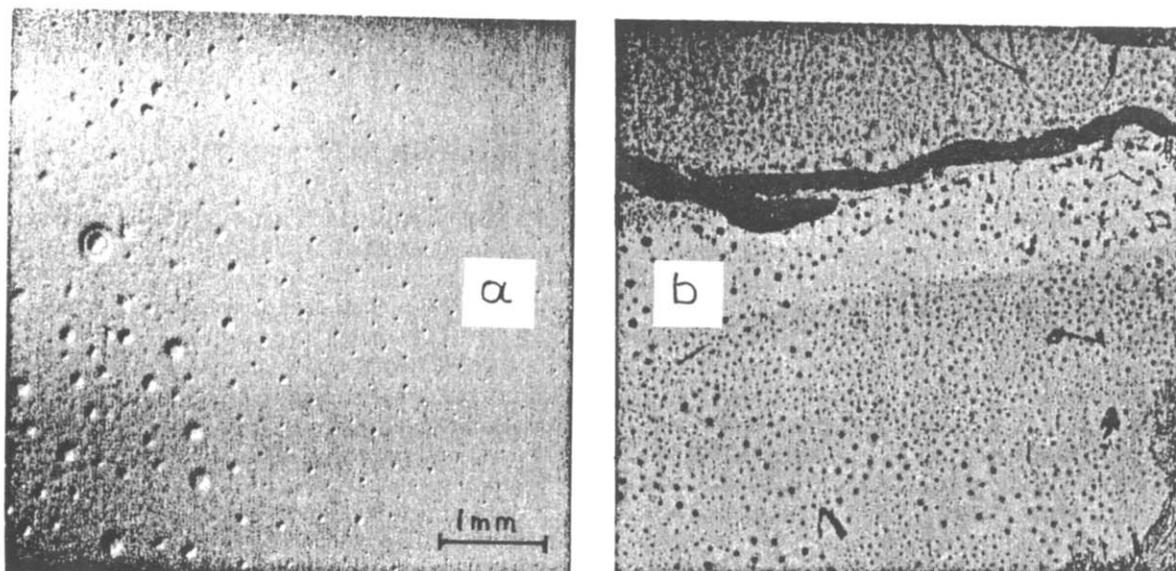


Fig. 1. Microscopy of residues on Si wafer. (a) p//Ar/ CH_4 , $D^* = 0.07 \text{ eV/C}$, $L_T = 161 \text{ eV}\mu\text{m}^{-1}$; (b) $^3\text{He}^{2+}$ // CH_4 , $D^* = 16.8 \text{ eV/C}$, $L_T = 10810 \text{ eV}\mu\text{m}^{-1}$.

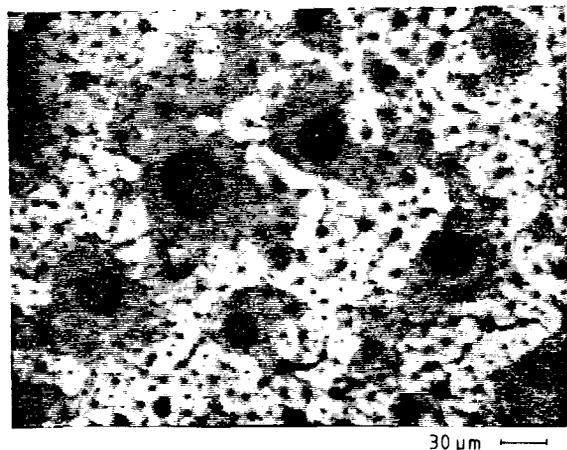


Fig. 2. SEM of residue on Si wafer; ${}^3\text{He}^{2+}/\text{CH}_4$, $D^* = 16.8$ eV/C, $L_T = 10810$ eV μm^{-1} .

