

CURRENT DENSITY EFFECTS AND THE IMPORTANCE OF CHARGE TRANSFER PROCESSES IN THE RADIOLYSIS OF METHANE: ASTROPHYSICAL IMPLICATIONS

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ABSTRACT

In order to get information about the influence of irradiation parameters and the addition of inert gases in radiolysis processes of astrophysical interest, methane gas targets were irradiated with 6.5 MeV protons at a pressure of 1 bar and room temperature. The yields for higher hydrocarbons like ethane or propane were obtained by gas chromatography analysis of irradiated gas samples. A series of experiments was performed adding inert gases like helium, argon, or nitrogen in various quantities to the methane gas. Charge transfer reactions were found to play an important role in the reactions induced by the irradiation. Current density and total absorbed dose were also proved to have large influence on the yields of produced hydrocarbons. Estimations of electron, ion, and radical densities are made, leading to an understanding of the reaction mechanism and comparisons to other rate coefficients are given. The relevance of the investigations for the chemistry and the simulation of various astrophysical systems is given.

Subject headings: laboratory spectra — molecular processes

I. INTRODUCTION

The chemical evolution of primitive gas mixtures under the influence of ionizing radiation is an important subject in cosmic chemistry (Draganic, Draganic, and Vujosevic 1984). The atmospheres of planets and their satellites contain primitive gases like methane, carbon dioxide, nitrogen, and argon as well as higher hydrocarbons, amines, or alcohols (Atreya 1986). The latter substances are produced in chemical reactions initiated by UV photons or by MeV protons and electrons (Khare *et al.* 1986). Similar processes occur in interstellar clouds under the influence of galactic cosmic rays or UV radiation (Herbst 1985; van Dishoeck 1986), and even in the solid state as cometary matter may have changed its composition under the influence of cosmic radiation (Moore *et al.* 1983; Johnson *et al.* 1987).

Various simulation experiments have been carried out to investigate these processes (for references see Sack 1989). However, the parameters appropriate for astrophysical systems, such as temperature, pressure, or radiation flux are often not well known or difficult to simulate in laboratory experiments. Sometimes these parameters vary strongly in a single object e.g., the pressure and the particle flux in the atmosphere of Jupiter at different heights (Atreya 1986). Hence an understanding of the effect of these parameters on radiolysis processes is important. Therefore the aim of the investigations described in this paper was not the exact simulation of an astrophysical system. Rather, we concentrated on investigating the influence of the total absorbed dose and the current density on the induced reactions and the reaction products. In order to get information about certain reaction pathways we also

studied the radiolysis of mixtures of gaseous methane with inert gases at room temperature.

II. EXPERIMENTAL DETAILS

a) Apparatus

Two different reaction vessels were used: In vessel I, shown in Figure 1 the influence of the addition of an inert gas to a methane target on the composition of the gas mixture after irradiation was studied. It consists of a Duran glass tube (1: 120 mm; ϕ : 43 mm), each side of which is closed with teflon flanges sealed with viton packing rings. The 6.5 MeV protons provided by the Erlangen Tandem-Van de Graaff accelerator enter the vessel through a window consisting of a 25 μ m capton foil. The protons leave the vessel through a 25 μ m capton foil after depositing 0.7 MeV in the gas. There are two feed throughs for gas inlet and outlet and two feed throughs with septums. This enables gas samples to be obtained with a gas-tight syringe. The proton current of ~ 330 nA was measured by an external Faraday cup. This current is amplified by an electrometer amplifier and integrated by a target current integrator to obtain the total absorbed dose. The cross section of the beam was constant within 20%. The reaction gases were mixed in a separate gas mixing device. The mixing vessel (volume: 2l) is evacuated to a pressure less than 10^{-3} mbar. Then the mixing vessel is filled with the reaction gases. Their partial pressure is measured by a semiconductor pressure sensor (Siemens KPY 14). After evacuation of the gas target to less than 10^{-4} mbar in order to remove gas and water contamination, it is filled with the reaction gas mixture; the pressure is adjusted to 1 bar. After every experiment the reaction vessel was cleaned in an acetone ultrasonic bath, dried, and afterward evacuated for ~ 30 minutes.

Reaction vessel II shown in Figure 2 was used to measure dependencies of the amounts of products on irradiation

¹ This paper is dedicated in memory of Alfred Hofmann. We regret his untimely death in 1989 February.

