

LABORATORY SIMULATION OF CHEMICAL INTERACTIONS OF ACCELERATED IONS WITH
DUST AND ICE GRAINS

K. Rössler
Institut für Chemie 1 (Nuklearchemie) der Kernforschungs-
anlage Jülich GmbH, Postfach 1913
5170 Jülich
Federal Republic of Germany

ABSTRACT.

Energetic ions or atoms in space may undergo hot chemical reactions upon penetration into interplanetary or interstellar dust grains, ice layers, cometary matter, and surfaces of planetary moons. The mechanistic pathways can be different from those of classical ion molecule interactions, photolytical and radiolytical processes. The kinetic energy of the hot reactant facilitates endothermic reactions and those with high energy of activation, among them atom-molecule interactions. The conditions of hot cosmic chemistry are simulated in laboratory experiments in order to obtain insight into the nature of chemical products and the reaction mechanisms of their formation. This paper reviews the methods of ion implantation, nuclear recoil in situ, nuclear recoil implantation, secondary knock-on processes and computer simulation of collision cascades. Carbon and nitrogen impact in frozen H_2O , NH_3 and CH_4 is shown to lead to the formation and radiolytic permutation of a series of organic molecules, among them e.g. formaldehyde, methanol, methylamine, cyanamide, formamidine and guanidine which may act as precursors for biomolecules.

I. INTRODUCTION

Reactions in the bulk of interplanetary or interstellar dust grains are less frequently treated by cosmic chemistry, compared to the reactions in the gas phase. Two prominent examples are the formation of H_2 molecules from H atoms on grain surfaces (1) and the photolytic or radiolytic reactions in mixed ice layers or frosts (2). A new type of cosmic solid state reactions has been discussed recently, the interaction of accelerated ions or atoms with interstellar grains (3-7). Species with kinetic energies ranging from a few eV to some MeV are frequently encountered in space, e.g., in the radiation belts of stars and planets, in interactions with solar (stellar) winds and cosmic rays, and upon collisions of dust or gas clouds. The impact of primary energetic particles such as electrons, protons, light and heavy ions may create secondary projectiles inside a solid by knock-on processes (8) and finally may lead to sputtering (9). Chemical reactions of accelerated species are studied for more than 50 years in nuclear chemistry. The

domain of hot atom chemistry treats the reactions of particles recoiling as a consequence of nuclear processes (10-14). Hot reactions are characterized by the fact that one of the reactants carries an appreciable amount of its kinetic energy into the reactive collision. This enables endothermic reactions and those with high energies of activation, such as atom-molecule interactions. The latter ones are only seldomly considered in cosmic chemistry higherto. Especially, the reactions of biogenic atoms such as carbon or nitrogen with interstellar dust and ice material, comets, planetary surfaces, etc. seems to be of interest with respect to the formation of organic material in space. Some first studies are concerned with the reactions of hot radioactive ^{11}C and ^{13}N with frozen H_2O , NH_3 and CH_4 at 77 K (6,15-19). These nuclear recoil techniques are compared to other solid state physical methods such as ion implantation, atomic beams, and computer simulation of collision cascades in solids. The different approaches are compared with respect to their aptitude to simulate energetic solid state processes in space.

