greater than 1 MeV the contribution of the photoelectric effect can be neglected and the entire interaction is through the production of Compton electrons. In Compton effect, a part of the incident energy is absorbed to eject the Compton electron. The interaction takes place with the shells of the most loosely bond outer electrons, which for all practical purposes can be considered as free. Hence, the contribution of the compton process to the total absorption coefficient depends entirely on the number of electrons per gram which varies with atomic number. Pair production involves interaction of photons with the nucleus and leads to complete disappearance of the incident photon and the appearance of an electron positron pair. The minimum photon energy must be 1.022 MeV. The excess energy is carried by positron and electron in the form of kinetic energy. The cross section for this process increases with atomic number. In the annihilation process of oppositely charged species two photons are created each with 0.511 MeV. The interaction of these photons, e.g. with water, proceeds entirely through Compton process. For all three mechanism of interaction of photons, generation of secondary electrons is the essential feature and all the chemical changes in a medium following photon irradiation are attributed to these electrons.

Charged particles loose their energy in matter through interaction with electrons or nuclei of the medium and hence slow down. The rate of energy loss suffered by a charged particle in traversing a unit path length, ($S = -dE/dx$) is called the "stopping power". This quantity is related to the charge and velocity of the incident particle and also to the physical properties of the medium. At low velocities, the energy lost by a charged particle is equal to the energy absorbed by the medium, in which case the stopping power is called the linear energy transfer LET (keV m^{-1}).

For incident electrons at low velocities the main stopping mechanism involves the excitation of molecular vibrations until the energy is reduced to about 0.5 eV. Below this energy, and when the medium is a condensed phase, the incident electron may excite interamolecular vibrations on its way and finally becomes thermalized. The value of the stopping power for electrons is in general lower than that for heavier particles. A special issue of high energy electrons is the production of Bremsstrahlung.

For accelerated ions there are two principal mechanism of energy transfer : elastic (nuclear) interactions, i.e. atomic collisions, and inelastic (electronic) interactions, i.e electronic excitation or ionization. The elastic processes occur at lower energies and preferentially with heavier particles. The borderline between the two domains is given by the rule of thumb, that the energy transferred by nuclear collisions E_n is of the order of that by electronic interactions E_e when :

$$\mathrm{E_{projectile}\,(keV) \approx M_{projectile}\,(a.m.u)}. \qquad (2)$$

The maximum energy transferred $\mathrm{E_{max}}$ in head– on collisions between a projectile with $\mathrm{M_1}$ and energy E and a target atom of $\mathrm{M_2}$ can be calculated to :

$$E_{\max} = \frac{4M_1M_2}{(M_1+M_2)^2}E \qquad (3)$$

If the transferred energy E is greater than the threshold energy for a displacement, a target atom will be knocked– on (secondary particle) and forced to leave its site. When its energy is sufficiently high, it will knock-on another target atom. Thus, a side branch of the collision cascade is generated. The actual amount of energy transfer under non head-on collisions can be calculated in the binary collision approximation from interaction potentials of Thomas–Fermi or Thomas–Fermi–

Molière type and many others [7-9]. Below an energy E_A the predominant interaction is with the whole atoms ("hard sphere collision) :

$$E_A = E_R \frac{2(M_1 + M_2)}{M_2} Z_1 Z_2 (Z_1^{2/3} + Z_2^{2/3}) \qquad (4)$$

where E_R signifies the Rydberg energy, 13.6 eV, and Z_1 and Z_2 the atomic numbers of the collision partners. For incident heavy ions capture and loss of electrons, i.e. neutralization or further ionization plays an important role also in view of the stopping [9]. At lower energies (10^3-10^4 eV) all projectiles will reach a charge state close to zero.

High energetic and in particular light particles undergo predominantly interactions which can be described theoretically by the Lindhard- Scharff- Schiött theory (LSS) and at higher energies (e.g. E > some 10^5 eV for H^+ or E > 1 MeV for He^{2+}) by the Bethe theory [4]. For very high energetic particles (e.g. H^+ at 10^8 eV) relativistic effects have to be considered.

There is, however, for high energy particles a contribution of nuclear processes to radiation damage also. The electrons produced by inelastic interaction are of relatively high energy (some eV to some keV) and will penetrate the lattice more or less rectangular to the direction of the projectile. These δ-electrons are ejected very rapidly and leave a core of singly positively charged ions which repulse each other, Figure 1. Since the bonds are loosened by lattice excitation, collisions and ionization, those ions or their fragments are driven out off the track by Coulomb repulsion (and ev. attraction by the δ-electron "cloud"). Energies from some eV to several keV can be reached by the ions giving rise to secondary knock– on processes with target atoms and ion-molecule reactions likewise. Not to forget that every fast particle at the end of its trajectory, when slowed down, will undergo nuclear