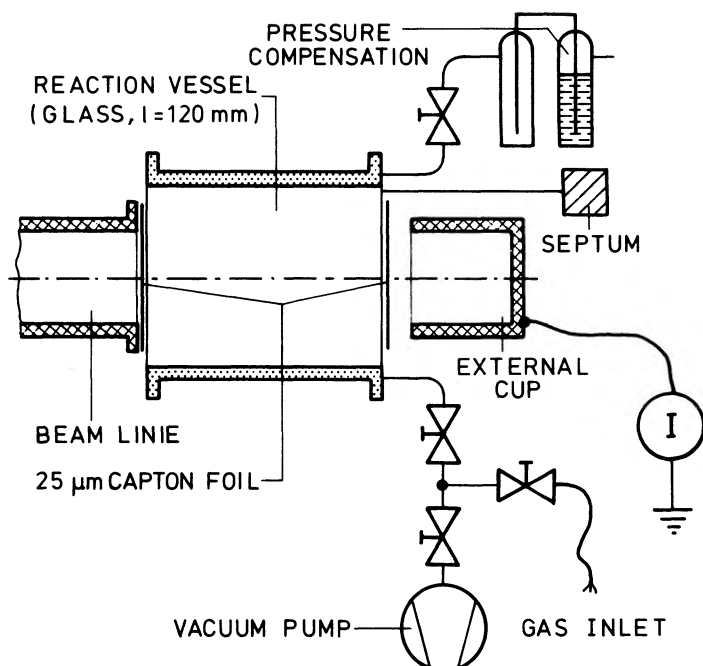


FIG. 1.—Experimental arrangement I

parameters like total absorbed dose and current density. To obtain high absorbed doses per target molecule at short irradiation times the volume of this vessel was minimized to ~ 7.5 ml. The short length of 4 cm results in a very sharp distribution of current density because the angular straggling of the proton beam in the reaction gas can be neglected. As described in § IIc the material of the wall of the vessel has no measurable influence on the composition of the gas mixture after irradiation, therefore, vessel II was made of stainless steel. The vessel has two windows of $25\ \mu\text{m}$ capton foil through

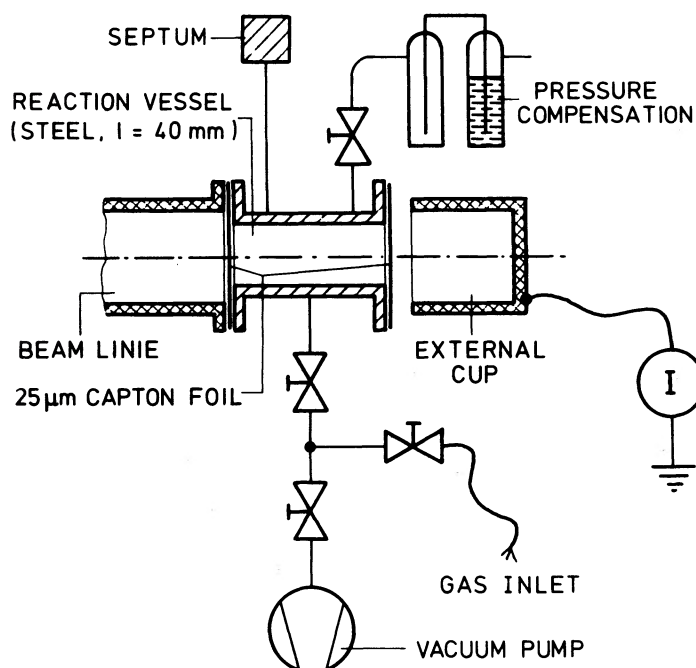


FIG. 2.—Experimental arrangement II

which the 6.5 MeV protons enter or leave the gas target depositing 0.24 MeV per proton. The foils are sealed with viton packing rings. It also has two feed throughs for gas inlet and outlet and another closed with a septum to take gas samples by a gas tight syringe.

In addition, two circular apertures with a diameter of 2 mm were used to define the cross section of the proton current. The first aperture is divided into four segments. On each segment the proton current is measured. Then the position of the proton beam is adjusted such that the same proton current is measured on each of the segments. This guarantees that the proton beam was concentric with the aperture system. By varying the focus of the beam the sum of the current on the segments was adjusted to $\sim 30\%$ of the target current measured by the external cup. The current density of the proton beam in the reaction gas was proved to be constant over the cross section of $3\ \text{mm}^2$ by scanning the beam.

b) Analysis by Gas Chromatography

Radiolysis of gases containing methane results in the formation of various saturated and unsaturated hydrocarbons. Hence gas chromatography was chosen as the method for analysis since it is very sensitive and allows the separation of complex gas mixtures. Immediately after the irradiation a gas sample of $400\ \mu\text{l}$ was taken with a gas-tight syringe and analyzed. A Packard model 427 gas chromatograph equipped with a Chrompak Hayesep Q column ($l = 2\ \text{m}$) was used. The carrier gas was helium with a flow of 30 ml per minute. The substances were detected by a flame ionization detector. In order to optimize the separation of the substances a temperature gradient program was applied (temperature interval: $50\text{--}200^\circ\text{C}$; temperature rise: 5°C per minute). For calibration various external gas standards were used.

c) Reproducibility and Error Estimation

The reproducibility of the product yields is determined by the errors of the total absorbed energy, incorrect partial pressures of the target gases and the reproducibility of the GC analysis. In a series of 10 irradiations of methane with a beam current of 330 nA and a total absorbed energy of 75 meV per target molecule the standard deviation for the main products of the radiolysis was found to be less than 10%. The accuracy of the mixing ratio of the reaction gases in the gas mixing device is especially important for experiments dealing with addition of inert gases. By the use of the semiconductor pressure sensor this error is confined below 5%.

