

## Interaction of MeV ions and VUV photons with polymers and high molecular hydrocarbons

R.M. Mahfouz<sup>1</sup>, M. Sauer, S.T. Atwa<sup>2</sup>, R.I. Kaiser and K. Roessler

*Institut für Nuklearchemie, Forschungszentrum Jülich, Postfach 1913, D-5170 Jülich, Germany*

Organic solids such as polymethylene, polyethylene, polyoxymethylene, aliphatic and cyclic paraffins, naphthalene, anthracene and kerogen were irradiated at 77 K with 10–20 MeV cyclotron ions (p, <sup>3</sup>He) and up to 10 eV photons. The products were analysed by quadrupole mass spectrometry (QMS), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and gas chromatography (GC). Besides radiolytic fragmentation, also synthesis of new and complex compounds was observed as a consequence of hot carbon chemistry. Vacuum ultraviolet (VUV) irradiation proved to be less effective in the buildup of new structures than MeV ions, due to its lower linear energy transfer.

### 1. Introduction

The interaction of solar and cosmic rays with extraterrestrial matter has extensively been simulated in frozen systems such as H<sub>2</sub>O, NH<sub>3</sub>, CO<sub>2</sub>, CH<sub>4</sub>, etc. and mixtures thereof [1–5]. Irradiation experiments were performed at low temperatures (5–77 K) and at radiation doses of several eV per target molecule in order to meet conditions in space. Much less work has been devoted to organic refractories despite the fact that they constitute an important part of solid matter in space. In polymers radiation results in cross linking and/or chain scission, gas evolution and eventually carbonization [6–9]. Radiation damage of polymers induced by electrons and/or  $\gamma$ -rays has been extensively studied because of their use in nuclear power facilities. The damage induced by energetic ions has not been treated so much, despite this being an important subject in view of application of organic material in radiation fields such as space [10]. Following studies in solid methane as a deliberately simple analog for organic solids [11–14], here a representative series of complex organic substances was selected: polymers such as PM, PE and POM; tetracosane and androstane for linear and cyclic paraffins, naphthalene and anthracene for polycyclic aromatic hydrocarbons, and kerogen as a mixture of naturally occurring hydrocarbons. It was interesting to compare the effects induced by vacuum photons and MeV ions which simulate two

main radiation sources in space: solar or stellar photons and the particle component of cosmic rays.

### 2. Experimental

The substances studied were: polymethylene (PM) and polyethylene (PE) in form of 50 to 500  $\mu$ m grains from ROW, Wesseling (Lupolen HD 6080 M and Lupolen LD 1800 SP 15), polyoxymethylene in 2 to 10  $\mu$ m grains (POM) in the specific form of p.a. paraformaldehyde from Merck, Darmstadt; naphthalene, anthracene and tetracosane p.a. from Merck, Darmstadt; androstane from Aldrich; kerogen in 5 to 10  $\mu$ m grains prepared from an oil slater from Messel quarry near Darmstadt by treatment with concentrated HCl and HF.

The VUV-irradiation chamber of about 12 l volume is shown schematically in fig. 1. A Hamamatsu L 1835 deuterium lamp was focussed with the aid of a MgF<sub>2</sub> lens onto a spot of 8 mm diameter on a LN<sub>2</sub> cooled sample platform. Some 10  $\mu$ m thick samples were pressed with a piston into cylindrical copper containers of 12 mm diameter which were fixed on the platform by conductivity silver. The pressing resulted in a homogeneous surface necessary for spectroscopy in reflectance. A quadrupole mass spectrometer from Balzers was mounted near to the sample in order to measure the evolving gases. A turbomolecular pump together with two LN<sub>2</sub> cold traps produced a vacuum of  $2 \times 10^{-7}$  mbar. The samples were irradiated up to 6 h with a photon flux of  $2.1 \times 10^{19} \text{ s}^{-1} \text{ m}^{-2}$  ( $\lambda = 110$  to 300 nm). The 8 mm spot, thus, was hit in 6 h by about  $4 \times 10^{19}$  photons. Assuming an average penetration depth of 1  $\mu$ m and neglecting the amount of reflection,

<sup>1</sup> On leave from Chemistry Department, Assiut University, Egypt.

<sup>2</sup> On leave from Chemistry Department, Zagazig University, Benha branch, Egypt.

a maximum dose of  $D^* \approx 130$  eV per carbon atom results for most of the organic targets. For details see refs. [15,16]. Table 1 shows a comparison of the UV intensity of the sun at 1 AU and the VUV source used in these experiments. It can be seen that the intensity of the VUV source is equal to that of the sun in the lower energy regime between 4.2 and 7.3 eV, but by a factor of 100 higher in the proper VUV regime between 7.3 and 11.3 eV.