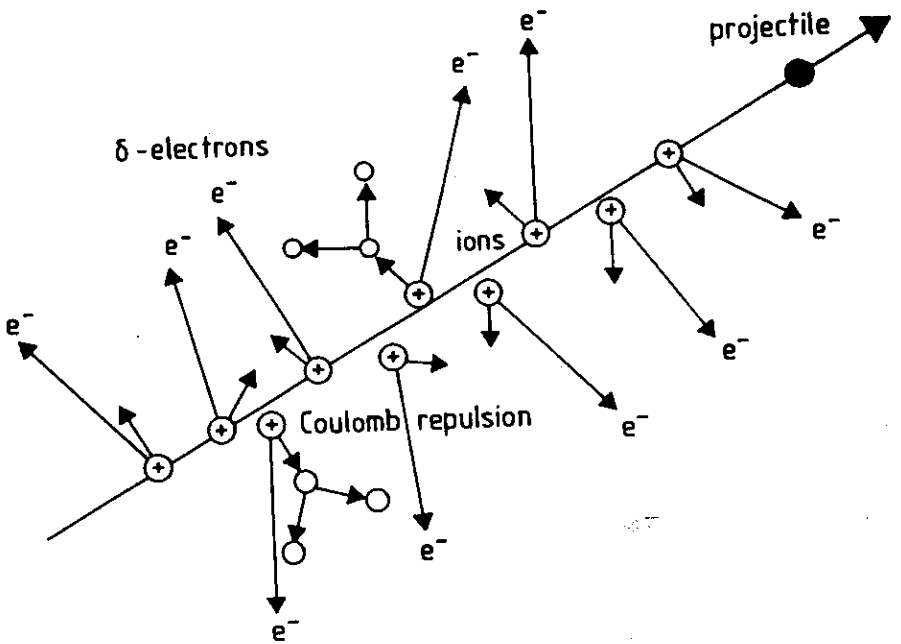


Fig. 1 : High energy projectile track; from [32].

collisions. In such, both low energetic heavy and high energetic light particles will produce kinetically energetic (hot) atoms.

I-2 Radiation Chemistry of Solid Hydrocarbons :

Most basic studies of radiation chemistry are concerned with low molecular weight compounds, and it is the changes in chemical structure and the intermediate states and mechanism that are of major concern **[2,3,10-13]**. Recently, the behavior of electrons at times shorter than those involved in atomic-molecular rearrangement is also becoming of interest. Studies in organic solids and macromolecular compounds and polymers are stimulated by potential application **[14-17]**. The effect of high energy radiation on organic materials is largely determined by the functional groups present and in general the radiolysis is initiated by the formation of single ions and excited molecules, but at higher doses they can be grouped together in spurs, blobs and short tracks **[3]**.

The positive ion formed in the interaction of radiation with matter may recombine with an electron and yield a molecule in a highly excited state. Consequently the energy released usually results in immediate dissociation into free radicals (photo-dissociation):

$$A^+ + e^- \rightarrow B + C^*. \qquad (5)$$

At least one of the products will be in an excited state and may undergo further decomposition. If A^+ is a stable structure, e.g. an aromatic ring, then the excitation energy is able to migrate rapidly and is not localized in any one bond, so that dissociation may not occur. In some gas phase reaction the positive ion may dissociate before undergoing neutralization, e.g. :

$$C_4H_{10}^+ \rightarrow CH_3 + C_3H_7^+. \qquad (6)$$

The carbonium ion $C_3H_7^+$ rearranges to a more stable unsaturated ion with elimination of hydrogen :

$$C_3H_7^+ \rightarrow \begin{matrix} {}^+CH_2 - CH = CH_2 \\ CH_2 = CH - {}^+CH_2 \end{matrix} + H_2. \qquad (7)$$

Another potential reaction is the formation of a stable molecule and an unsaturated free radical ion :

$$C_4H_{10}^+ \rightarrow CH_4 + C_3H_6^+. \qquad (8)$$

In studying radiation chemical reactions induced by high energy radiation, Linde **[18]** defined the radiation chemical yield as the quantity M/N, where M is the number of molecules produced or made to react by the radiation and N is the number of ion pairs formed. A more common measure of the radiation chemical yield is the G-value which is defined as the number of molecules produced or made to react per 100 eV of absorbed radiation energy. Assuming that the energy required to form an ion pair is about 32.5 eV, the value for air, G is approx. 3 (M/N). In condensed systems the G-value is used to estimate radiation chemical yields since N cannot be measured. Linde **[18]** found that when excitation, decomposition, hydrogenation, polymerization, and a variety of other reactions were carried out, the value of M /N was nearly always at least 2 and was often considerably greater. When M /N = 2, it was resonable to assume that negative and positive ions both undergo reaction. When M /N exceeded 2, it was proposed that the reacting molecules formed clusters around the positive ion. That was then assumed to be neutralized by an electron (or a negative ion), resulting in the release of energy at least corresponding to the ionization potential of the neutral molecule formed, i.e. 9-15 eV. This large amount of energy can be sufficient to cleave a bond in some of the clustered molecules. When M /N is 20 and larger, e.g. in the case of polymerization of acetylene, the cluster theory is inadequate since clusters of improbable size were to

modifies its physical properties, such as flow and mechanical behaviour, conductivity, light emission, melting and solubility, and these are of major practical interest. In fact, the chemical changes involved in the radiation of polymers are relatively small, and it is because such chemical modifications on a very minor scale produce such maior physical modification that the radiation treatment of polymers has acquired its present industrial importance **[17]**.

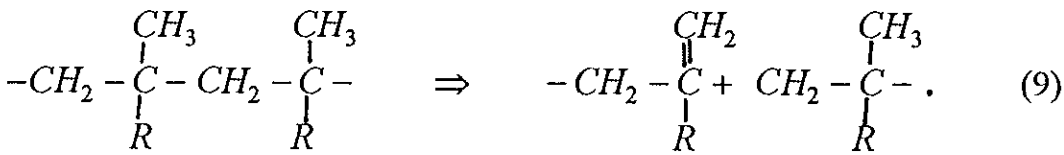
The same is true for radiobiology where doses are so low that chemical changes can only be minute. Nevertheless they result in major biological effects. The explanation both for polymers and biopolymers is usually that they involve macromolecules in which minor changes at appropriate places have great influence on molecular morphology.

The reactions which occur in polymers when exposed to high energy radiation may be classified into two groups :

a) Crosslinking of the polymer chain leading to an increase in molecular weight and at very high doses to the formation of an insoluble network.
b) Scission of the molecular chains which results in a decrease of the average molecular weight.