The identification of the products was performed by the use of calibrated standards of hydrocarbons up to a chain length of five carbon atoms. They were supplied by Chromopack. The peaks of saturated and unsaturated hydrocarbons with up to three carbon atoms were separated, except ethene and ethyne, which overlapped. Amines and nitriles did not influence the identification of these substrates. Butane and pentane isomers could not be identified in detail. Hence the different peaks of their isomers are numbered. The yields are calculated using the calibration factors of *n*-butane and *n*-pentane, respectively.

For the radiolysis methane 2.5, nitrogen 5.0, helium 5.0, and argon 5.0, supplied by Linde AG were used. Besides the methane, the gases have no measurable contamination. Methane was contaminated by 740 parts per million (ppm) ethane and ethyne, but this contamination can be neglected when compared with the amount of ethane of 23,000 ppm, produced, e.g., on irradiation of methane with a total deposited

energy of 75 meV per target molecule. The influence of the walls of the vessel on the yields of products was tested with experimental setup I. Plates of glass, teflon, stainless steel, and aluminum with $65 \times 20 \text{ mm}^2$ area were placed inside the vessel; the distance to the beam was 12 mm. In no case did these plates influence the yields of the produced gaseous hydrocarbons.

Furthermore the temperature of the irradiated gas was measured at different distances from the beam in vessel I using a Phillips 6442A/00 thermocouple with a very low heat capacity. At 0.5 minute after the beginning of the irradiation of methane with a proton current of $1 \mu\text{A}$ the thermocouple reached the equilibrium temperature. At 1 mm from the beam the gas temperature adjusted to 33°C . At 5 mm and 10 mm the equilibrium temperature was 32°C and 31.8°C . This small temperature gradient and the low absolute temperature of the gas despite a power of 0.5 W is evidence for the presence of considerable convection inside the reaction vessel.

Finally, with a modified vessel I gas samples were taken at different distances from the beam directly after 50 s irradiations of methane. The measured yields of hydrocarbons were independent of the position of the syringe. Hence the products are distributed homogeneously in the vessel.

III. RESULTS

a) Irradiation of Methane

Reaction vessel I was used for the irradiation of methane with 6.5 MeV protons. The proton current was $1 \mu\text{A}$; this is equivalent to a current density of $14 \mu\text{A cm}^{-2}$. As the irradiation time was 27 minutes the total absorbed energy can be calculated to 7 eV per target molecule. This very high dose was applied in order to detect very large molecules like benzene which are produced in small concentrations. Only in this experiment a more sophisticated GC analysis than the method described above was performed. Experimental details are described in Rudolph, Johnen, and Khedim (1986).

Various hydrocarbons were detected in the irradiated gas sample: they are depicted in Table 1. Most products are saturated hydrocarbons. By comparing, e.g., *n*-hexane and benzene, a preference for the production of aromatic hydrocarbons can be seen.

TABLE 1

YIELDS OF PRODUCTS IN ppm	
Products	Yields
Ethane	$49600 \pm 5\%$
Ethene	$492 \pm 6\%$
Ethyne	$92.0 \pm 12\%$
Propane	$7870 \pm 10\%$
Propene	$125 \pm 19\%$
<i>i</i> -butane	$987 \pm 9\%$
1-butene	$48.7 \pm 19\%$
<i>n</i> -butane	$1270 \pm 7\%$
<i>i</i> -pentane	$1070 \pm 10\%$
<i>n</i> -pentane	$114 \pm 10\%$
<i>n</i> -hexane	$7.3 \times 10^{-4} \pm 15\%$
<i>n</i> -heptane	$< 3 \times 10^{-5}$
<i>n</i> -octane	$< 3 \times 10^{-5}$
<i>n</i> -nonane	$< 3 \times 10^{-5}$
<i>n</i> -decane	$< 3 \times 10^{-5}$
Benzene	$10.0 \pm 15\%$
Toluene	$8.93 \pm 15\%$
<i>o</i> -xylene	$< 3 \times 10^{-5}$
<i>p</i> -xylene	$< 3 \times 10^{-5}$
<i>m</i> -xylene	$< 3 \times 10^{-5}$

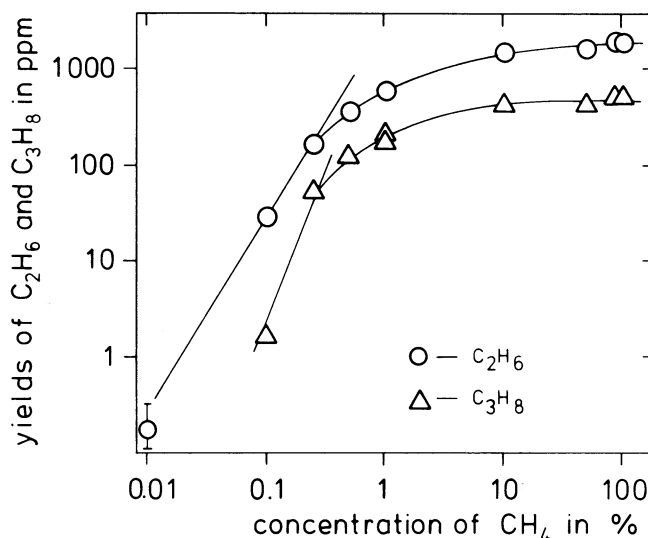


FIG. 3.—Yields of ethane and propane after irradiation of methane/argon gas mixtures; proton current: 330 nA; total absorbed energy: 75 meV per target molecule.