The fourth group consists of about 1% aromatic species. Mono- and polysubstituted benzene derivatives were synthesized in all irradiated open and closed targets, whereas the formation of more complex poly-

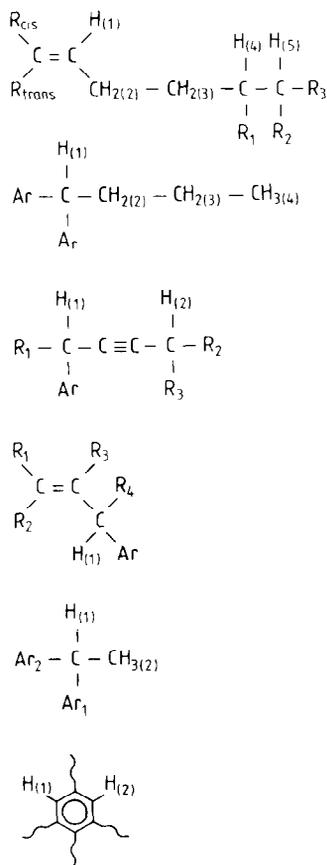


Fig. 3. Molecules detected by ${}^1\text{H-NMR}$ (Ar = aryl).

~ 1 % aromatic species

experiments	aromatic molecules
all:	
${}^3\text{He}^{2+}/\text{CH}_4$ a) 10.2 eV/ CH_4	
b) 16.8 eV/ CH_4	

Fig. 4. Aromatic molecules detected in residues by ${}^1\text{H-NMR}$, HPLC and GC-MS.

cyclic aromatic hydrocarbons (PAHs) like naphthalene, anthracene, phenanthrene and pyrene (fig. 4) was restricted to ${}^3\text{He}^{2+}$ irradiations of highest $L_T(\text{CH}_4)$ in open targets and metal cuvettes. Proton irradiated CH_4 in closed metal cuvettes showed no PAH formation, although the irradiation doses of 1.4–2.8 eV per carbon atom overlapped with the ${}^3\text{He}^{2+}$ dose range ($D^* = 0.1$ to 15 eV per carbon atom [11]). It indicates a dependence on a critical linear energy transfer for the formation of PAHs.

This is also reflected in the results of integrated ${}^1\text{H-NMR}$ studies of the soluble fraction in the open targets. The protons were divided according to their chemical shifts into four groups of aliphatic, olefinic, aromatic and aliphatic protons at C atoms connected with $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ bonds or aryl groups. The yields were correlated in fig. 5 with dose and linear energy transfer. The dramatic increase of aromatic protons at the extent of aliphatic is the dominant feature. No formation of PAHs was observed for proton irradiations despite of equivalent doses.

The detected unsaturated species indicate hydrogen elimination. The H:C ratio of the residues in closed metal cuvettes shows a constant profile of 2 over the

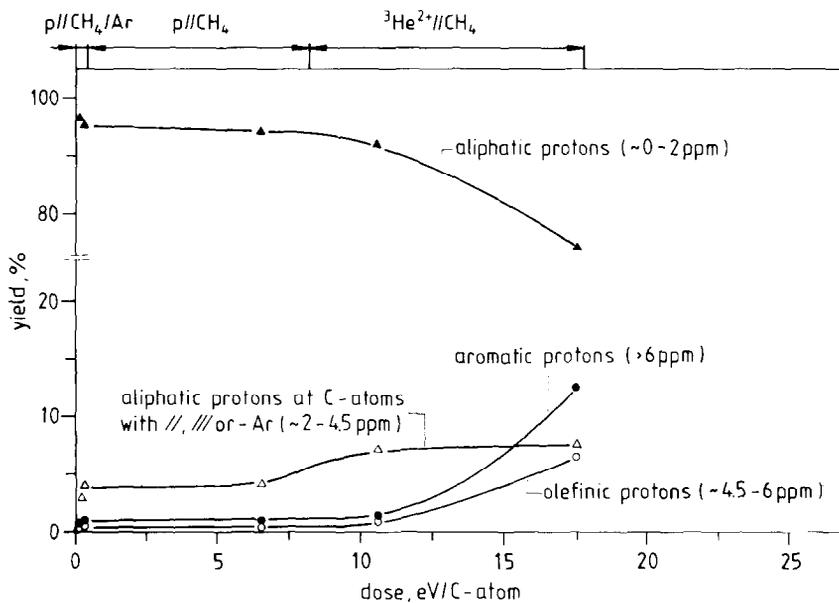


Fig. 5. Abundance of different types of protons in ^1H -NMR spectra of CDCl_3 solutions of residues as depending on dose and energy density.