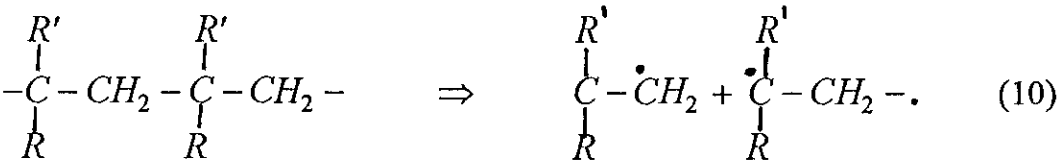
Both processes occur simultaneously in many polymers, and the classification depends on which is predominant. The presence of oxygen is very important for the choice of one of reaction pathways. Scission and cross-linking can be accompanied by the elimination of hydrogen and the formation of small volatile molecules such as CH_4, C_2H_6, CO and CO_2.

A mechanism **[10, 17]** which has been suggested for scission considers a rearrangement, particularly favoured in the presence of an α-methyl group :



(9)

However, a more general mechanism includes the formation of polymer radicals as an early step :



(10)

I-3 Hot Atom Chemistry in Solid Hydrocarbons :

Ions or atoms which are injected with high energies into solids do not only create reactive defects and excited states but may also undergo specific chemical reactions different from the classical thermal ones. They impart their kinetic and/or electronic energy to the reaction complex and form excited molecules or intermediate states which can be stabilized by a variety of reaction channels. These reactions are called hot or high energy or suprathermal. The expression {hot-atom chemistry} applies in particular to solids where fast neutralization processes will change most of the ions injected into neutrals, at least at the end of their trajectory when chemical reactions are likely to occur. Hot-atom chemistry has received quite a lot of attention in nuclear chemistry and physics. The chemical reactions induced by radioactive atoms recoiling from nuclear processes have been studied since 61 years (1934, Szilard-Chalmers effect) and have been intensively applied to isotope enrichment, labelling and doping of materials **[21-27]**.

Hot ions and atoms are not in thermal equilibrium with their surrounding. This is in general the case for energies exceeding some 0.1 eV. Atoms escaping planetary atmospheres with energies of (0.3 to 0.5) eV are called hot. This term,

even if very often used, is somewhat misleading since by definition a temperature cannot be attributed to single particles. The equation 1 eV = 10^4 K holds only when a group of atoms or ions possesses this energy (e.g., in a hot grain). Heat is a collective phenomenon in equilibrium. For a single hot atom the surrounding is cold. Figure 2 shows that hot species can easily overcome activation energy thresholds of reaction. A very important aspect of suprathermal reactions is their velocity. They can be much faster than thermal ones since the activation energy barrier can be overcome in one single attack **[27]**. An important factor in suprathermal chemistry is that hot atoms can also be electronically excited and, thus, add their excitation energy to overcome the reaction threshold **[27, 28,32]**.

The lower and the upper energy limits for suprathermal reactions are given by the facts that **(a)** the energy barrier for a typical hot process, i.e. a slightly endothermic reaction, has to be overcome (in the order of 2 to 3 eV) and **(b)** the new bond or molecule to be formed must be stable at least for one vibrational period. This limits the maximum energy for the gas phase to about 20 eV and to 50 eV for the solid state. Molecules which carry more than these energies will fragment immediately and the projectile will continue its trajectory. Chemical interactions of this kind should rather be regarded as polarization effects and should be attributed to inelastic loss phenomena. Figure 3 shows the energy limits in form of a cross-section curve. The upper limit for reactions in the solid state is higher than for the gas phase due to the easier deexcitation of product molecules. Figure 4 displays an energy scale of interactions of a high-energy projectile entering a solid with 1 MeV down to thermalization at the end of its trajectory, from **[32]**.

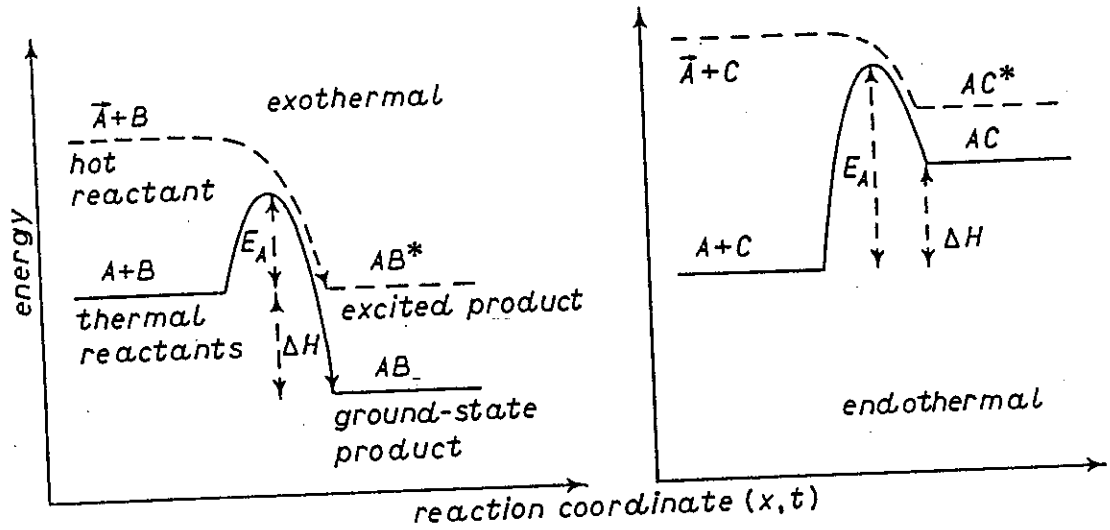


Fig. 2 : Schematic view of energetics of thermal and hot reactions in exo-and endothermal processes, from [32].

