

Emission of organic products from the surface of frozen methane under MeV ion irradiation

R.I. Kaiser, R.M. Mahfouz¹ and K. Roessler

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

10 μm layers of CH_4 freshly condensed onto a cold finger at 10–15 K were irradiated with 10–20 MeV protons and $^3\text{He}^{2+}$ ions. The gases emitted during irradiation and successive warming to ambient temperature were monitored by quadrupole mass spectrometry (QMS). C_2H_2 and C_2H_4 were the primary volatile products at low temperatures. They were converted with increasing irradiation time and dose into C_2H_6 , C_3H_6 and heavier hydrocarbons up to C_8 . During the warmup phase even more complex hydrocarbons up to C_{12} were emitted including substituted benzenes (xyloles), naphthalene derivatives and anthracene and/or phenanthrene. The preferential formation of unsaturated compounds in the first reaction steps underlines the role of hot carbon atoms in the radiation induced complexation of solid organic matter, starting with their insertion into C–H bonds. The interaction of cosmic rays with organic solids in space includes these suprathreshold reactions as one of the most prominent processes.

1. Introduction

Frozen CH_4 serves as a deliberately simple model substance for organic solids to study the radiation induced buildup of complex molecules such as e.g. in chemical evolution in space [1,2]. It is well known that irradiation of gaseous or solid methane creates a variety of hydrocarbons [3–11]. Two mechanistic approaches compete: (1) ion-molecule reactions [5,9,12] and (2) hot (suprathreshold) carbon insertion into C–H bonds [2–4,6,8,10,11,13]. The observation of polycyclic aromatic hydrocarbons [8,10,11] led to the postulate of a multicenter reaction within the collision cascade of an energetic ion. Hot carbon and hydrogen atoms, formed by knockon, as well as CH , CH_2 and CH_3 radicals should cooperate in a concerted reaction to form larger units. Electron irradiation or VUV photolysis do not lead to complex products [14]. The intermediate formation of excited methylcarbene [CH_3CH]* by insertion of hot carbon into the C–H bond plays a central role. Recent experiments in solid methane at 77 K used 20 MeV $^3\text{He}^{2+}$ ions from a cyclotron, closed metal cuvettes in a cryostat for the CH_4 [7,8,10] and chromatographic techniques for the analysis (GC, HPLC). In this work, a new approach is made with CH_4 frozen onto a cold finger at 10 K in vacuum. The previous experiments represent chemical reactions in

the bulk of frozen organic solids, the present ones the reactions at or near the surface.

This paper concentrates on a study of the emission of volatile organic products during the irradiation at low temperatures and in the warmup phase to ambient temperature. An important issue of this work is the study of the effects of deposited energy density. Linear energy transfer L_T can be changed from 180 to 10810 $\text{eV } \mu\text{m}^{-1}/\text{CH}_4$ using MeV protons and $^3\text{He}^{2+}$ ions, diluting the CH_4 in one set of experiments by argon. A parallel paper [13] treats the analysis of the solid residues. It should be mentioned that the study of the fundamental mechanisms of complexation of organic matter is not only important for space chemistry e.g. for the problem of formation of PAHs [15], but also for the formation of amorphous hydrogenated carbon layers a-C:H in practical technological application [16].

2. Experimental

Methane and argon were obtained with 99.9995% and 99.999% purity from Messer Griesheim. For matrix isolation of CH_4 they were mixed in the ratio 12 Ar (96 mbar) to 1 CH_4 (8 mbar) in a special gas mixing chamber. The gases were condensed onto a 15 K cold finger mounted onto a bath cryostat [11]. The condensation proceeded with a rate of $145 \mu\text{mol h}^{-1}$ as monitored by Fourier transform infrared spectroscopy: ν_{as} and δ_{as} features were integrated in absorbance from

¹ On leave from Chemistry Department, Assuit University, Egypt.

