EXPERIMENTAL AND COMPUTATIONAL STUDY OF THE RADIATION–INDUCED DECOMPOSITION OF FORMALDEHYDE. IMPLICATIONS TO COMETARY NUCLEI

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Abstract. The radiation-induced decomposition of aqueous solutions of formaldehyde was studied at 298 and 77 K in order to obtain an insight into the possible role of ionizing radiation on cometary chemistry. Aqueous solutions of 1.0 mol dm^{-3} formaldehyde were exposed to γ-radiation in the dose range from 0.01 kGy to 1.2 MGy. The radiation chemical yield of decomposition of formaldehyde was determined to be: $G(-CH_2(OH)_2)$=26.3$\pm$1.2 at 298 K and $G \leq 0.48$ at 77 K.

Based on previous estimates of the total dose of ionizing radiation that comets have accumulated over 4.6 billion years, we predict a radiation-induced depletion of formaldehyde as a function of depth in comet nuclei: 100% destruction in the outer layers (0–20 m) and $\approx$ 10% destruction in the interior layers.

1. Introduction

Radiation chemical processing of comets by cosmic radiation during their life time in Oort's cloud has been considered as a source for new molecular species (Huebner, 1987; Strazzulla, 1987; Khare *et al.*, 1989). For example, while the identification of polyoxymethylene (POM, an oligomer of formaldehyde) is still controversial (Mitchell *et al.*, 1989), Huebner has suggested that POM could have been formed by the action of cosmic radiation on the surface layers of comet nuclei (Huebner, 1987). Furthermore, it has been suggested that the dark surfaces of cometary nuclei could be attributed to radiation effects (Cruikshank, 1989). Estimates of the contribution of ionizing radiation, both internal (decay of imbedded radionuclides) and external (cosmic rays) to the absorbed dose inventory of cometary nuclei have been made by Draganić and coworkers (Draganić *et al.* 1984, 1987; Ryan and Draganić, 1986; Draganić and Draganić, 1988). Their calculations seem to indicate that ionizing radiation may have had a more important role than is generally admitted (Mukhin *et al.*, 1989; Mitchell *et al.*, 1989; Greenberg, 1987).

The purpose of this work** is to investigate the radiation-induced decomposition

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of formaldehyde in cometary nuclei and to establish if ionizing radiation played a role in chemically altering the pristine nature of comets. The reason for selecting an aqueous formaldehyde system is that water is a major constituent of comets, comprising about 80% of volatile ices (Greenberg, 1987, 1989; Oró, and Mills, 1989), and formaldehyde is relevant because:

(1) It is among the most abundant carbon containing molecules in comets (Greenberg, 1987, 1989; Oró, and Mills, 1989), and it is also present in carbonaceous chondrites (Breger *et al.*, 1972);

(2) Frozen anhydrous formaldehyde has a large radiation yield of polymerization: $G \approx 10^7$ (molecules per 100 e.V) at 140 K, $G \approx 10^5$ at 77 K, and $G \approx 10^3$ at 4 K (Goldanskii *et al.*, 1973);

(3) If the identification of POM is correct (Huebnear, 1987; Huebner *et al.*, 1989), it may have been formed from formaldehyde;

(4) Cometary bombardment of the primitive Earth would have provided formaldehyde among other organics for terrestrial chemical evolution (Oró and Berry, 1987); and

(5) No systematic study of the radiolysis of aqueous formaldehyde has been done relevant to either cometary chemistry or terrestrial chemical evolution.

2. Experimental Procedure

The purification of water and cleaning of glassware were carried out by standard procedures used in radiation chemistry (Draganić and Draganić, 1971). The chemicals used were of the highest purity commercially available.

2.1. SAMPLE PREPARATION AND IRRADIATION

Methanol-free formaldehyde solutions were prepared by dissolving commercial paraformaldehyde (5.3 g) in triple distilled water (0.15 dm³). The mixture was heated at about 353 K for half an hour, and finally the residue was filtered out. Oxygen-free aqueous 1.0 mol dm⁻³ formaldehyde solutions at their natural pH (≈ 6.7) were prepared according to the ampoule or syringe techniques (Draganić and Draganić, 1971) from methanol-free formaldehyde solutions.

Irradiations were carried out in two ^{60}Co units at dose rates of 5 and 120 Gy min⁻¹. The irradiations were done at 298 K. Some preliminary data were also obtained at liquid nitrogen temperature (77K).