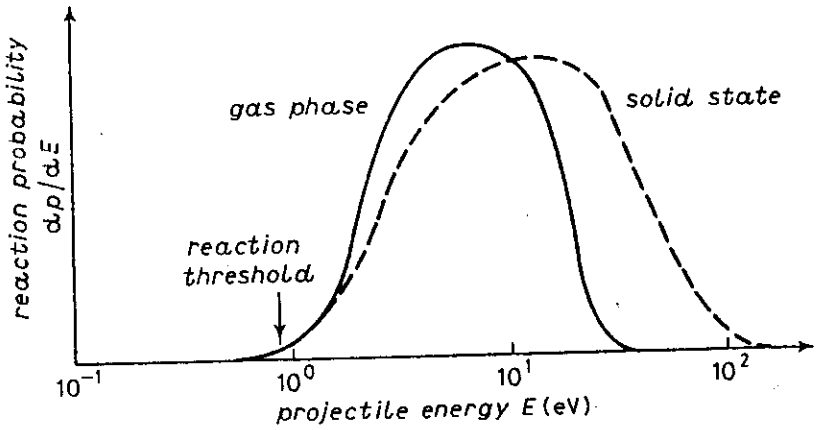


Fig. 3 : Schematic representation of cross-section curves for hot reactions in gas and solid, from [32].

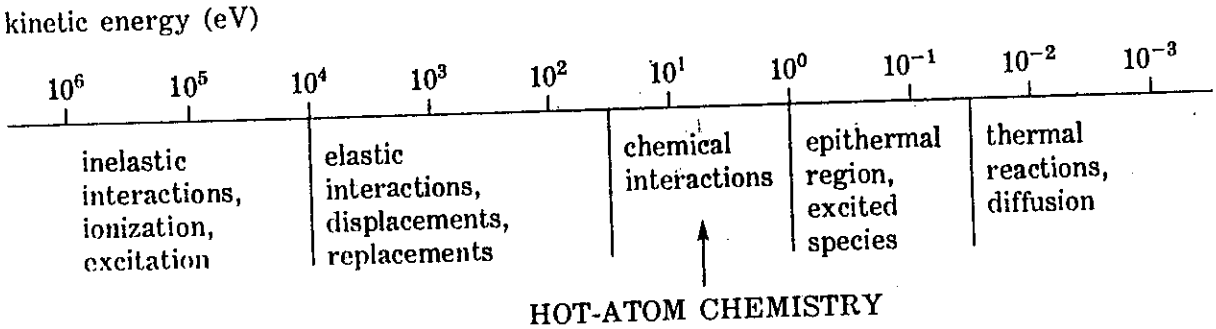


Fig. 4 : Energy scales of interactions of hot species; from [32].

Besides hot atoms or ions there are also hot molecular fragments such as, e.g., methyne CH, methylene CH_2, methyl CH_3, nitrene NH, amine NH_2 and hydroxyl OH, furthermore hot molecules and hot clusters or grains.

Until now in research of chemical effects of nuclear transformations and ion implantion the problem of hot-reaction kinetics is still unsolved. The reason for this is the nonequilibrium character of these processes which prevents the application of simple energy distribution functions such as the Maxwell– Boltzmann equation. Furthermore these reactions are very fast and in general performed by few isolated reactants only such as in the case of nuclear recoil.

The classical Arrhenius equation for reaction kinetics of binary collisions in thermal equilibrium is :

$$k(T) = A \exp[-E_A / kT], \tag{11}$$

where $k(T)$ is the temperature-dependent velocity constant, A the pre-exponential factor, E_A the activation energy, k the Boltzmann constant and T the temperature. The pre-exponential factor A is :

$$A = \sqrt{2}\, \pi\, \sigma^2\, \varpi N, \tag{12}$$

where the expression $\sqrt{2}\pi\sigma^2$ signifies the reaction cross-section. σ^2 should better be written as $(\sigma_1 + \sigma_2)^2$, the gas kinetic diameters of the reaction partners. This term becomes relatively high for ion-molecule interactions. ϖ signifies the average velocity, *i.e.* in the thermal case the temperature. It is this term which is affected by the high velocity of the hot atom. N is the number density of the target and, thus, high for solids. The activation energy E is in general considered as the energy threshold to be crossed by the relative translational motion of the reaction partners. This is, however, a simplification since the reaction probability depends also on the

inner (electronic excitation) energy and the geometrical configuration [28]. The mean velocity constant can also be expressed as :

$$k(T) = \int_0^{\infty} \underbrace{f(T,V)}_{\text{velocity distribution}} \overbrace{\sigma(V)}^{\text{cross-section}} dV. \qquad (13)$$

$k(T)$ can be formulated in a general way in terms of energy E as :

$$k(T) = \left[\left(\frac{2}{kT}\right)^{3/2}\left(\frac{1}{\pi\mu}\right)^{1/2}\int_0^{\infty} E\sigma(E)\exp\left[\frac{E_o - E}{kT}\right]dE\right]\exp[-E_o / kT], \quad (14)$$

where $\sigma(E)$is the energy-dependent cross-section. The pre-exponential factor A (the term in brackets) depends on the form of $\sigma(E)$ and the amount of E. Figure 5 shows the overlap of Maxwell– Boltzmann (thermal) energy distribution with a typical cross-section curve of Figure 4. Both reactant and target atom or molecule are in thermal equilibrium. Only the few atoms receiving for a short moment an excess energy higher than the threshold can react, not considering the relatively rare tunnelling processes. It can easily been followed, that hot atoms with kinetic energies exceeding some eV will react with high cross sections.