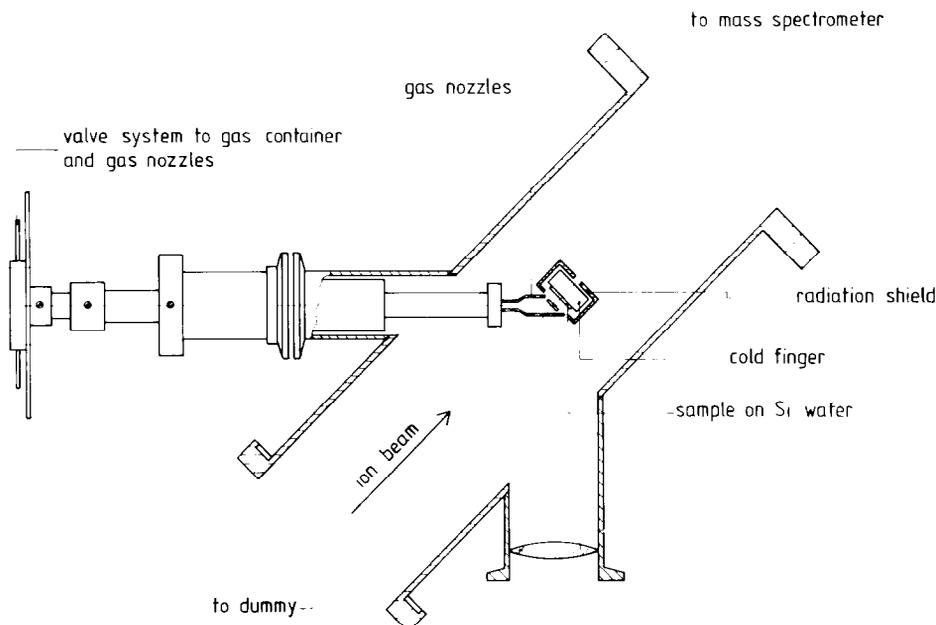


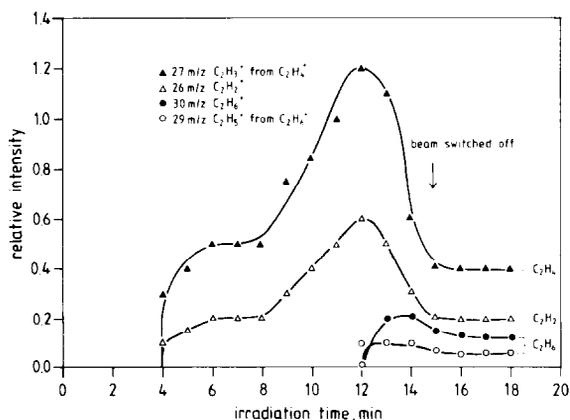
Fig. 1. Schematic view of the irradiation arrangement.

3149–2949 cm^{-1} and 1349–1249 cm^{-1} respectively and thickness was calculated using integrated absorbance coefficients $A(\nu_{\text{as}}) = 193500 \text{ cm}^{-2}$ and $A(\delta_{\text{as}}) = 129700 \text{ cm}^{-2}$ [17]. The basic vacuum of 10^{-7} mbar (by a turbomolecular pump) was reduced to 2×10^{-5} mbar during condensation. $11.3 \pm 0.5 \mu\text{m}$ layers of frozen CH_4 , and $9.6 \pm 1.7 \mu\text{m}$ of the Ar/ CH_4 mixture containing $1 \pm 0.2 \mu\text{m}$ CH_4 were formed. Fig. 1 shows the schematic view of the irradiation apparatus. The cold finger carried a 2 cm^2 large (111) Si wafer as a substrate for the condensate. The gases were provided by a system of gas nozzles [2,11]. The 17.6 MeV p and 16.9 MeV $^3\text{He}^{2+}$ ions from the CV 28 compact cyclotron of Forschungszentrum Jülich delivered between 0.02 and 0.12 MeV to the gas condensates before being stopped in the cold finger. All parts viewed by the ion beam were made of pure AlMg3F18 in order to avoid the generation of long lived radioactivities. The beam currents used were 0.25 and $0.5 \mu\text{A cm}^{-2}$. The irradiation times varied from 5 to 90 min giving rise to doses between 0.07 and 16.8 eV per carbon atom. During irradiation the temperature of the sample increased up to 45 K.