2. CHEMICAL REACTIONS OF IMPLANTED IONS

The chemical consequences of implantation of biogenic ions into some inorganic substances have been studied by means of radioactive and stable isotopes. Besides the formation of carbides and nitrides by implantation of carbon and nitrogen ions into metals and semiconductors, many properly "chemical" systems have been reported, cf. e.g. (20-26). Table I presents a selection of insulator systems ranging from alkali halides to targets with more cosmic relevance such as SiO_2 and water ice. In general, simple products are observed, most of them by means of optical spectroscopy. The advantage of the in situ analysis by optical spectroscopy, which applies to many systems in Table I (with exception of the radioactive implants), is however ruled out to a certain degree by the radiolytical effects of the high radiation doses delivered by the implants. Optical spectroscopy in absorption requires, even for molecules with very high (C_2) and high (CO_2) molar extinction coefficients in the range of 10^4 to $10^5 \text{ cm}^2 \text{ mole}^{-1}$ (23), the implantation of some 10^{15} to some 10^{17} ions cm^{-2} . Table II. reports the radiation dose (total fluence) - in eV delivered per target molecule in the penetration range of the projectiles - for carbon implants in H_2O -ice ($\sigma = 0.87 \text{ g cm}^{-3}$). It can be seen, that the doses are relatively independent of the energy and that they are very high in the range of 50 to 5000 eV per target molecule for 10^{15} and 10^{17} ions cm^{-2} . The second disadvantage is that also the fluxes (dose rates) are equally high. In order to obtain some 10^{17} implants cm^{-2} in a reasonable time the beam intensity cannot be much lower than 0.1 to 1 μA ($6 \cdot 10^{11}$ to $6 \cdot 10^{12}$ ions sec^{-1}). Other methods of in situ analysis such ESR and ^{13}C -NMR require high concentration of implants, likewise. The only feasible improvement consists in optical spectroscopy via laser induced fluorescence of the chemical products. Here some 10^{14} to 10^{15} ions cm^{-2} would be sufficient for an effective measurement. The high energy deposition by the laser may, on the other hand, be detrimental for metastable radicals and intermediates. In order to establish a good comparison of the simulation experiments with real

cosmic chemistry, temperatures of the targets should be kept in the region between 4 and 10 K by the aid of cryostats. Especially for water ice, slight changes of temperatures in the 4 to 20 K and the 77 to 115 K region result in different mobility of radiolytic H[•] or OH[•] radicals, responsible for reducing or oxidizing the primary products of the implantation, cf. (7,18,19). The major disadvantage, however, remain the too high doses and dose rates, compared to interstellar conditions.

Table I. Chemical products formed by ion implantation into some simple solids

projectile	energy keV	target	temp. K	products	analysis** method	ref.
³⁵ S ⁺	60	NaCl, KCl	298	S ²⁻ , S ⁰ , SO ₃ ²⁻ , SO ₄ ²⁻	RC	20
³² P ⁺	60	"	298	PI, PIII, PV	"	20
¹² C ⁺ , ¹⁴ N ⁺	20-200	KCl	298	CN ⁻	UV	21
¹² C ⁺ , ¹³ C ⁺	250	AX***	5	C ₂ ⁻ (C ₂ , C ₃)	VIS, UV	22, 23
¹ H ⁺ , ² H ⁺	15	Al ₂ O ₃	298	Al ₂ O ₂ (OH)	IR	24
¹ H ⁺ , ² H ⁺		TiO ₂	298	OH, OD	IR	25, 26
¹² C ⁺	150	MgO, Al ₂ O ₃ , SiO ₂ , CaF ₂	5	no C ₂ ⁻	VIS, UV	22, 23
¹² C ⁺	15	minerals lunar samples	298	simple organic	MS	3, 4
¹² C ⁺ , ¹³ C ⁺	40	SiO ₂	298	CO ₂ , CO	IR	5, 27, 28
¹⁴ C ⁺	0.007 -0.48	H ₂ O	113	CO, CO ₂ , CH ₄ CH ₃ OH, CH ₂ O HCOOH etc.	RC	29, 30
¹² C ⁺ , ¹³ C ⁺	40	H ₂ O	77	CO ₂	IR	31
¹² C ⁺ , ¹⁴ N ⁺	40	H ₂ O	77	CNO(?)	IR	31
¹⁴ N ⁺	250	H ₂ O	6	NO ₂ , HNO ₂	IR	19, 32
¹¹ C ⁺	10 ⁻² -10 ³	C ₂ H ₄	77	twelve ¹¹ C labelled organic	RC	33

* RC = radiochem. separations, e.g. chromatography; UV, VIS, IR = optical spectroscopy in absorption; MS = mass spectroscopy of ejected ions