The classical procedure of hot-atom chemistry represents even more than ion implantation the method which has produced most of the information on supra-thermal processes up to the present. It makes use of the recoil of the product nuclide following nuclear reactions. The advantage of the nuclear-recoil methods is that it creates a radioactive atom. Figure 6 describes the process in the example of the $^{14}N(p,\alpha)^{11}C$ reaction with ≥ 8 MeV protons from a cyclotron. The nuclear reaction creates an intermediate excited ^{15}O nucleus which deexcites by emission of an α-particle. The remaining ^{11}C nucleus obtains a kinetic energy of 2 to 3 MeV, according to the law of conservation of energy and momentum. It recoils from its original lattice site, breaks its covalent or lattice bonds, dissipates its energy by

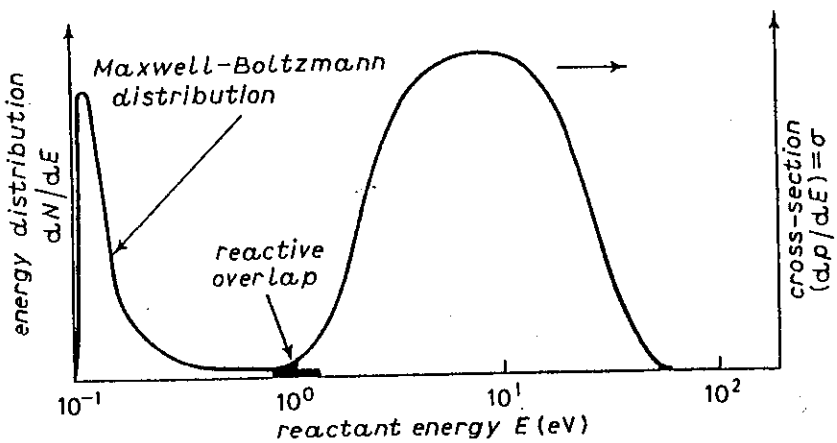


Fig. 5 : Thermal-reaction characteristics (Maxwell- Boltzman), from [32].

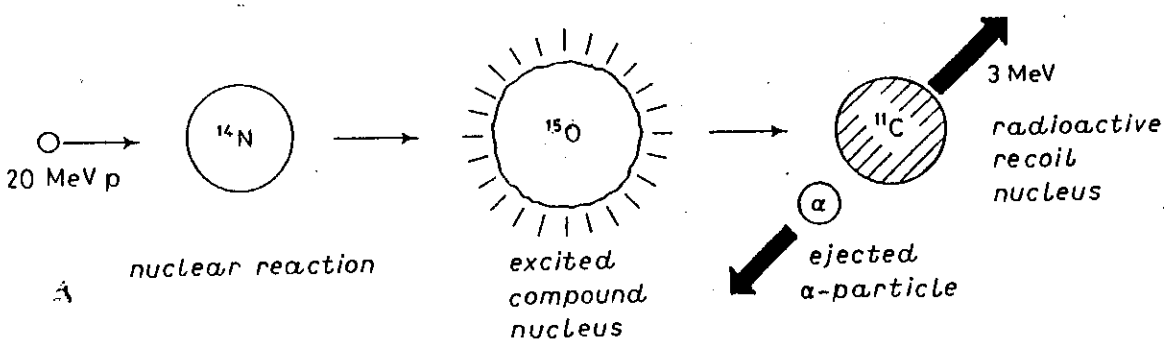


Fig. 6 : Schematic representation of the nuclear reaction $^{14}N(p,\alpha)^{11}C$ leading to the recoil of ^{11}C, from [32].

elastic (S_n) and inelastic (S_e) collisions and finally can react suprathermally before being thermalized. There are many nuclear reactions leading to "biogenic" recoil atoms (*H(T), C, N, O, P, S*) such as $^{3}He(n, p)^{3}H$, $^{12}C(^{3}He, ^{4}He)^{11}C$, $^{14}N(p, \alpha)^{11}C$, $^{12}C(d, n)^{13}N$, $^{16}O(\gamma, n)^{15}O$, $^{32}S(n, p)^{32}P$ and $^{35}Cl(n, p)^{35}S$. Most of the cyclotron– or accelerator-particle-induced nuclides are positron emitters of relatively short half–life. Provided neutrons or accelerator particles are available, it is possible to create hot atoms in a manifold of target substances of cosmic relevance **[28]**.

The consequences of recoil atoms in solid hydrocarbons, in particular of hot carbon atoms, have been reported in many publications **[21, 23 – 27, 29 – 37]**. A general mechanistic scheme is given in Fig. 7 for the formation of low molecular hydrocarbons labelled by ^{11}C in the reactions of recoil carbon from the nuclear reaction $^{12}C(^{3}He, ^{4}He)^{11}C$ in solid CH_4 at 77 or 10 K, from **[37]**. These products are formed by H–abstraction of ^{11}C to $^{11}CH_4$, ^{11}C insertion into CH_4 to yield a metastable intermediate, methylcarbene $(CH_3\text{-}CH)^*$, which in turn may react by H–elimination to C_2H_2, by intramolecular H–transfer to C_2H_4, by H–pick up to C_2H_6, by CH_3–addition to C_3H_8 or C_3H_6, etc. The dependence of the radiochemical yields of these short chain aliphates and olefins on the radiation dose given by the $^{3}He^{2+}$–ions is shown in Fig. 8, from **[30]**. However, not only these simple but also more complex products are formed such as e.g. C_7H_{16}, benzene, toluene and a series of polycyclic aromates. Even amorphous carbon had been found in small amounts **[30–37]**. Fig. 9, from **[34]**, depicts some of these complex compounds. Their formation is partly due to a new solid state reaction mechanisms : the multicenter reaction **[31–37]**. Fig. 10 exhibits the computer calculation of a typical cascade by an energetic carbon atom in solid CH_4, projected into one plane, from **[35]**. Only the hot carbon and hydrogen atoms formed are shown. It can be seen, that they concentrate in a zone with a radius of approx. 10 Å at the end of the cascade with