A quadrupole mass spectrometer of Balzers was mounted behind the cold finger and measured the volatile gases emanating from the samples during irradiation and in the warmup phase to room temperature (ca. 10 h with heating rates between 0.1 and 0.5 K min^{-1}).

3. Results

The mass spectra taken during irradiation show signals from $1 \leq m/z \leq 113$. Among the species containing one carbon atom, $m/z = 14$ [CH_2] $^+$ is stronger than 16 [CH_4] $^+$. $m/z = 13$ [CH] $^+$ and 15 [CH_3] $^+$ show only weak intensity. Molecules with two carbon atoms such as in $m/z = 26$ [C_2H_2] $^+$, 27 [C_2H_3] $^+$ (fragment from C_2H_4^+), 29 [C_2H_5] $^+$ (fragment from C_2H_6^+) and 30 [C_2H_6] $^+$ were detected with lower yields than the C_1 species. Figs. 2 to 4 show the time dependence of the intensity of mass peaks of C_2 -species. In proton

Fig. 2. Time resolved mass peaks from a 17.6 MeV proton irradiation ($0.25 \mu\text{A cm}^{-2}$) of Ar/ CH_4 (12:1) at 15 K.

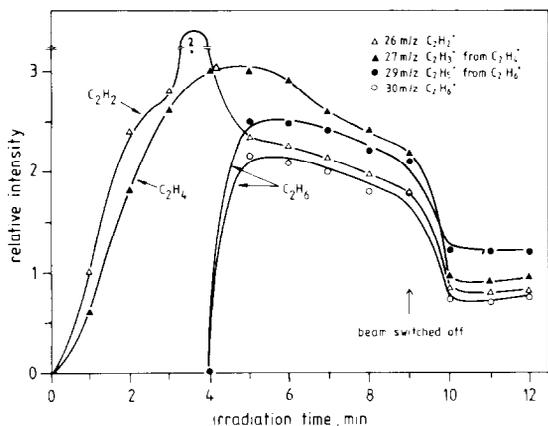


Fig. 3. Time resolved mass peaks from a 17.6 MeV proton irradiation ($0.25 \mu\text{A cm}^{-2}$) of CH_4 at 15 K.

irradiated Ar/ CH_4 (fig. 2) C_2 species were liberated 4 min after start of irradiation. C_2H_4 shows higher intensity than C_2H_2 . Both peaks follow a similar time dependence. They increase till about 12 min after start. At this time the C_2H_6 signal appeared at the extent of C_2H_2 and C_2H_4 . Pure CH_4 ice showed a liberation of C_2H_2 and C_2H_4 shortly after the start of proton irradiation (fig. 3). At the beginning, C_2H_4 is somewhat more intense than C_2H_2 but decreases rapidly when at about 5 min the C_2H_6 peak shows up. The intensities of all peaks show a broad plateau till switchoff. The $^3\text{He}^{2+}$ ion irradiation of pure CH_4 ice (fig. 4) yielded very intense peaks that the QMS was overflowed. After switching off the beam, all three systems showed weaker signals of a slow outdiffusion. It can be seen that the intensity of the signals increased drastically when going from p//Ar/ CH_4 to p// CH_4 and $^3\text{He}^{2+}$ // CH_4 systems. When integrating the yields of the products from figs. 2 and 3, a

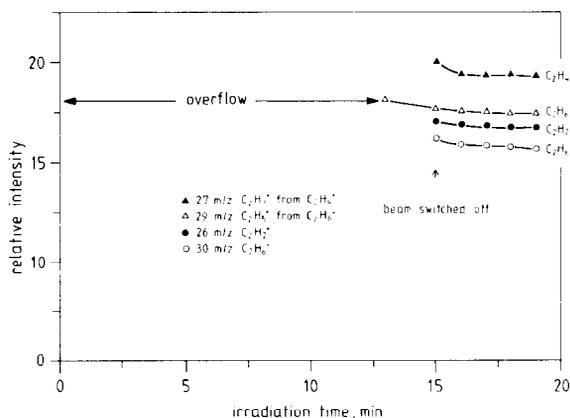


Fig. 4. Time resolved mass peaks from a 16.9 MeV $^3\text{He}^{2+}$ irradiation ($0.25 \mu\text{A cm}^{-2}$) of CH_4 at 15 K.