*** A = Na, K, Rb, Cs; X = F, Cl, Br, I

3. CHEMISTRY OF SECONDARY PROJECTILES (UPON KNOCK-ON, SPUTTERING)

Energetic particles in solids create a number of secondary projectiles by knock-on processes. Provided the energy of the latter ones is large enough, tertiary projectiles are formed and so on. Computer simulation of collision cascades in SiO₂ and H₂O-ice shows that by a 10⁴ eV hydrogen primary about 20 and by carbon between 50 and 100 secondaries are formed with energies between some few eV and 10⁴ eV (8). These particles can perform hot chemical reactions, which might be of special importance for frozen H₂O-NH₃-CH₄, etc. mixtures and contribute to the radiolytical reactions, cf. (3⁴). This hot chemistry underlies the formation and chemical sputtering of molecules and molecular ions during the bombardment of ices with fast ions (9).

TABLE II. Dependence of radiation dose D^{*} (total fluence) delivered to H₂O-ice (ρ=0.87) by carbon implants with various energies.

energy of 12C ⁺ , eV	mean pene- tration, nm cf. [8]	n(H ₂ O) cm ⁻² in the impl. layer	D [*] , eV per target molecule for 10 ¹⁵ or 10 ¹⁷ ions cm ⁻²	
10 ²	0.7	2 · 10 ¹⁵	50	5000
10 ³	6.5	1.9 · 10 ¹⁶	53	5300
10 ⁴	62	1.8 · 10 ¹⁷	55	5500
10 ⁵	600	1.7 · 10 ¹⁸	57	5700

Numerous systems have been studied via mass spectrometry of the ejected ions, such as H₂O, NH₃, CO₂, SO₂, CH₄, N₂, H₂ and O₂ and mixtures thereof, cf. e.g. (9,34-42). Of interest is the observation of formaldehyde D₂¹³C¹⁸O emerging from an ion bombarded surface of a ¹³C¹⁸O₂-D₂¹⁶O ice film at 9 K (9). The probable mechanism of formation may be an insertion of a secondary energetic ¹³C into the O-D-bonds of D₂¹⁶O. Besides the sputtering of ices there are interesting studies on the ejection of volatiles out of carbon films during bombardment with hydrogen at energies between 100 eV and 30 keV, cf. (43). Synergistic effects have been studied in the erosion of graphite and TiC by D⁺ ions, H⁰/Ar⁺-molecular and ion beams and H⁰/e⁻-molecular and electron beams (44-46) and the emission of CH₃, CH₄(CD₄) has been observed. Due to the sensitive methods of detection, irradiation doses can be kept somewhat lower than in the case of analysis of the primary's chemical fate. However, the information on the bulk chemistry is often obscured by surface effects and aggregation in the gas phase before detection.

4. NUCLEAR RECOIL IN SITU AND NUCLEAR RECOIL IMPLANTATION

Formation of energetic primaries at much lower irradiation doses ranging from 10⁻⁴ to some 10² eV per target molecule is possible via recoil processes after nuclear reactions. Biogenic recoil atoms can be