b) Addition of Inert Gases

In three series of experiments various quantities of the inert gases helium and argon and also nitrogen were added to the methane target. Although nitrogen may react with methane to form amines, nitrogen can be treated as an inert gas because its reactivity is extremely low, as observed in various radiolysis experiments (e.g., Schuster, Sack, and Hofmann 1989). The gas mixtures which contained between 1% and 99.99% of inert gas were irradiated with a beam current of 330 nA ($j = 4.7 \mu\text{A cm}^{-2}$). The deposited energy was adjusted to 75 meV per target molecule. The yields of ethane and propane obtained at irradiation of methane/argon mixtures are depicted in Figure 3.

The amounts of ethane produced divided by the percentage of primary methane are shown in Figure 4. The other hydrocarbons show qualitatively the same behavior.

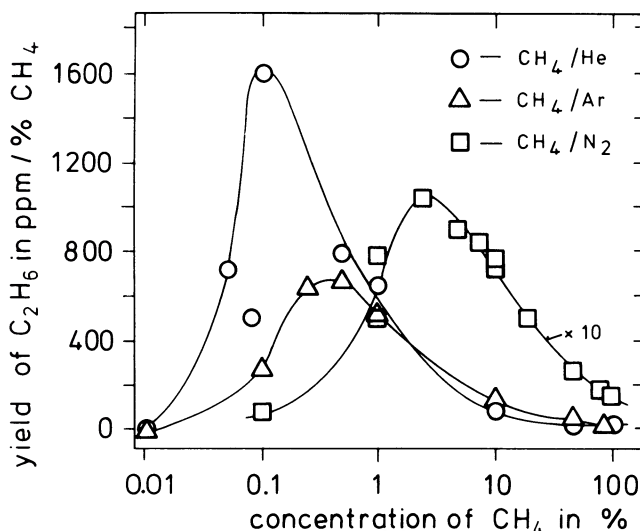


FIG. 4.—Yield of ethane divided by the methane concentration obtained from mixtures of methane with different inert gases; proton current: 330 nA; total absorbed energy: 75 meV per target molecule.

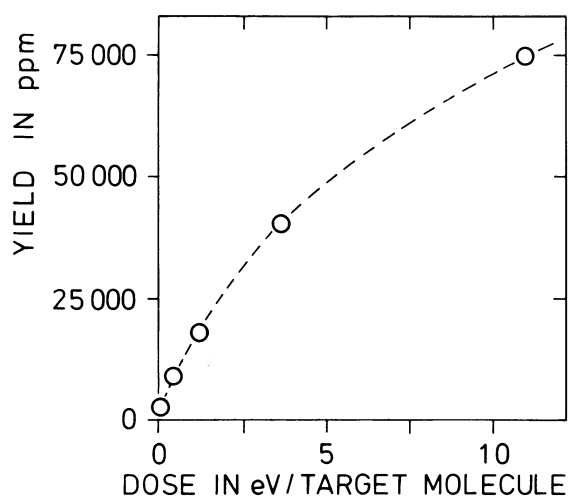


FIG. 5.—Yield of ethane dependent on the total absorbed energy after the irradiation of methane with a proton current of 200 nA.

c) Variation of Current Density and Total Absorbed Dose

In another series of experiments methane targets were irradiated with 6.5 MeV protons using different beam currents. The current was varied between 0.81 nA ($j = 0.026 \mu\text{A cm}^{-2}$) and 900 nA ($j = 29 \mu\text{A cm}^{-2}$). In addition the irradiation time was varied between 1.1 s and 121 minutes so that the total absorbed dose was varied between 1.68 and 11000 meV per target molecule. In Figure 5 the yield of ethane obtained in experiments with a constant proton current of 200 nA is shown versus the total absorbed dose. At high total absorbed doses the yield rapidly become nonlinear with increasing dose.

Figures 6–7 show the dependence of the yields of ethane, two butane isomers, and a pentane isomer on the current density for a constant dose of 136 meV per target molecule. These yields depend on the current density even at relatively low current density and the dependencies differ qualitatively for the different products. Finally, the dependence of the yield of ethane on the current density at different total absorbed energies is given in Figure 8. The yields are depicted as

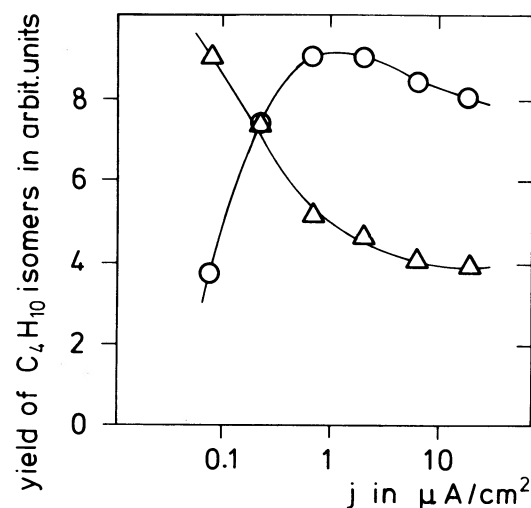


FIG. 7.—Yields of two butane isomers dependent on the current density after the irradiation of methane; total absorbed energy: 136 meV per target molecule.