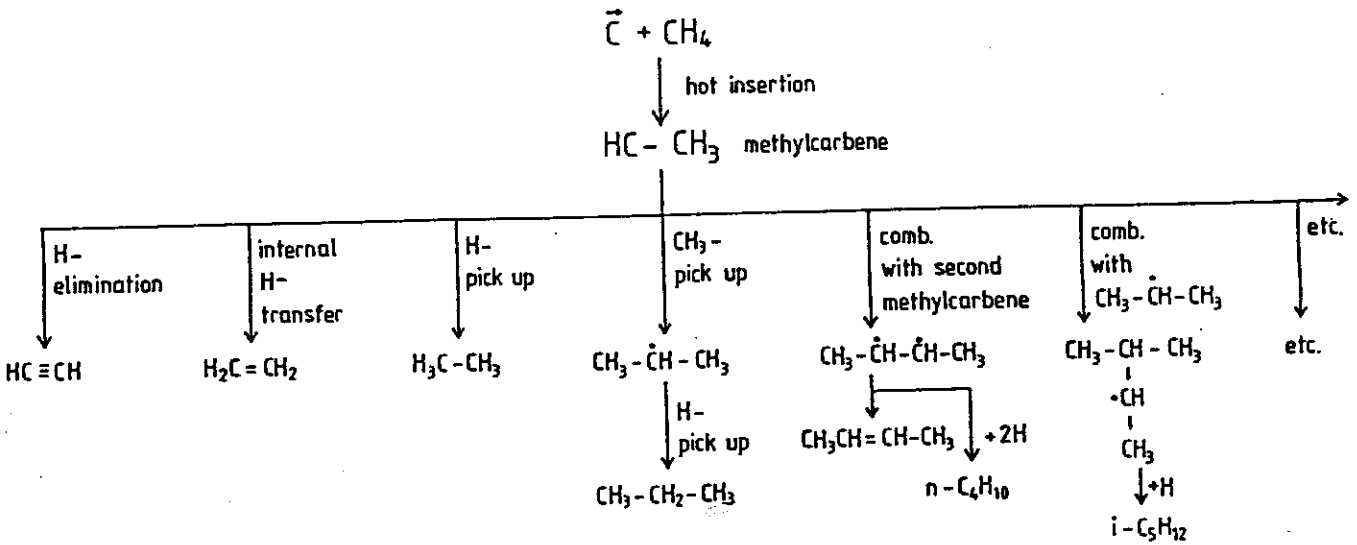


Fig. 7 : Mechanistic scheme for the formation of small ^{11}C-labelled products in the hot atom interaction of recoil ^{11}C from the nuclear reaction $^{12}C(^{3}He, ^{4}He)^{11}C$ in solid CH_4 at 77 K, from [37].

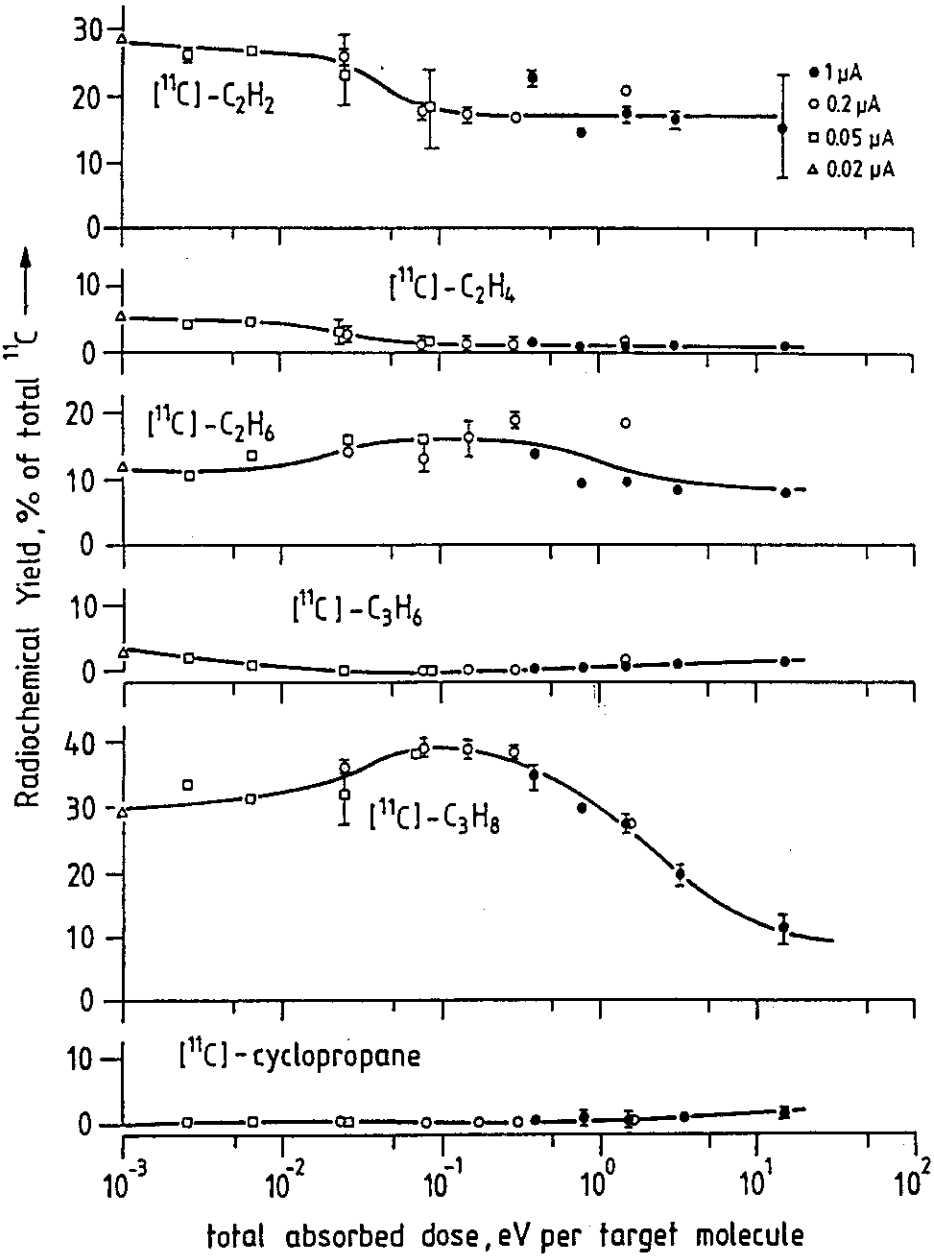


Fig. 8 : Dose dependence of the radiochemical yields of some of the ^{11}C-labelled hydrocarbons in the interaction of 20 MeV $^3He^{2+}$-ions with solid CH_4 at 77 K, from [30].