produced by a multiplicity of reactions ranging from the thermal neutron induced ${}^3\text{He}(n,p){}^3\text{H}$, ${}^{14}\text{N}(n,p){}^{14}\text{C}$, and ${}^{35}\text{Cl}(n,p){}^{35}\text{S}$ to those by cyclotron accelerated particles in the multi MeV range, e.g., ${}^{14}\text{N}(p,\alpha){}^{11}\text{C}$, ${}^{16}\text{O}(p,\alpha){}^{13}\text{N}$ and ${}^{14}\text{N}(d,n){}^{15}\text{O}$, cf. (7,10). The product nuclei obtain kinetic energies from several 100 eV to some MeV depending on the type of nuclear process. They can be projected in situ by activating a target component or implanted from the outside from another gaseous, liquid or solid source material, e.g. BN fine grains for implanting ${}^{11}\text{C}$ via the ${}^{14}\text{N}(p,\alpha){}^{11}\text{C}$ reaction into admixed LiH grains (15,16). That the irradiation doses can be kept much lower than in the ion implantation studies, comes from the fact that the projectiles are radioactive and can be followed by radiochemical techniques such as radiogas -, high performance liquid - and thin layer chromatography. Thus 10^7 to 10^{10} implants can be analyzed for their chemical fate. The radiation dose stems primarily from the activating particles (protons, deuterons, neutrons etc.) and not from the collision cascade of the primary as in the case of the ion implantation or sputtering studies. The disadvantages of the nuclear method are the target evaporation, melting or dissolving steps prior to the chromatographic analysis, which may change important metastable intermediates in the cold solid into different final products. Also, only reactions of single atoms can be studied. The small number of recoil atoms is not sufficient to form compounds containing two or more of them. Despite these disadvantages, the fact that (via the radioactivity) a 100 % balance of the products of a certain implant is possible and the low dose range render the nuclear method as a powerful tool for studies of cosmic solid state chemistry. Recent examples are the systems ${}^{11}\text{C}/\text{H}_2\text{O}$ (77 K), ${}^{13}\text{N}/\text{H}_2\text{O}$ (77 K), ${}^{11}\text{C}/\text{NH}_3$ (77 K) and ${}^{13}\text{N}/\text{CH}_4$ (77 K) (7,15-19) which demonstrated the formation of products which are important for cosmic chemistry with respect to chemical evolution such as NH_3 , CH_4 , formaldehyde, cyanamide, methylamine, NH_2OH , CH_3OH , formamidine and guanidine. These systems showed the primary hot reactions at doses $\leq 10^{-2}$ eV per target molecule and at increasing radiolysis, e.g. in H_2O ice, reduction by H^\cdot radicals, and at highest doses ($>10^1$ eV per target molecule) oxidation by the reactive OH^\cdot and O_2H^\cdot radicals. Thus, products are constantly changed by radiolysis (7). From the effects of temperature, dose and dose rate extrapolation to cosmic conditions seem to be possible.

6. CONCLUSION

The three experimental methods for studying hot reactions in solids of astrophysical interest have advantages and disadvantages with respect to information on the proper in situ reactions at lowest temperatures. Thus, they have to complete each other and proper mechanistic information should be based on intercomparison of the results obtained by at least two of the methods. Computer simulation of collision cascades provides the necessary solid state physical background information for the chemical studies.