G-values. They show that the dependence on the current density is qualitatively similar at different doses and that only at the very lowest dose is G independent of current density at low current densities.

IV. DISCUSSION

a) Primary Processes

Particles with nonrelativistic velocities like the 6.5 MeV protons used in our experiments, dissipate their energy into two types of inelastic processes, the ionization and the excitation of target molecules. For ionization mainly outer shell electrons of the target molecules are removed with kinetic energies up to a few keV (Wilson and Toburen 1975). These secondary electrons result in one to two further ionizations per one primary ionization (Burns and Barker 1968). For a W -value (average energy required for one ionization) of 27 eV (György and Wojnarovits 1981) and an energy loss of 57 keV cm^{-1} (Janni 1982) for 6.5 MeV protons in methane under

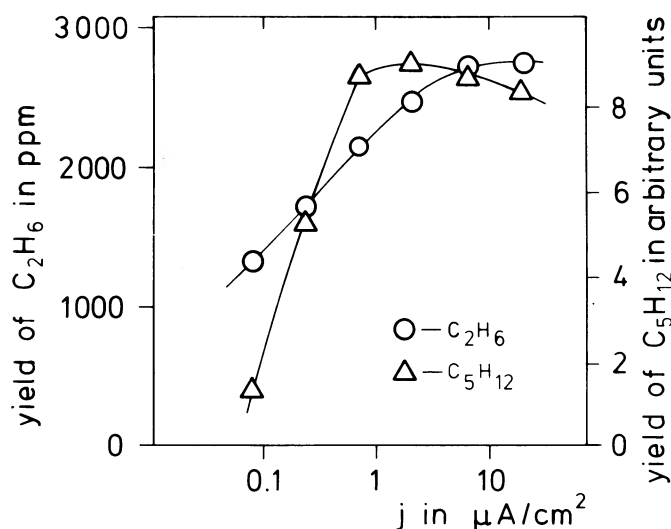


FIG. 6.—Yields of ethane and pentane dependent on the current density after the irradiation of methane; total absorbed energy: 136 meV per target molecule.

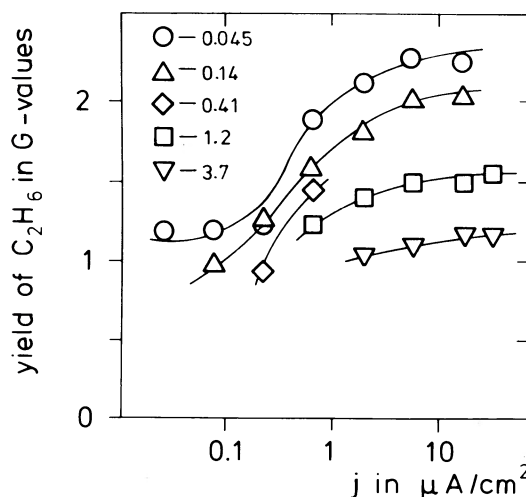


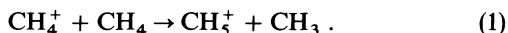
FIG. 8.—Yield of ethane after irradiation of methane as a function of current density at various total absorbed energies (in eV per target molecule).

atmospheric pressure $\sim 2 \times 10^3$ ions per cm of the proton track are produced.

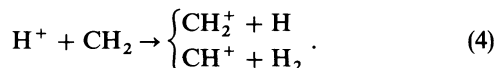
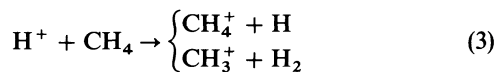
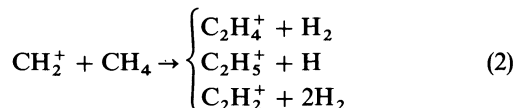
These primarily formed CH_4^{+*} undergo fragmentation mostly independent of the projectile type and energy; a typical cracking pattern is: CH_4^+ : 47%; CH_3^+ : 39%; CH_2^+ : 10%; CH^+ : 3.3%; C^+ : 0.7% (Malhi *et al.* 1987). H^+ and H_2^+ are minor products, hence many H radicals and molecular hydrogen are produced in these fragmentations. Inner shell ionization takes place in the primary processes with a probability of less than 1% for these proton energies (McElroy, Ariyasinghe, and Powers 1987). Also double ionization can be neglected compared to the outer shell processes. In addition, excitation of methane molecules can form reactive species in the target gas. However, this forms only a small fraction of the total so that the amount of radicals produced by dissociation of excited molecules can be neglected (Miller and Green 1973).