dose range from 0.1 to 15 eV per carbon atom [11]. The H:C ratio of the residues obtained by irradiations of open CH_4 targets decreases from original 4 to a value of 1.4 (fig. 6), indicating that hydrogen elimination is favoured in open targets over closed systems.

4. Discussion

The dualism of irradiation dose and energy density seems to be an ideal tool to explain the experimental results.

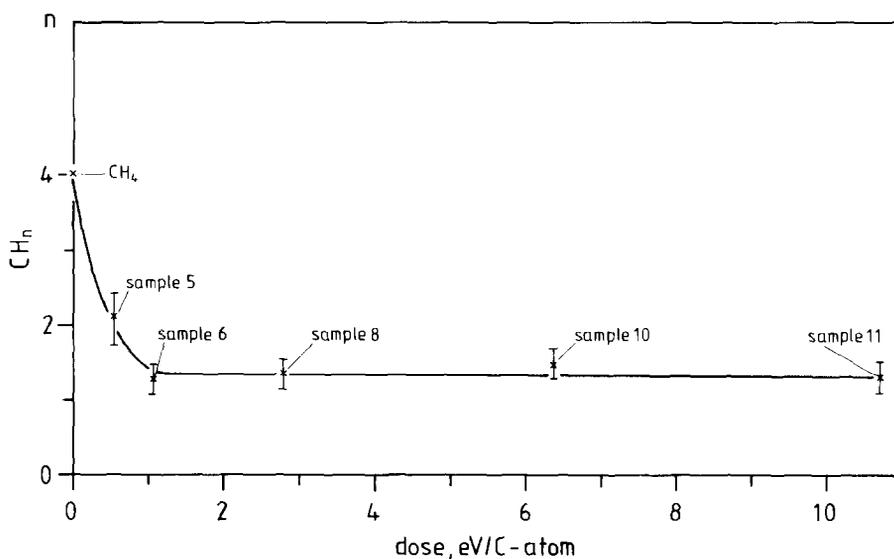


Fig. 6. Dose dependence of H/C ratio in residues measured by RBS-ERDA.

The formation of a few % polycyclic aromatic hydrocarbons is governed by a critical linear energy transfer of about 2 to 10 keV μm^{-1} which induces a multi-center reaction [11–15, 18], i.e. aggregation of the individual insertion products of hot carbon secondaries into CH₄ (in particular methylcarbene) and CH, CH₂ and CH₃ radicals in *one* collision cascade. If $L_T(\text{CH}_4)$ is below this critical value, the concentration of radicals in the activated zone is too low to recombine in the relaxation phase to complex two- or three-dimensional molecules.

In this conceptual framework, the total radiation dose which is correlated to overlapping cascades seems to be of minor importance in the buildup of PAHs compared to energy density effects. The classical hot atom reactions such as insertion, abstraction and addition [17] cannot explain the syntheses of PAHs. Radiation chemical mechanisms do not seem to play a role at 0.1 eV per carbon atom [11]. Successive reactions in overlapping cascades should contribute only with some 100 eV per carbon atom to a radiolytical formation of complex molecules.

This is important for space where the very long irradiation times at relatively low dose of 10² cm⁻² s⁻¹ of ions in the MeV region can lead to partial annealing of the defects. Thus, the necessary energy deposition and accumulation of subreaction-centers for the formation of PAHs hardly is reached by cascade overlap. This underlines the role of heavier ion irradiation in the prebiotic buildup of complex molecules. When performing simulation experiments on cosmic ray effects, more attention has to be given to these particles even when less abundant in space.