2.2. ANALYSES

Molecular hydrogen was extracted from irradiated solutions into a gas-evacuated chamber and introduced by a Töepler pump into a Varian 1400 gas chromatograph equipped with a thermal conductivity detector. A column (4 ft long, 1/4 in e.d.) packed with silica-gel (40/50 mesh) was employed for the analysis using argon with a flow rate of 30 cm³ min⁻¹.

Hydrogen peroxide was measured according to the method of Allen *et al.* (1952).

The molar extinction coefficient in the presence of formaldehyde was determined to be: $\epsilon_{350 \text{ nm}} = 25\,496\ (\pm 1\%)\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$.

Formaldehyde was determined by potentiometric titration of the weak anion produced by the addition of sodium bisulfite with an accuracy of $\approx 1\%$. It was also determined by high performance liquid chromatography (HPLC) using the chromatographic conditions reported below.

HPLC was used for the separation of low molecular weight organic acids (such as formic acid) as well as of simple, non-ionic compounds (such as formaldehyde and methanol). A Varian 5000 liquid chromatograph was used with a variable UV-visible wavelength detector fixed at 210 nm. An ion-moderated partition chromatographic column (Aminex HPX-87H, 300×7.8 mm) purchased from Bio-Rad Laboratories was used for the analysis. The elution was performed with a 0.001 mol $\text{dm}^{-3}\ H_2SO_4$ solution with a flow rate of 0.6 $\text{cm}^3\ \text{min}^{-1}$.

Gas chromatography-mass spectrometry (GC-MS) was used for the analysis of formaldehyde, formic acid, methanol and other potential products. The analysis was carried out in a Hewlett Packard gas chromatograph 5890 coupled to a mass detector series HP-5970 operated at 70 eV. A capillary column from Hewlett Packard (HP-1, 12 m $\times$ 0.2 mm $\times$ 0.33 μm film thickness) was used for the analysis. Helium was used as the carrier gas with a flow rate of 2 $\text{cm}^3\ \text{min}^{-1}$. The column temperature was maintained isothermal at 30 °C for 10 min and then varied from 30 °C to 210 °C at 1 °C min^{-1}.

The radiation chemical yields (G) of products or solutes were expressed as the number of molecules destroyed or formed per 100 eV of energy absorbed, and were calculated from the slopes of concentration-dose plots according to Navarro-González et al., 1989. The deviations on G values were calculated from the standard error of the slopes obtained by linear regression analyses.

3. Computer Modeling

The computer program used, ACUCHEM, was developed by Braun et al. (1988) from the U.S. National Institute of Standards and Technology. ACUCHEM is based on deterministic kinetics methods to solve numerically the system of differential equations describing the temporal behavior of spatially homogeneous, isothermal, multicomponent chemical reactions. The chemical kinetics data base for modeling the radiolysis of liquid water and dilute solutions was compiled from the reference data reported by Buxton et al. (1988) and has been described in detail (Navarro-González, 1989). Reaction 1 in Table I summarizes the chemical effect produced by the irradiation of liquid water at pH 3–13 with γ-rays or fast electrons with energies in the range from 0.1 to 20 MeV. The fate of such molecular and radical products is modeled with 54 chemical reactions. Some of the main reactions included in the mechanism are given in Table I (reactions 2–7). In addition, reactions 8 to 25 in Table I were included in the chemical kinetic data base to model the radiation-induced decomposition of formaldehyde in aqueous solutions. Reaction