The QMS spectra were recorded before and during irradiation at 80 K and thereafter when warming to ambient temperature. The residues were analysed by FT-IR spectroscopy in diffuse reflectance (Nicolet DX 300 with a "praying mantis" unit from Harrick). Then the samples were heated 45 min at 150°C in a pyrex container and the emanating gases were analysed with a Shimadzu GC-9A gas chromatograph with flame ionization detector (FID) on a Poropak Q column. For details see ref. [16].

Ion irradiation was carried out in the CV 28 compact cyclotron of Forschungszentrum Jülich with 17 MeV p and 15 to 20 MeV  $^3\text{He}^{2+}$  ions and typical beam currents of 1 or 2  $\mu\text{A cm}^{-2}$ . Irradiation times were varied from 1 to 30 min, giving rise to radiation doses  $1 \leq D^* \leq 100$  eV per carbon atom of the target. The samples were enclosed in 1 mm deep stainless steel cuvettes covered with a 25  $\mu\text{m}$  thick Ti-foil. These targets were mounted in a  $\text{LN}_2$  cryostat in such a way that the radiation entered from the side of the Ti-foil and penetrated the solids hereby delivering some 5 to 8

Table 1

Comparison of VUV intensities of sun at 1 AU and Hamamatsu L1835 source

$\Delta\lambda$ [nm]	Photon flux [ $\text{s}^{-1} \text{m}^{-2}$ ]	
	Sun (1 AU)	L 1835
110–170	$2.8 \times 10^{16}$	$4.1 \times 10^{18}$
170–300	$22.9 \times 10^{18}$	$17.0 \times 10^{18}$

MeV. The beam was stopped in the stainless steel back plate of the target array.  $\text{LN}_2$  cooling was sufficient to keep the sample temperature below 150 K even at the highest beam intensity used. For details cf. ref. [11]. The analysis of the irradiated samples was carried out by FT-IR spectroscopy in transmission in KBr pellets and gas chromatography after heating as described above. Some additional spectra were taken with a Jobin-Yvon S3000 micro Raman spectrometer.

### 3. Results

The results of the VUV irradiation are summarized in table 2. MgO as a standard (p.a. from Merck, Darmstadt) did not show any change. Naphthalene did not exhibit fragmentation or spectral change. Kerogen developed gases only after heating to 150°C. Small hydrocarbons containing up to nine carbon atoms ( $\text{C}_9$ ) were observed. Their amount increased with the radiation dose. The strongest GC peak was that of  $\text{C}_6$ .

PM did not yield QMS signals, whereas PE showed aliphatic hydrocarbons with three, four and five carbon atoms. A slight yellow color was observed for both polymers by visual inspection stemming from the formation of conjugated double bonds. The FT-IR bands between 800 and 1000  $\text{cm}^{-1}$  increased very much (fig. 2). Heating resulted in the liberation of hydrocarbons containing up to six carbon atoms.

Polyoxymethylene yielded a series of compounds in QMS, in particular when warming up to ambient temperature after irradiation (fig. 3). Some of them are products from photolysis in the solid state ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_2\text{O}$ ,  $\text{HCOOH}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{HO-CH}_2\text{-O-CH}_2\text{-OH}$ , etc.), some result from cleavage of larger fragments in the ion source ( $\text{HO-CH}_2\text{-O}^+$ , etc.). FT-IR spectra showed a strong increase of the formerly very weak band at 1738  $\text{cm}^{-1}$ , which is connected to the formation of an ester.

The results of MeV ion irradiation at about 80 K are rather preliminary. They are summarized in table 3. Even a strong treatment of 30 min with 2  $\mu\text{A cm}^{-2}$   $^3\text{He}^{2+}$  ions did not bring about a change of the FT-IR spectra of PM and PE. However, Raman spectra of PE showed for the highest dose of about 100 eV per carbon atom the formation of polycyclic aromatic hy-