$\text{C}_2\text{H}_4/\text{C}_2\text{H}_2$ ratio of 2.25 was obtained for p//Ar/ CH_4 and one of 0.98 for p// CH_4 .

Much less intensive than the signals of the two carbon containing species were those for three carbon containing and heavier molecules. They were detected only in later stages of the irradiation and in the warmup phase. Among them are linear alkanes from propane ($m/z = 29, 28, 37, 44, 43, 39, 41, 42$ with decreasing intensity) to octane ($m/z = 113$). Furthermore cyclopropane or propene (C_3H_6 , $m/z = 42, 44$) and allene or propine (C_4H_4 , $m/z = 40$) were observed. Higher alkenes and alkadiens were also found ($m/z = 111, 97, 95, 83, 81, 71, 69, 55$).

During warmup all peaks showed a strong increase and heavier ions up to $m/z = 178$ were observed. Among the species additionally liberated from the ice were linear alkanes up to dodecane $m/z = 169$ [$\text{C}_{12}\text{H}_{25}$] $^+$ and linear alkenyl and alkadienyl species up to $m/z = 165$ [$\text{C}_{12}\text{H}_{21}$] $^+$.

Signals of $m/z = 91$ and 105 are attributed to mono- and disubstituted benzenes, [C_7H_7] $^+$ and [C_8H_9] $^+$ resp., those at $m/z = 130$ and 104 to 1,4-dihydronaphthalene, those at $m/z = 132$ to 1,2,3,4-tetrahydronaphthalene and finally that at 178 to anthracene or phenanthrene.

4. Discussion

The mass spectra recorded during irradiation demonstrate one of the most important differences of the open target versus the closed cuvettes [7,8], i.e. the outdiffusion of H_2 , CH_2 , CH_4 , etc. which accelerates the transformation of CH_4 into higher molecular units. Data on diffusion of the observed species under the present conditions are not available in literature. Thus, a quantitative evaluation of the mass spectra is not possible. However, the qualitative information is valuable enough. The correlation of the two carbon containing products in figs. 2 and 3 shows clearly that C_2H_2 , C_2H_4 and C_2H_6 depend on the same precursor, i.e. excited methylcarbene [$\text{CH}_3\text{-CH}$] * formed by insertion of hot carbon into CH_4 . If CH_2 insertion would compete, the C_2H_6 peak should appear at the very beginning of the irradiation when CH_2 signal is strongest. CH_2 is formed via successive hydrogen abstraction by hot carbon atoms or radiolysis of CH_4 . It seems, however, to be thermalized soon. Thus, it might be too inactive for insertion. C_2H_6 is formed only when the hydrogen concentration is high enough for H-pickup by thermalized methylcarbene. Additionally, the yield of C_2H_6 increases at the extent of the unsaturated two carbon species. This underlines the role of methylcarbene as the intermediate for saturated and unsaturated two carbon containing products. Recombination of CH_3 radicals to C_2H_6 can be neglected

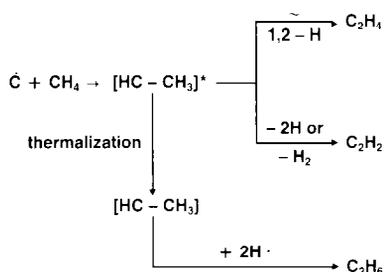


Fig. 5. Basic processes in the formation of two carbon containing species by hot carbon in the solid state.

because they were detected at minor concentrations by QMS. Furthermore, CH_3 is only mobile at temperatures > 100 K, thus, recombination cannot take place. Fig. 5 presents an overview on the basic processes. In contrast to the synthesis of ethane in the solid state, C_2H_6 can be formed in the gas phase by insertion of CH_2 in a C-H bond of CH_4 [6].