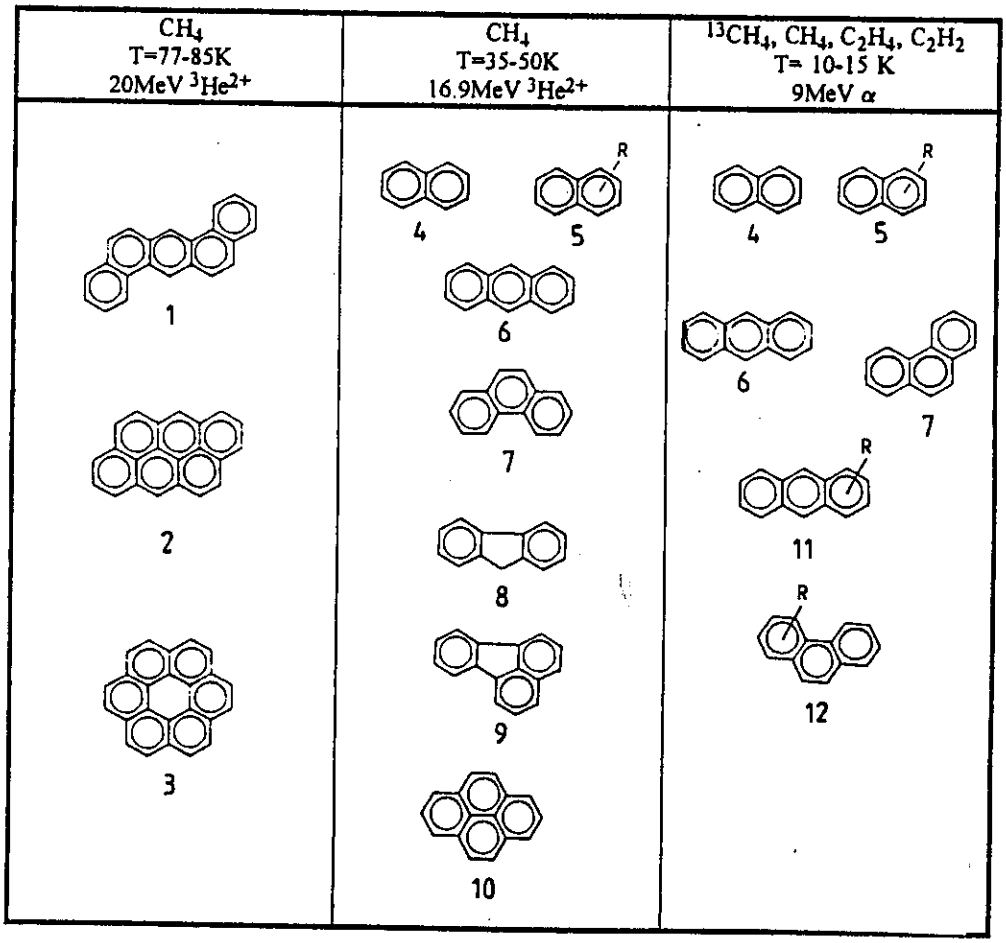


Fig. 9 : Complex products formed in solid CH_4 at 10 K by He^{2+} ions irradiation, from [34].

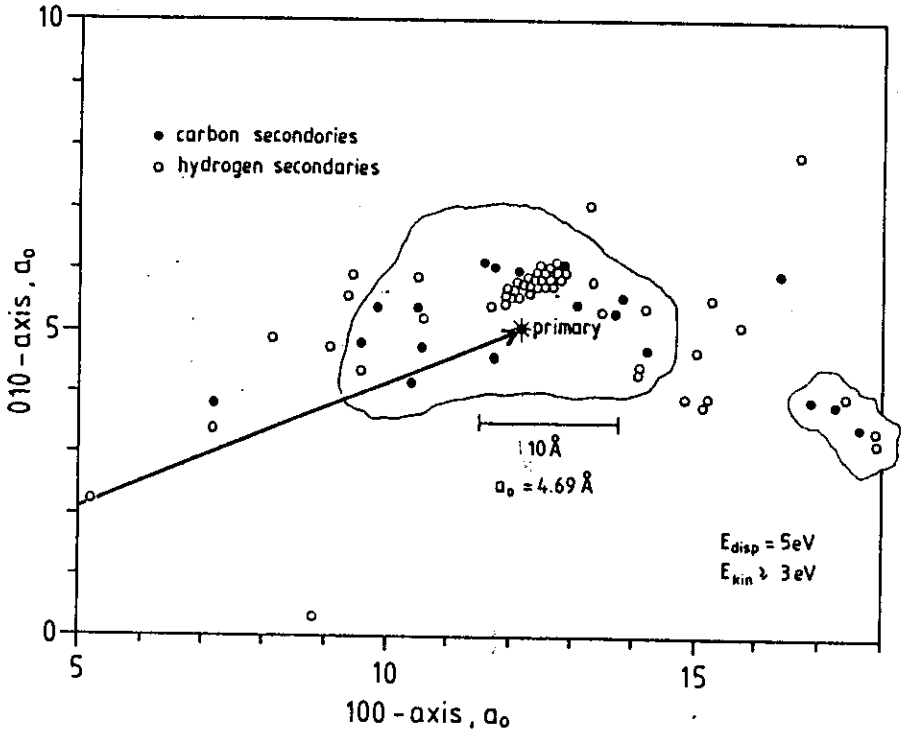


Fig. 10 : Multicenter mechanism in solid CH_4 when hit by an energetic carbon atom. Computer simulation of collision cascades; projection onto one plane; only hot carbon and hydrogen atoms are shown; from [35].

more than 15 hot carbon atoms. Thus, multiple interactions of hot atoms, intermediate radical products, radicals by radiation and general excitation brings about the formation of the complex structures.