Last but not least, a clear separation between closed ice targets (bulk ices in the interior of comets, icy planets and satellites, etc.) and those exposed to vacuum (ice surfaces such as on interstellar and planetary grains) has to be taken into account. Bulk ices do not allow easy hydrogen release to space, and the molecules formed in the interior are protected against oxidation. Obviously, hydrogen elimination by hot atom chemistry and sputtering is more pronounced on ice surfaces where the different reduction potentials lead to different chemistry and an increasing carbonization. This could provide a potential source for amorphous carbon formation in space.

Acknowledgements

The authors thank Prof. Dr. G. Götz, Jena, for helpful discussions of the RBS-ERDA spectra. They

are indebted to the CV 28 cyclotron crew of Forschungszentrum Jülich for irradiations, Mrs. Karin Busse, Münster, for recording the NMR spectra, Dr. E. Wallura of IRW, Jülich, for SEM measurements and Hewlett Packard, Ratingen, for assistance in GC-MS.

References

- [1] G. Stöcklin, H. Stangl, D.R. Christman, J.B. Cumming and A.P. Wolf, *J. Phys. Chem.* 67 (1963) 1735.
- [2] M.H. Moore, B. Donn, R. Khanna et al., *Icarus* 54 (1983) 388.
- [3] C. Calcagno, G. Foti and G. Strazzulla, *Radiat. Eff.* 91 (1985) 79.
- [4] G. Strazzulla, *Icarus* 61 (1985) 48.
- [5] W.L. Brown, L.J. Lanzerotti and K.J. Marcantonio, *Nucl. Instr. and Meth.* B14 (1986) 392.
- [6] J. Bénit, J.P. Bibring and F. Rocard, *Nucl. Instr. and Meth.* B32 (1988) 349.
- [7] B.N. Khare, C. Sagan, W.R. Thompson et al., *Icarus* 79 (1989) 350.
- [8] K. Roessler, in: *Solid State Astrophysics*, eds. E. Bussoletti and G. Strazzulla (North-Holland, Amsterdam, 1991) p. 197.
- [9] G. Strazzulla and R.E. Johnson, in: *Comets in the Post-Halley Era*, eds. R.L. Newburn et al. (Kluwer, Dordrecht, 1991) p. 243.
- [10] A. Patnaik, K. Roessler and E. Zádor, *Adv. Space Res.* 9 (6) (1989) 49.
- [11] A. Patnaik, K. Roessler and E. Zádor, *Radiochim. Acta* 50 (1990) 75.
- [12] K. Roessler, G. Eich, A. Patnaik and E. Zádor, *Lunar Planet. Sci. Conf.* XXI (1990) 1035.
- [13] K. Roessler, in: *Polycyclic Aromatic Hydrocarbons and Astrophysics*, eds. A. Léger et al. (Reidel, Dordrecht, 1987) p. 173.
- [14] K. Roessler and G. Eich, *E-MRS Meeting June 1987*, vol. XVII (Editions de Physique, Paris, 1987) p. 167.
- [15] R.I. Kaiser, Report Jül-2492, Forschungszentrum Jülich (1991) p. 130.
- [16] R.I. Kaiser, R.M. Mahfouz and K. Roessler, these Proceedings (6th Int. Conf. on Radiation Effects in Insulators, Weimar, Germany, 1991) *Nucl. Instr. and Meth.* B65 (1992) 468.
- [17] G. Stöcklin, *Chemie heisser Atome* (Verlag Chemie, Weinheim, 1969).
- [18] K. Roessler, these Proceedings (6th Int. Conf. on Radiation Effects in Insulators, Weimar, Germany, 1991) *Nucl. Instr. and Meth.* B65 (1992) 55.