Table I

Reactions used in simulations of irradiated solutions of aqueous formaldehyde

No.	Reaction			Constant[a]	Remark
1	H_2O	$\xrightarrow{\gamma\text{-ray}}$	$0.6\ H\cdot + 2.6\ e_{aq}^- + 2.6\ H +$ $2.7\ \cdot OH + 0.7\ H_2O_2 + 0.45\ H_2$	$G(-H_2O)=4.1$	Buxton et al., 1988
2	$H\cdot$	$+\ H\cdot$	$\longrightarrow\quad H_2$	$k=7.8\times10^9$	Buxton et al., 1988
3	$H\cdot$	$+\ e_{aq}^-$	$\xrightarrow{H_2O}\ H_2 + OH^-$	$k=2.5\times10^{10}$	Buxton et al., 1988
4	$H\cdot$	$+\ \cdot OH$	$\longrightarrow\quad H_2O$	$k=7.0\times10^9$	Buxton et al., 1988
5	e_{aq}^-	$+\ e_{aq}^-$	$\xrightarrow{2H_2O}\ H_2 + 2OH^-$	$k=5.5\times10^9$	Buxton et al., 1988
6	e_{aq}^-	$+\ H^+$	$\longrightarrow\quad H\cdot$	$k=2.3\times10^{10}$	Buxton et al., 1988
7	$\cdot OH$	$+\ \cdot OH$	$\longrightarrow\quad H_2O_2$	$k=5.5\times10^9$	Buxton et al., 1988
8	$CH_2(OH)_2$	$+\ e_{aq}^-$	$\longrightarrow\quad \cdot CH_2OH + OH^-$	$k=1.0\times10^7$	Buxton et al., 1988
9	$CH_2(OH)_2$	$+\ H\cdot$	$\begin{cases} \longrightarrow\ \cdot CH(OH)_2 + H_2 \\ \longrightarrow\ \cdot CH_2OH + H_2O \end{cases}$	$k_a=3.3\times10^6$ $k_b=6.7\times10^5$	Anbar et al., 1975; Buxton et al., 1988
10	$CH_2(OH)_2$	$+\ \cdot OH$	$\longrightarrow\quad \cdot CH(OH)_2 + H_2O$	$k=1.0\times10^9$	Buxton et al., 1988
11	$\cdot CH_2OH$	$+\ \cdot CH_2OH$	$\longrightarrow\quad (CH_2OH)_2$	$k=1.5\times10^9$	Ross and Neta, 1982
12	$\cdot CH(OH)_2$	$+\ \cdot CH(OH)_2$	$\longrightarrow\quad CH_2(OH)_2 + HCO_2H$	$k=3.6\times10^8$	Ross and Neta, 1982
13	$\cdot CH_2OH$	$+\ H_2O_2$	$\longrightarrow\quad CH_2(OH)_2 + \cdot OH$	$k=4.0\times10^4$	Ross and Neta, 1982
14	HCO_2H		$\rightleftharpoons\quad HCO_2^- + H^+$	$K=1.8\times10^{-4}$	Weast et al., 1985
15	$\cdot CH_2OH$	$+\ CH_2(OH)_2$	$\longrightarrow\quad \cdot CH(OH)_2 + CH_3OH$	$k=1.0\times10^5$	Ross and Neta, 1982
16	$\cdot CH(OH)_2$	$+\ CH_2(OH)_2$	$\longrightarrow\quad \cdot P_2$	$k=8.0\times10^1$	This work
17	$\cdot P_2$	$+\ CH_2(OH)_2$	$\longrightarrow\quad \cdot P_3$	$k=8.0\times10^1$	Assumed[b]
18	$\cdot P_3$	$+\ CH_2(OH)_2$	$\longrightarrow\quad \cdot P_4$	$k=8.0\times10^1$	Assumed[b]
19	$\cdot P_4$	$+\ CH_2(OH)_2$	$\longrightarrow\quad \cdot P_5$	$k=8.0\times10^1$	Assumed[b]
20	$\cdot P_5$	$+\ CH_2(OH)_2$	$\longrightarrow\quad \cdot P_6$	$k=8.0\times10^1$	Assumed[b]
21	$\cdot P_6$	$+\ CH_2(OH)_2$	$\longrightarrow\quad \cdot P_7$	$k=8.0\times10^1$	Assumed[b]
22	$\cdot P_7$	$+\ CH_2(OH)_2$	$\longrightarrow\quad \cdot P_8$	$k=8.0\times10^1$	Assumed[b]
23	$\cdot P_8$	$+\ CH_2(OH)_2$	$\longrightarrow\quad \cdot P_9$	$k=8.0\times10^1$	Assumed[b]
24	$\cdot P_9$	$+\ CH_2(OH)_2$	$\longrightarrow\quad \cdot P_{10}$	$k=8.0\times10^1$	Assumed[b]
25	$\cdot P_n$	$+\ \cdot P_m$	$\longrightarrow\quad$ Oligomers	$k=1.0\times10^8$	Assumed[c]

where n and m vary from 2 to 10

[a] Rate constants and equilibrium constants are denoted by k and K, respectively. Rate constants have units of $dm^3\ mol^{-1}\ s^{-1}$. Radiation chemical yields (G) are the number of molecules formed or destroyed per 100 eV.
[b] Rate constants are assumed to be of the same order of magnitude as that of reaction 16.
[c] Rate constants are assumed to be of the same order of magnitude as that of reaction 12.

16 (Table I) was derived by computer fitting of the decomposition of formaldehyde and of the pH-dose response using reaction 12 as the competing reaction.