Another interesting fact is that the intensity of C_2H_4 is higher than that of C_2H_2 in Ar/ CH_4 system. Integrated yields calculated from the values in figs. 2 and 3 give C_2H_4/C_2H_2 ratios of 2.25 for proton irradiated Ar/ CH_4 and 0.98 for the system p// CH_4 . In the matrix isolated case the $[CH_3-CH]^*$ intermediate prefers 1,2-H-rearrangement before elimination to C_2H_2 occurs. The larger lattice constant of argon may provide an increased free volume for methylcarbene and the positive activation volume for H-migration followed by deexcitation.

Higher molecular species are formed by longer irradiation times, i.e. doses from 0.5 eV per carbon atom on. Cyclic and polycyclic products are favoured with increasing energy density in the series p//Ar/ $CH_4 < p//CH_4 < ^3He^{2+}/CH_4$ with $L_T = 160 < 1800 < 10810$ eV $\mu m^{-1}/CH_4$, respectively, cf. refs. [11,13].

The experiments demonstrate the validity of the hot (suprathedral) carbon approach for MeV ion irradiation of simple organic solids.

Acknowledgements

One of the authors (R.M.M.) is indebted to Internationales Büro of Forschungszentrum Jülich for a grant.

The authors thank Mr. E. Biel for experimental assistance, Prof. Dr. G. Stöcklin for helpful discussions and the CV 28 cyclotron crew for the irradiations.

References

- [1] G. Strazzulla and R.E. Johnson, in: Comets in the Post-Halley-Era, eds. R.L. Newburn et al. (Kluwer, Dordrecht, 1991) p. 243.
- [2] K. Roessler, in: Solid State Astrophysics, eds. E. Bussoletti and G. Strazzulla (North-Holland, Amsterdam, 1991) p. 197.
- [3] C.F. MacKay and R. Wolfgang, J. Am. Chem. Soc. 83 (1961) 399.
- [4] G. Stöcklin, H. Stangl, D.R. Christman, J.B. Cumming and A.P. Wolf, J. Phys. Chem. 67 (1963) 1735.
- [5] D.R. Davis, W.F. Libby and W.G. Meinschein, J. Chem. Phys. 45 (1966) 4481.
- [6] G. Stöcklin, Chemie heisser Atome (Verlag Chemie, Weinheim, 1969).
- [7] A. Patnaik, K. Roessler and E. Zádor, Adv. Space. Res. 9 (6) (1989) 49.
- [8] A. Patnaik, K. Roessler and E. Zádor, Radiochim. Acta 50 (1990) 75.
- [9] N.J. Sack, R. Schuster, A. Hofmann, A. Khedim and R. Koppmann, Ap. J. 360 (1990) 305.
- [10] K. Roessler, G. Eich, A. Patnaik and E. Zádor, Lunar Planet. Sci. Conf. XXI (1990) 1035.
- [11] R.I. Kaiser, Report Jül-2492, Forschungszentrum Jülich (1991) p. 130.
- [12] W.W. Duley and D.A. Williams, Interstellar Chemistry (Academic Press, London, 1984).
- [13] R.I. Kaiser, J. Lauterwein, P. Müller and K. Roessler, these Proceedings (6th Int. Conf. on Radiation Effects in Insulators, Weimar, Germany, 1991) Nucl. Instr. and Meth. B65 (1992) 463.
- [14] R.M. Mahfouz, M. Saver, S.T. Atwa, R.I. Kaiser and K. Roessler, these Proceedings (6th Int. Conf. on Radiation Effects in Insulators, Weimar, Germany, 1991) Nucl. Instr. and Meth. B65 (1992) 468.
- [15] K. Roessler, in: Polycyclic Aromatic Hydrocarbons and Astrophysics, eds. A. Léger et al. (Reidel, Dordrecht, 1987) p. 173.
- [16] K. Roessler and E. Eich, E-MRS Meeting June 1987, vol. XVII (Editions de Physique, Paris, 1987) p. 167.
- [17] J. Pearl, M. Ngoh, M. Ospina and R. Khanna, J. Geophys. Res. 96 (1991) 477.