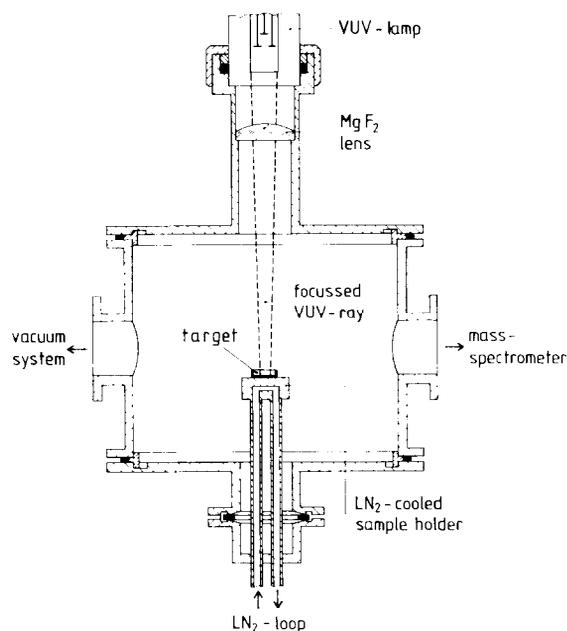


Fig. 1. Scheme of the VUV irradiation chamber.

Table 2  
Results of analysis of some organic refractories and polymers irradiated 6 h with VUV photons at 80K

Substance	Gas by QMS	Residues		
		Visual inspect.	FT-IR reflectance	GC/FID after heating 150°C
MgO-standard	–	no change	no change	no peaks
Naphthalene	naphthalene + fragments	no change	no change	decomposition
Kerogen	not	no change	no change	organic fragments up to C <sub>9</sub> (C <sub>6</sub> strong)
Polymethylene	not	slightly yellow –C=C–C=C–	double bonds 800–1000 cm <sup>-1</sup> vinyl-type	organic fragments up to C <sub>6</sub>
Polyethylene	C <sub>3</sub> , C <sub>4</sub> , C <sub>5</sub> -species	slightly yellow –C=C–C=C–	double bonds 800–1000 cm <sup>-1</sup> vinyl-type	organic fragments up to C <sub>6</sub>
Polyoxymethylene	CO, HCO CH <sub>2</sub> O, HCOOH, CH <sub>3</sub> OH, H <sub>2</sub> CO <sub>2</sub> , CH <sub>3</sub> O HO–CH <sub>2</sub> –O, HO–CH <sub>2</sub> –O–CH <sub>2</sub> , HO–CH <sub>2</sub> –O–CH <sub>2</sub> –O, CH <sub>3</sub> –O–CH <sub>2</sub> , CH <sub>3</sub> –O–CH <sub>2</sub> –O–CH <sub>2</sub> ,	slightly yellow	new $\nu(\text{C}=\text{O})$ → esters	decomposition

drocarbons. Naphthalene, anthracene, tetracosane and androstane suffered a general radiolytic decrease of the intensity of all IR-bands, however did not show the formation of new band systems. The gases evolved after heating at 150°C consisted of hydrocarbons, in the case of PM with max five carbon atoms per molecule. The fragments from the other substances

contained ten and more carbons. Fig. 4 shows details of gas chromatograms of polyethylene and naphthalene. It can be seen that the products in the two cases are quite different, showing a greater complexity for naphthalene. The products induced by 17 MeV protons consist in both cases of few, relatively discrete peaks as majority components. These are linear

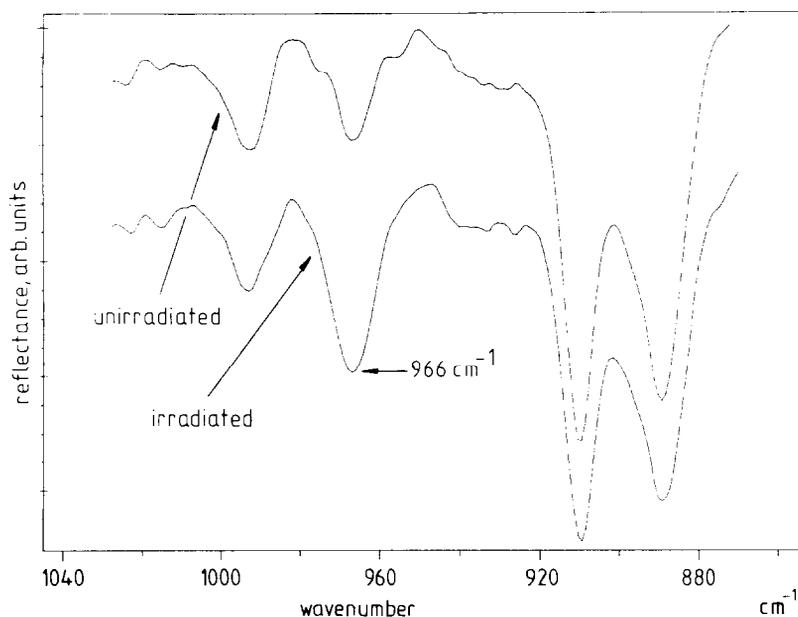


Fig. 2. FT-IR spectrum in diffuse reflectance of polyethylene irradiated at 80 K for 6 h with VUV photons.