b) Principal Reaction Pathway

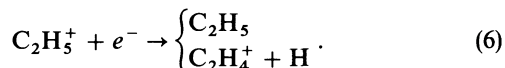
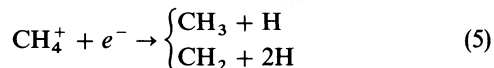
The various species produced in the primary processes mentioned above will react in a number of different ways as described, for example, in Duley and Williams (1984). Methane ions will react with target methane molecules according to



Further important ion-molecule reactions are, e.g.,

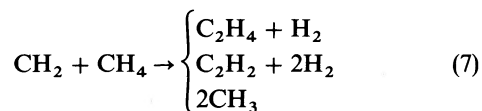


These reactions have coefficients of the order of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$. In neutralization reactions many radicals are produced:

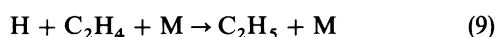
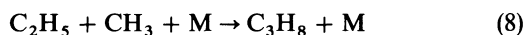


Rate coefficients of the latter reactions are of the order of $10^{-7} \text{ cm}^3 \text{ s}^{-1}$. The ionization energy deposited leads mostly to the dissociation of the neutralized ion as can be seen in equations (5)–(6).

The reactive radicals produced in primary and neutralization processes will react mainly with methane:



Also radical-radical reactions occur:



These reactions lead finally to the formation of the higher hydrocarbons (Földiák 1981). It is seen that hydrogen molecules are produced already in many ion-molecule and neutralization processes explaining its high yield in radiolysis experiments (e.g., Schuster, Sack, and Hofmann 1989).

The reactions given above can be classified in another way. There are reactions between reactive species like ions or radicals and stable target molecules. The latter are mostly methane molecules; in experiments with high total absorbed doses of radiation these may also be stable products like molecular hydrogen or ethane. Examples for these reactions are equations (1)–(3), (7). The other type are reactions among reactive species (e.g., [4]–[6] and [8]–[10]). These reactions have competitive processes: e.g., two CH_3 radicals, which are produced in reaction (5), may react to ethane (eq. [11]) or they may recombine with hydrogen atoms to form methane (eq. [12]). These reaction rates are dependent on the density of reactive species. For instance, at high radical densities various reactions among different radicals are possible, at low densities recombination processes are more probable. Another example are the neutralization reactions: because they are dependent on the electron density, they are in competition with ion-molecule reactions: e.g., equations (5) and (1). Therefore, the density of reactive species like electrons, ions, or radicals determines the importance of reactions of reactive species with target molecules, with other reactive species, and of recombination processes.

c) Addition of Inert Gases

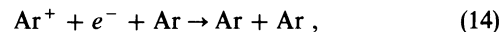
The addition of inert gases to a methane gas target, as described in § IIIb should indicate the importance of the different reaction pathways in § IVb. The curves in Figure 3 measured with a methane/argon gas mixture may be divided into three parts, where different reaction pathways are supposed to be important.

At high methane concentrations (above 5%) the yields of ethane and propane are almost independent of the methane concentration in the primary gas mixture. Energy deposited in the inert gas can be transferred to the methane molecules by charge transfer reactions:



Due to the high methane concentration and the high reaction rate coefficient, of 10^{-10} – $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Duley and Williams 1984), this reaction dominates and is not influenced by the neutralization of argon ions with electrons. The CH_4^+ ions produced in the charge transfer reactions react similar to the CH_4^+ formed by primary ionization of methane. Higher hydrocarbons may be formed after neutralization of the ions in radical reactions according to chapter 4.2. Argon atoms have only small influence on these processes.

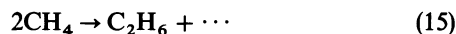
At methane concentrations between 0.1% and 5% the curve in Figure 3 has a bend. The charge transfer reactions compete with neutralization of argon ions with electrons:



this three body reaction has a atmospheric pressure rate coefficient of $1.3 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ (Mahan and Person 1963). Indeed as the electron concentration is higher than 10^{12} cm^{-3} , as will be estimated in § IVd and the neutralization coefficient is about 4 orders of magnitude higher than the coefficient for charge transfer reactions these two types of reactions can compete at a methane concentration of $3 \times 10^{16} \text{ cm}^{-3}$. This is equivalent to only 0.1% CH_4 in the primary gas mixture. This

illustrates the consistency between our results and the charge transfer and neutralization rate coefficients given in literature (e.g., Duley and Williams 1984) as well as with our estimations of electron densities (see § IVa).

Furthermore neutralization of CH_4^+ influences the formation of hydrocarbons. Due to the low-methane concentrations also the importance of radical-radical reactions is increased. At very low methane concentrations (below 0.1%) the slope of the curves in the double logarithmic depiction in Figure 3 is 2 for ethane and 3 for propane. The law of mass action implies the sum formulae:



Considering the complexity of reaction pathways which take part in the formation of hydrocarbons, this result is remarkable.

It should be noted that at methane concentrations below 0.1% a relevant amount of ions may be produced by the Jesse effect (Hurst and Klotz 1976): Not only argon ions, but also excited argon atoms transfer their energy to methane molecules and may ionize them.