I-4 Astrophysical Implications :

The solar system is replete with physical and chemical information that broadens our perspective about processes affecting chemical evolution and the origin of life **[27, 32, 38–42].** Knowledge gained from planetary exploration by means of space crafts has greatly expanded our understanding of the detailed prebiotic chemistry occuring in the Earth's solar system environment. It has also contributed to a more expanded view of life as a planetary phenomenon. Continued exploration increases our knowledge of chemical evolution and the origin of life on earth and will allow better estimates of the likelihood of such processes occuring elsewhere beyond the solar system **[38].**

The raw material from which the building blocks of life have evolved consists of the chemical elements of the periodic table. Examination of the crust of the earth, the oceans, and the atmosphere provides us with the information about the abundance of these elements on the earth. Data on the elemental composition of matter beyond the earth came from several sources. The spectroscopic analysis of light from stars reveals the nature of the elements in them. Cosmic ray particles can supply us with samples of extraterrestrial matter. Meteorites and lunar samples have given us valuable knowledge of the composition of the solar system **[38].**

In space the elements (H, C, N, O, ... etc) which are required for organic molecules are the most abundant. There are a large number of molecular species which have been identified in the interstellar gas indicating that there is a very active chemical factory in space. Among the abundant simple molecules are CO, H_2CO,

HCN, H_2O, NH_3, CH_3OH,..... etc. However, the most complex and abundant molecules are not in the gas but rather must be in small solid particles called interstellar dust which float about in the gas. Although both gas and dust temperatures are basically governed by radiation from the stars, dust is generally much colder than gas and the interstellar medium is far from thermal equilibrium. The mean temperature of the dust grains, which is reached by a balance between absorption of radiation from the ambient field and emission of radiation by the small dust grains, is only about 10 K. It is only near energetic sources of radiation such as stars, that grain temperatures become as high as 50 or 100 K, and only in few cases, when the grains get very close to hot stars temperatures for a complete evaporation would occur as showed by Greenberg **[39, 42]**.

Polycyclic aromatic hydrocarbons (PAHs) are among the major substances that are proposed to explain a class of infrared bands, the so-called unidentified infrared bands, detected in emission toward a wide variety of galactic sources rich in ultraviolet flux. Mennella et. al. **[43]** studied the infrared thermal emission spectra of three PAHs, coronene, chrysene and 1-methylcoronene, and the results support the hypothesis that PAHs in space are arranged in condensed form. Salama and Allamandola **[44]** studied the UV-VIS optical absorption spectra of PAHs cations and discussed how PAHs convert interstellar UV-VIS radiation into the infrared.

In general, the dust components present in the interstellar medium can be divided into two classes depending on their formation history **[45]**. First, there is the stardust, such as silicates, amorphous carbon, polycyclic aromatic hydrocarbons (PAHs) and graphite, which are made in a high-density, high-temperature environments in the oxygen-rich or carbon-rich outflow mainly from late-type giants and planetary nebulae. Second, there are dust components that are formed in the

interstellar medium itself. This includes icy grain mantles, consisting of simple molecules (e.g., H_2O, NH_3,...etc.) inside dense-clouds, as well as an organic refractory dust component, consisting of more complex molecules. The presence of both of these dust components in the interstellar medium was confirmed by infrared observations **[38,39]**. It is assumed that there is a chemical, evolutionary link between these two dust components, i.e., the organic refractory dust component is formed by energetic processing (UV photolysis, cosmic ray bombardment or hot reactions) of the icy grain mantles **[27, 32, 35-37, 39, 42, 46-48]**.

I-5 Literature Review and Objectives of the Present Study :

The interaction of solar and cosmic rays with extraterrestrial matter has extensively been simulated in frozen systems such as H_2O, NH_3, CO_2, CH_4, etc and mixtures thereof **[25, 27, 29–37, 39, 42]**. 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 **[49–53]**. Radiation damage of polymers induced by electrons and /or γ-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.

In the present study it is desirable to study the effect of radiation of MeV ions from a cyclotron (H^+, $^3He^{2+}$ and $^4He^{2+}$ projectiles) and VUV photons on five organic substances : normal paraffins such as tetracosane $C_{24}H_{50}$, cycloparaffin as androstane $C_{19}H_{32}$, polycyclic aromatic hydrocarbons as naphthalene $C_{10}H_8$ and

anthracene $C_{14}H_{10}$ and kerogen from oil slater containing long aliphatic chains and polycyclic aromatic compounds. All these substances were selected as model substances of solid hydrocarbons in space. In addition, some molecular layers of tetracosane and androstane have been deposited on mineral grains such as siderite, pentlandite and pyrrhotine. The analysis of the irradiated samples was carried out by Fourier transform infrared spectroscopy (FT-IR) in transmission and diffuse reflectance and gaschromatography (GC/FID) of volatile reaction products. Of particular interest in this thesis is to compare between the effects induced by MeV ions and vacuum-UV photons which simulate two main radiation sources in space: the particle component of cosmic rays and solar or stellar photons.