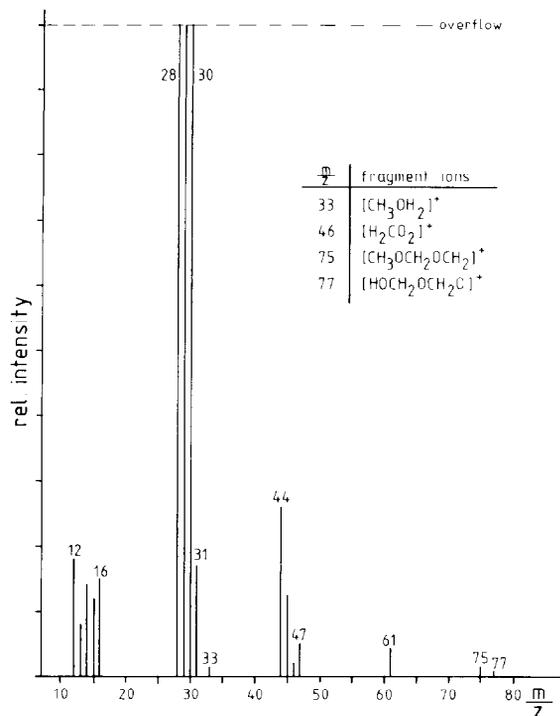


Fig. 3. Quadrupole mass spectrum of polyoxymethylene after 6 h irradiation with VUV-photons at 80 K in the warm-up phase at 250 K ( $p = 7 \times 10^{-7}$  mbar).

aliphatic compounds such as pentane, hexane, etc., with a lower background of branched and cyclic compounds. The  ${}^3\text{He}^{2+}$  ions gave rise in both cases to an increased background of complex products, most probably including cyclic compounds, but no specific majority component.

#### 4. Discussion

VUV irradiation of solid hydrocarbons creates fragments up to  $\text{C}_6$  and double bond structures in the polymer residues. The mechanisms of these processes are well understood and described in literature (e.g. refs. [8,9,17]). Kerogen, PM and naphthalene seem to be rather stable against photolysis, even at the high

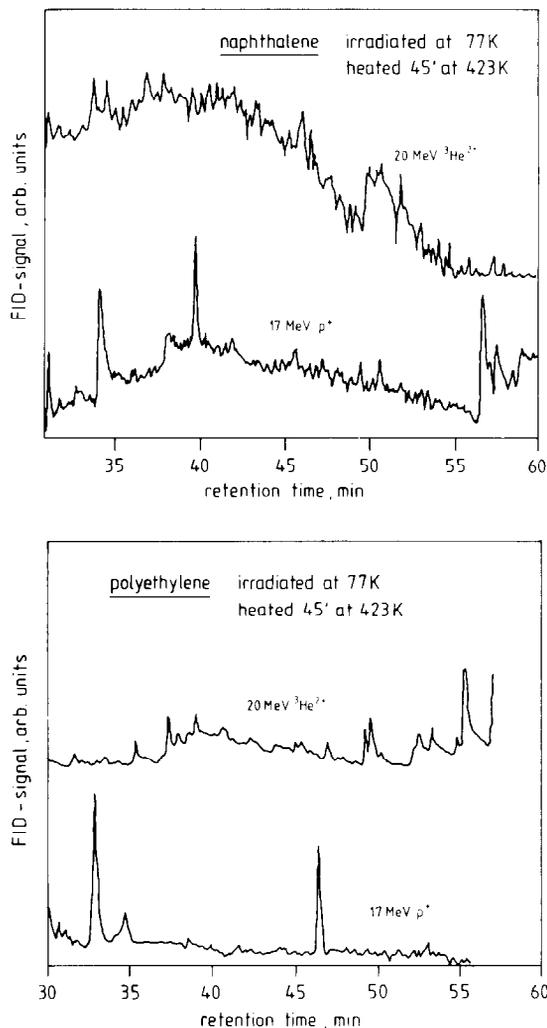


Fig. 4. Gas chromatograms (details) of gases emanating at 150°C out of polyethylene and naphthalene irradiated at 80 K for 10 min with  $2 \mu\text{A cm}^{-2}$  17 MeV p and for 30 min with  $2 \mu\text{A cm}^{-2}$  20 MeV  ${}^3\text{He}^{2+}$ .

