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RADIATION CHEMISTRY OF CARBON AND NITROGEN COMPOUNDS IN H_2O AND NH_3 ICES ; RELEVANCE FOR CHEMICAL EVOLUTION IN SPACE

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Abstract : Radiolysis and photolysis of ice and ice-mixtures lead to the formation of new chemical compounds. Preexisting chemical compounds can be changed by the interaction with radicals formed in the frozen matrices and by direct radiolysis. The actual product distribution in an icy substrate is a function of radiation dose (fluence) and dose rate (flux). The reactivity of irradiated H_2O-ice depends on the equilibrium concentration, the mobility and reaction velocity of $H^\bullet$, $HO^\bullet$ or $HO_2^\bullet$ radicals, electrons, etc. The nuclear recoil process (1,2) offers an elegant method to introduce carrier-free probes without disturbing the macroscopic composition of the matrix. The kind of products formed by the radioactive atom is indicative for the redox properties of the ice. The accompanying radiation, e.g. of protons to induce the $^{14}N(p,\alpha)^{11}C$ process in NH_3 or the $^{16}O(p,\alpha pn)^{11}C$ in H_2O, allows to modify the radiation load. Fig. 1 shows the typical behaviour of ^{11}C products in H_2O-ice at 77 K as a function of the deposited proton dose (2). A neutral phase at low doses is characterized by relatively constant yields of the major products CH_2O, CH_3OH and CO_2. It is followed by a reducing phase at medium dose (CH_3OH increase) and an oxidizing phase at higher dose (CO_2 becomes the only product).

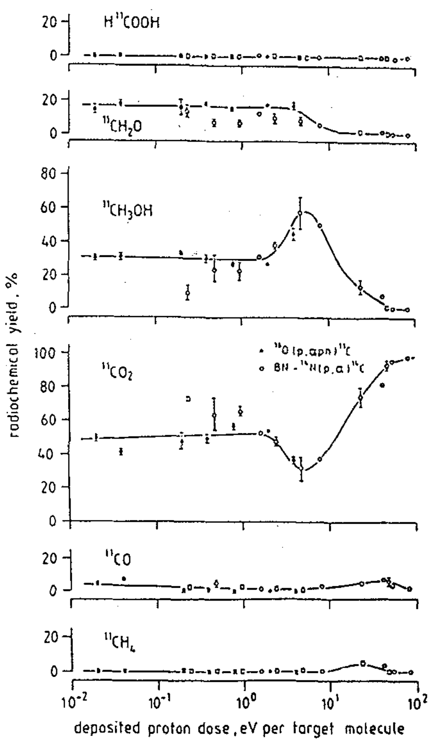

Fig. 1 : ^{11}C nuclear recoil product distribution in H_2O-ice at 77 K as a function of dose.

A similar behaviour is observed for ^{13}N from the nuclear reaction $^{16}O(p,\alpha)^{13}N$. The increase and decrease of the yields of the reduced or oxidized products, respectively, can be considered as a kind of "radiolytic recycling".
A dose behaviour of H_2O-ice towards ^{11}C and ^{13}N and that of NH_3-ice towards ^{11}C is summarized in Fig. 2. The O/H ratio of the carbon and nitrogen compounds, averaged over all products at one dose , is normalized by the O/H ratio of the target.

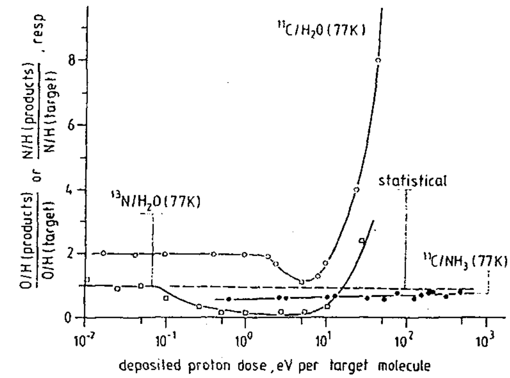

Fig. 2 : Averaged O/H or N.H ratio of ^{11}C and ^{13}N nuclear recoil products in H_2O and NH_2-ice at 77 K.

A value of 1 signifies that products are formed statistically from the O and H components of the lattice. A value beyond 1 means oxidation, a value below reduction. The radiolytic recycling is due to the fact that $H^{\bullet}$ radicals which are by far more mobile than the $HO^{\bullet}$ govern the reactions. At higher radical concentrations a reaction can occur on site, the mobility becomes less decisive, and the $HO^{\bullet}$ radicals can exert their greater reactivity. The ice becomes oxidizing. It is of interest to note that the average N/H ratio of the $^{11}C/NH_3$ system figures always in the reduced regime, since $HN^{\bullet}$ radicals are not as reactive as $HO^{\bullet}$, and the entire dose regime is governed by the $H^{\bullet}$ radicals. An admixture of NH_3 will shift the reducing phase of water ice to higher doses. This has been checked in H_2O/NH_3 (3 : 1) at 77 K, where substantial amounts of $^{11}CH_3OH$ and $H^{11}CONH_2$ were formed at doses up to 10 eV.
The findings are of importance for the chemical reactions in icy bodies in space. The addition of rather abundant NH_3 (and CH_4) increases the reducing character and, thus, enables the build-up of organic molecules at medium to high radiation doses. In systems governed by $HO^{\bullet}$ only inorganic products could be expected, such as CO, CO_2 and NO_2.

References

(1) Rössler K. and Nebeling B., Reactions of energetic carbon and nitrogen in H_2O, NH_3 and CH_4 ices and implications in cosmic chemistry, this conference.
(2) Rössler K., Proc. 3rd Int. Conf. Radiations Effects in Insulators, Guildford (UK) 15-19 July 1985, in press.

COMMENTS

J.M.WARMAN

I think it's worth pointing out that the chemical products studied by Dr. Roessler represent only an extremely small fraction of the total chemical change occuring within a system due to the incidence of an high energy cosmic ray. The products are in fact only those which are formed at the very end of the energy degradation path of the particle and which include that particle in their chemical structure. During the degradation of the initial particle energy a cylindrical core of 10 to 20 Å in diameter of ionisation and excitation of the bulk medium is formed. Using a reasonable estimate of the average energy to form a chemical product of 100 eV one can estimate that for an incident particle of initial energy A MeV there will be 10^4 A times as many molecules of products derived from the bulk material (eq. hydrogen and hydrogen peroxide for water ice) as are formed including the initial nucleus. This does not however diminish the potential great importance of these minor products since as was clearly shown they can provide the more complex building blocks which may lead to eventual development of complex molecules similar to those found in earthly biological systems.

Answer :

Besides the high energy cosmic ray particles there are many low energy (eV to some 10 eV) ones by e.g. photodissociation, low energy solar wind, secondary knock on processes, which lead to hot reactions, but not necessarily to destruction of the matrix.

J.F. CRIFO

Can you tell whether at this time there is theoretical means of predicting the reactions or whether one has to rely only on experiment ?

Answer :

Computer studies by the aid of program MARLOWE (binary collision simulation), cf K. ROESSLER, ,G. EICH, in Properties and Interactions of Interplanetary Dust, R.H. GIESE, P. LAMY (Eds.) *REIDEL, DORDRECHT* 1985, 351/6.