The addition of nitrogen or helium instead of argon to a methane target results qualitatively in the same behavior of the ethane and propane yields. Only the negative bend of the curves is shifted toward higher and lower methane concentrations, respectively. This is depicted in Figure 4, where the yields of ethane divided by the portion of methane in the primary gas mixtures are shown for mixtures with helium, argon and nitrogen. The maximum shows the methane concentration in the primary gas mixture, where the transition between supportance of ethane formation by charge transfer reactions and its obstruction by neutralization reactions occurs.

For example due to the high-ionization potential of helium (22.5 eV), which is ~ 10 eV higher than the ionization potential of argon, charge transfer reactions between helium and methane have a reaction coefficient much higher than the one between argon and methane. In addition, the neutralization coefficient of helium ions is lower than the corresponding value of argon. Hence the competition between neutralization and charge transfer reactions occurs at lower methane concentrations; the maximum in Figure 4 is shifted to the left side. For the nitrogen/methane system just the opposite argumentation is valid. Higher neutralization coefficients and lower charge transfer coefficients lead to a maximum in Figure 6 at 2.5% methane.

d) Effect of Variation of Current Density and Total Absorbed Dose

As mentioned in § IVb the density of reactive species plays an important role in the radiolysis of methane. The importance of reactions among them is increased at higher densities of reactive species compared to reactions of reactive species with stable molecules. Therefore, variation of current density j , which in our experiments is proportional to the power density $dP/dV = (j/e)dE/dl$ (dE/dl : linear energy transfer), leads to a variation of the density of primary events.

As stated in § IVa the average energy for the production of one primary ion at the radiolysis of methane is ~ 30 eV. In our experiments the power density was varied between 1.5 mW cm^{-3} and 1640 mW cm^{-3} . Hence the rate coefficients k_p for

the production of one primary ion can be calculated with the equation

$$k_p = dP/dV \times (30 \text{ eV})^{-1} \times [\text{conc}(\text{CH}_4)]^{-1}, \quad (17)$$

to be between $2 \times 10^{-5} \text{ s}^{-1}$ and $2 \times 10^{-2} \text{ s}^{-1}$. The formation rate of ions $d\text{conc}(P)/dt$ (and also for electrons e^-) can then be calculated as

$$d\text{conc}(N)/dt = \text{conc}(P) \text{conc}(e^-) 2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}. \quad (18)$$

These ions may now react in ion-molecule reactions. Nevertheless they (or their consequent products) will finally be neutralized with electrons. A typical rate coefficient for their neutralization reactions is $2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ (Duley and Williams 1984). Therefore the neutralization rate (= formation rate of neutrals N) can be calculated to

$$d\text{conc}(N)/dt = \text{conc}(P) \text{conc}(e^-) 2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \quad (19)$$

For the state of equilibrium the equation

$$d\text{conc}(N)/dt = d\text{conc}(P)/dt, \quad (20)$$

must be valid. From that the concentration of ions and electrons can be estimated to have been varied between $5 \times 10^{10} \text{ cm}^{-3}$ and $2 \times 10^{12} \text{ cm}^{-3}$.

As mentioned in § IVb the primary ions may react either via ion-molecule reactions or via neutralizations. Although the ion-molecule reactions are more frequent by orders of magnitude than these neutralizations because of the high-methane concentration, the increase of the concentration of electrons with increasing power density may have considerable effects for the reaction pathway. The radicals produced in neutralizations are the species which finally produce the higher hydrocarbons.

In a similar way we can now estimate the concentration of neutral radicals. Although some of them may already have been produced in primary processes the main source for the production of neutrals are the neutralization reactions.

Radicals will react in neutral reactions with methane target molecules or with other radicals to stable products. It is difficult to determine an exact rate coefficient for these radical-radical reactions; we estimate it to $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Hence the formation rate of stable products S can be written as

$$d\text{conc}(S)/dt = [\text{conc}(N)]^2 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}. \quad (21)$$

Again for the state of equilibrium

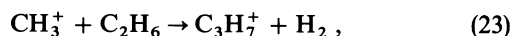
$$d\text{conc}(S)/dt = d\text{conc}(N)/dt, \quad (22)$$

the density of radicals can be estimated to vary between $2 \times 10^{12} \text{ cm}^{-3}$ and $7 \times 10^{13} \text{ cm}^{-3}$. This is the reason for a second competition process: higher radical densities enhance reactions among radicals, at lower radical densities reactions of radicals with methane target molecules are favored.

So two competing processes have been discussed which depend on the density of ions/electrons and radicals. The strong dependencies of the yields of products on the current density as measured in our experiments demonstrate the importance of this competition.

The saturation effect (see also Kovacs, Cserep, and Földiák 1975) in the production of hydrocarbons with increasing dose, as mentioned under § IIIc can be explained by two effects. First, produced higher hydrocarbons will be destroyed again by the ionizing radiation. The second effect which we consider to be even more important is an enhanced polymerization with

increasing dose. Ion-molecule reactions of ions with higher hydrocarbons like



will reduce the relative amount of volatile hydrocarbons. This results in a residue on the walls of the reaction vessel, which is supposed to consist of high, nonvolatile hydrocarbons.