doses applied. The most sensitive substance was POM. The presence of the ester of formic acid  $\text{HCOOR}$  can be considered as an intermediate step in the formation

Table 3

Preliminary results of analysis of organic refractories and polymers irradiated with 17 MeV protons and 15–20 MeV  ${}^3\text{He}^{2+}$  ions at 80 K

	Residues by FT-IR and Raman	Gas evolved after 45' at 150 K $\rightarrow$ GC/FID
Polymethylene	no change	few fragments $\leq \text{C}_5$
Polyethylene	PAHs <sup>a</sup> , amorphous carbon <sup>a</sup>	fragments $\geq \text{C}_{10}$
Naphthalene	general radiolysis, no specific new peaks	fragments $\geq \text{C}_8$
Anthracene	general radiolysis, no specific new peaks	fragments $\geq \text{C}_8$
Androstane	general radiolysis, no specific new peaks	fragments $\geq \text{C}_8$
Tetracosane	general radiolysis, no specific new peaks	fragments $\geq \text{C}_8$

<sup>a</sup> At  ${}^3\text{He}^{2+}$  irradiation and  $D^* \geq 100$  eV per carbon atom.

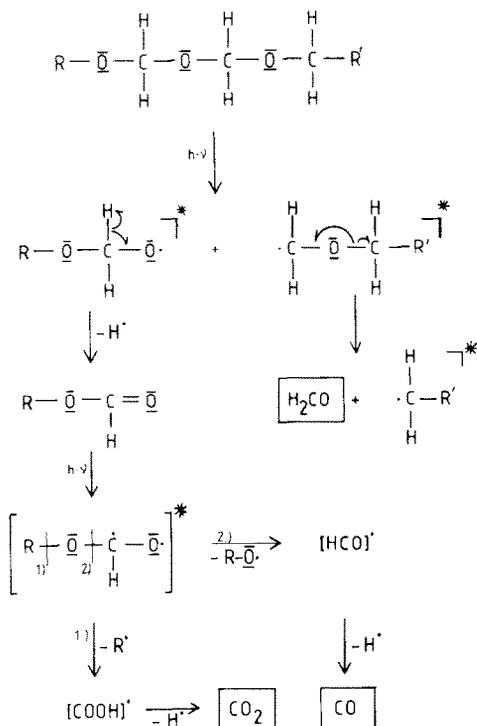


Fig. 5. Scheme of photolytic cleavage of POM.

of CO and CO<sub>2</sub> such as described in fig. 5.  $\alpha$ -cleavage of the ester leads to  $\cdot COOH$  radicals and finally to CO<sub>2</sub>,  $\beta$ -cleavage in a kind of Norrish I reaction to  $\cdot CHO$  and CO. The CH<sub>3</sub>O-terminal group may be due to H radical attack to  $\cdot CH_2-O-R$ . VUV photolysis leads to scission of bonds and local reactions, but not to the buildup of new complex units. The formation of hot hydrogen atoms with energies in the 1–2 eV range by photodissociation leads to local changes of pre-existing fragments. Only few hot carbons are formed and their concentration within the activated spot induced by one photon is too low to trigger the multicenter reaction which was recently discussed for the collision cascades by energetic ions [11–14,18]. Despite the high overall dose, the linear energy transfer is rather small:  $L_T = 5$  to  $10 \text{ eV } \mu\text{m}^{-1}$ . This is different for MeV ions. 17 MeV protons show a  $L_T$  value in the order of  $2 \text{ keV } \mu\text{m}^{-1}$ , 20 MeV  $^3\text{He}^{2+}$  ions a value of about  $10 \text{ keV } \mu\text{m}^{-1}$  for most of the organic solids [13]. The high density of radiolytic damage and the presence of hot carbon atoms from knock on processes with energies exceeding some eV may lead to the multicenter reactions. Thus, synthesis of new and complex compounds can compete with pure radiolytic fragmentation. The protons create fragments or products containing more than eight carbon atoms. 20 MeV  $^3\text{He}^{2+}$  ions lead to the formation of a wild set of high molecular products including polycyclic aromatic structures. This is due to the higher energy density in the cascades, even if the

overall dose is lower than in the case of VUV irradiation. Obviously, low doses of heavy ions can induce more changes than high doses of light particles or electromagnetic radiation.

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