REFERENCES

1. W.D. Watson, Rev.Mod.Phys. 48 (1976) 513/52
2. J.M. Greenberg, Sci.American 250 (1984) 96/106
3. J.P. Bibring, Y. Langevin, M. Maurette, R. Meunier, B. Jouffrey, C. Jouret, Earth Planet.Sci.Letters 22 (1974) 205/14
4. M. Maurette, Nucl.Instr.Meth. 132 (1975) 579/86
5. J.P. Bibring, F. Rocard, Radiat.Eff. 65 (1982) 159/65
6. K. Rössler, M. Vogt, 7th Int.Conf.Origins of Life, Mainz, FRG, 10-15 July 1983, Abstract C1-26
7. K. Rössler, H.-J. Jung, B. Nebeling, Adv.Space Res. 1985, in press (COSPAR 1984, F.3.3.1 and F.5.1)
8. K. Rössler, G. Eich, this issue
9. W.L. Brown, L.J. Lanzerotti, R.E. Johnson. Science 218 (1982) 525/31
10. G. Stöcklin, Chemie heißer Atome, Verlag Chemie, Weinheim 1969 (french version: Chimie des atomes chauds, Masson et. Ci., Paris 1971)
11. F.S. Rowland (ed.), Hot Atom Chemistry Status Report, IAEA, Vienna 1975
12. G. Harbottle, A.G. Maddock (eds.), Chemical Effects of Nuclear Transformations in Inorganic Systems, North Holland, Amsterdam 1979
13. T. Tominaga, E. Tachikawa, Modern Hot Atom Chemistry and its Applications, Springer Verlag, Berlin 1981
14. T. Matsuura (ed.), Hot Atom Chemistry, Kodansha, Tokyo 1984
15. K. Rössler, H. Lattke, C. Mathias, L.M. Al Shukri, M. Vogt, J.Lab.Comp.Radiopharm. 19 (1982) 1618/9
16. M. Vogt, Report Jül-1855 (June 1983)
17. K. Rössler, M. Vogt, Proc. 7th Int.Congr.Radiation Research, J.J. Broerse et al. (eds.), Martinus Nijhoff Publ., Amsterdam 1983, A6-05
18. B. Nebeling, Report-Jül-1973 (February 1985)
19. K. Rössler, K. Schurwanz, Report-Jül-1990 (April 1985)
20. A.G. Maddock, in (11), 33/48, and ref. cited herein
21. W.A. Metz, E.W. Thomas, Nucl.Instr.Meth. 194 (1982) 505/8
22. K. Rössler, A.R. Manzanares, Report Jül-1924 (June 1984)
23. K. Rössler, A.R. Manzanares, B. Stritzker, in Induced Defects in Insulators, P. Mazzoldi (ed.), Les Editions de Physique, Paris 1984, 193/9
24. D.M. Gruen, B. Siskind, R.B. Wright, J.Chem.Phys. 65 (1976) 363/78
25. M. Guermazi, P. Thevenard, P. Faisant, M.G. Blanchin, C.H.S. Dupuy Rad.Effects 37 (1978) 99
26. A. Perez, Nucl.Instr.Meth. B1 (1984) 621/7
27. F. Rocard, J.-P. Bibring, Phys.Rev.Lett. 48 (1982) 1763/6
28. J.P. Bibring, Y. Langevin, F. Rocard, J.Geophys.Res. 87 Suppl. (1982) A446/50
29. A.G. Maddock, University of Cambridge (U.K.), private communication
30. I.M. Evans, Ph.D.Thesis, University of Cambridge (U.K.) 1970
31. J.-P. Bibring, F. Rocard, Adv.Space Res., 1985, in press (COSPAR 1984, F.3.3.2)

32. K. Rössler, M. Batista, B. Nebeling, K. Schurwanz, Terra Cognita 5 (1985) 128
33. J. Dubrin, C. MacKay, R. Wolfgang, J.Am.Chem.Soc. 86 (1964) 645
34. W.L. Brown, W.M. Augustyniak, E. Simmons, K.J. Marcantonio, L.J. Lanzerotti, R.E. Johnson, J.W. Boring, C.T. Reimann, G. Foti, V. Pirronello, Nucl.Instr.Meth. 198 (1982) 1/8
35. V. Pirronello, G. Strazulla, G. Foti, E. Rimini, Nucl.Inst.Meth. 182/183 (1981) 315/7
36. G. Strazulla, V. Pirronello, G. Foti, Astr.Astrophys. 123 (1983) 93/7
37. J. Schou, H. Sørensen, P. Børgesen, Nucl.Instr.Meth. B5 (1984) 44/57
38. L.E. Seiberling, C.K. Meins, B.H. Cooper, J.E. Griffith, M.H. Mendehall, T.A. Tombrello, Nucl.Instr.Meth. 198 (1982) 17/25
39. R.A. Haring, A. Haring, F.S. Klein, A.C. Kummel, A.E. de Vries, Nucl.Instr.Meth. 211 (1983) 529/33
40. R.A. Haring, A.W. Kolfschoten, A.E. de Vries, Nucl.Instr.Meth. B2 (1984) 544/9
41. A.E. de Vries, R. Pedrys, R.A. Haring, A. Haring, F.W. Saris Nature 311 (1984) 40
42. L.J. Lanzerotti, W.L. Brown, K.J. Marcantonio, R.E. Johnson, Nature 312 (1984) 139/40
43. J. Roth, Topics in Applied Physics 52 (1983) 91/146
44. E. Vietzke, K. Flaskamp, V. Philipps, J.Nucl.Mat. 111/112 (1982) 763/8
45. E. Vietzke, K. Flaskamp, V. Philipps, J.Nucl.Mat. 128/129 (1984) 564/9
46. E. Vietzke, K. Flaskamp, V. Philipps, J.Nucl.Mat. 128/129 (1984) 545/550