V. CONSEQUENCES FOR ASTROPHYSICAL SYSTEMS

In experiments which dealt with the addition of inert gases, it was shown that charge transfer reactions play an important role in the radiolysis of methane/inert gas mixtures. This could explain the observations of CHON molecules in systems which consist mostly of nitrogen, carbon dioxide, and water and only traces of methane and other reactive substances. As proved in former experiments irradiation of nitrogen/carbon dioxide/water mixtures yields only neglectable amounts of higher organic components (Schuster *et al.* 1989). Our present measurements have shown that, due to charge transfer processes, the addition of small amounts of methane to these gases yields relatively high amounts of organic products. Our experiments are consistent with reaction coefficients for charge transfer and neutralization reactions.

Furthermore current density (power density) was proved to be an important parameter for the radiolysis of methane with MeV protons. Strong dependencies of the yields of hydrocarbons on this parameter have been measured at power densities of $\sim 1 \text{ mW cm}^{-3}$ – 1 W cm^{-3} . The results are qualitatively consistent with former measurements: Holroyd (1961) studied the radiolysis of neopentane with 3 MeV electrons. Variation of dose rate, which is an equivalent parameter to power density, gave dependencies of the yields of various hydrocarbons on this parameter at $\sim 80 \text{ mW cm}^{-3}$. Also Meisels (1965) found dependencies on the dose rate at the radiolysis of ethylene.

Woodward and Back (1963) irradiated hydrocarbons with γ radiation. They measured strong dependencies of the yields of products on the power density at $\sim 2 \times 10^{-5} \text{ mW cm}^{-3}$. In previous investigations (Sack *et al.* 1988; Schuster *et al.* 1989), we measured dependencies of the yields of amines, alcohols, and amino acids on the power density at the irradiation of gas mixtures of methane, nitrogen, water, and other gases with 6.5 MeV protons of a power density of about 100 mW cm^{-3} . Hence it can be stated that power density influences the reactions over a large interval of this parameter.

Compared to the average MeV proton fluxes in planetary atmospheres, which are normally of the order of $10^6 \text{ cm}^{-2} \text{ s}^{-1}$, our fluxes are by orders of magnitudes higher: they were varied between 1.6×10^{11} and $1.8 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$. Hence our results are better applied to such phenomena as auroras, where higher particle fluxes can occur.

But the most important conclusion of our investigations is concerning the application of laboratory data of simulation experiments to the real planetary atmosphere. Several simulation experiments have been performed which dealt with the irradiation of simple gas mixtures. As particle fluxes in those experiments are $\sim 10^{12} \text{ s}^{-1}$, it was suggested that it was possible to simulate several thousand years of the atmosphere in some minutes in the laboratory. But as these fluxes are

similar to ours, the results presented here show strong dependencies of radiolytical yields on particle flux between 1.6×10^{11} and $1.8 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$. Therefore it is obvious that one has to be very careful in applying results obtained at $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ to atmospheres where the fluxes are by 6 orders of magnitude lower.

The above measurements may be used to discuss an aspect of the chemistry of irradiated ices. Comets are supposed to consist mainly of primitive gases like water, carbon monoxide, carbon dioxide, or methane (Mendis 1986). During their storage in the Oort cloud the outer layer (some meters) of the frozen nucleus is irradiated with galactic cosmic rays (Johnson *et al.* 1987). In the track of a projectile, e.g., a MeV proton, in the ice ions and radicals are produced; some reactions like ion-molecule or neutralization reactions will immediately take place. But because of the low temperature of the ice radicals may be stored for a considerable period of time (Johnson *et al.* 1987). Nevertheless the low temperature processes are not well understood.

When the Oort cloud is perturbed by, e.g., a passing star (Fernandez and Ip 1987) some comets will be moved onto heliocentric orbits. When approaching the Sun the surface of the comet warms up (Mendis 1986) and reactions of the stored radicals will take place. Such reactions have been observed in laboratory simulation experiments (Moore *et al.* 1983; Greenberg 1980).

If the radicals are accumulated over the billions of years, their density is determined by the total absorbed dose of radiation. This may then be an equivalent parameter to the power density in our experiments. Because of the increasing relevance of reactions between reactive species with increasing radical density it can be stated that an increase of the total absorbed dose in cometary ice will not only lead to higher yields of products during warming up. It will even lead to changes in the relative distribution of products, because, as shown in our experiments, at higher radical densities the production of some substances will be favored and the yields of others may decrease.

However it is doubtful whether the radicals will really be stored in the cometary ice for the billions of years. Quantum mechanical tunneling processes may lead to chemical reactions even at very low temperatures (Goldanskii 1979). The diffusion of radicals in the ice is not clear. Even local reassembling of the ice may allow chemical reactions because of heating up the ice. Taking all this into account it cannot be excluded that also the dose rate may play an important role in cometary chemistry.

As our experiments have demonstrated the importance of irradiation parameters and of the concentration of inactive gases, future investigations should deal with questions like radical diffusion and reactions in cometary ice mixtures to clear up the relevance of these parameters in low-temperature ice systems.

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