For modeling the radiolysis of aqueous solutions of formaldehyde in the frozen stage at 77 K, we would have to consider the following stages:

(1) Energy deposition. It occurs in the rigid, icy, matrix with heterogeneous formation of reactive species with low mobility;

(2) Thawing process. It leads to increased mobility of the reactive intermediates and their reactions; and

(3) Liquid phase. The remaining reactive species disappear in chemical reactions.

It should be noted that the kinetic data to model a frozen aqueous system as

that examined in this work are not available, and we have used those for the liquid system (Table I). This is certainly a very crude approximation but enable us to obtain an overall preliminary picture of the process involved. In this extrapolation, we have assumed that the relative ratios for the rate constants used in the chemical kinetic data base (Table I) are unchanged at low temperatures. This assumption is partially supported by the fact that the relative reaction rates of solvated electrons with a variety of solutes in ice at 77 K quantitatively parallel those in liquid water at 300 K (Kevan, 1967); and also because the product distribution is unchanged from 298 K to 77 K (Draganić et al., 1985). In addition, we have made the following considerations for modeling the radiolysis of the frozen system at 77 K:

(1) The net chemical effect on the radiolysis of frozen water is similar to that of liquid water (Table I), except that hydrated electrons (e_{aq}^-) would be replaced by trapped electrons (e_t^-). The crystalline structure of ice appears to favor energy dissipation without reaction, and caging and subsequent recombination of radicals, so that the yields are considerably lower than in liquid water (Kevan, 1968; Spinks and Woods, 1976);

(2) G(-H_2O) falls from 4.1 at 298 K to 3.4 in ice at 263 K, 1.0 at 195 K, and 0.5 at 73 K (Allan et al., 1959);

(3) G(H_2O_2) has been determined to be 0.1 (Siegal and Rennick, 1966; Draganić et al., 1985);

(4) Using the equation of material balance for the oxidizing species G(-H_2O) =G($\cdot$OH)+2G(H_2O_2), we derived that G($\cdot$OH)=0.3. This value is consistent with the yield of stabilized $\cdot$OH radicals determined experimentally at 77 K by Siegel et al. (1961);

(5) It is concluded that G(H_2)=G(H_2O_2) based on a G(H_2)=0.1 for oxygen-saturated aqueous solutions at 77 K (Ghormley and Stewart, 1956).

(6) Using the equation of material balance for reducing species G(-H_2O) =2G(H_2)+G($\cdot$H)+G(e_t^-), we derived that G($\cdot$H)+G(e_t^-)=0.3. This value is consistent with a G(H_2)=0.4 for oxygen-free aqueous ethanol solutions at 77 K (Allan et al., 1959); and

(7) The production of trapped electrons (e_t^-) has been estimated to be G(e_t^-)=2 $\times$ 10^{-4} (Eiben and Taub, 1967); therefore, G($\cdot$H)=0.3.

4. Results and Discussion

4.1. RADIATION-INDUCED DECOMPOSITION OF FORMALDEHYDE AT 298 K

The experimental and theoretical decomposition of formaldehyde as a function of dose are shown in Figure 1. The experimental radiation chemical yield of decomposition of formaldehyde was determined to be 26.3 $\pm$ 1.2. We attributed this high value to a chain oligomerization reaction initiated by the radical $\cdot$CH(OH)$_2$ with formaldehyde. Computer fitting of the experimental data on the initial yield of decomposition of formaldehyde (dotted line in Figure 1) gives k($\cdot$CH(OH)$_2$ +
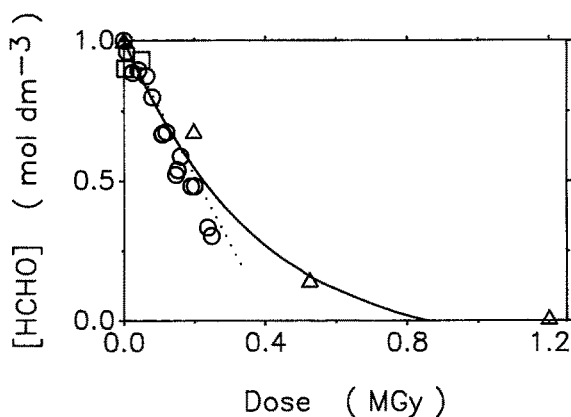
Fig. 1. γ-Radiation-induced decomposition of 1.0 mol dm^{-3} CH$_2$(OH)$_2$ in liquid water at 298 K. Titration (○), HPLC (△) and from Irie, 1989 (□). Solid line was obtained by computer simulation. Dotted line shows the initial trend used to derived k$_{16}$ by ACUCHEM.

CH$_2$(OH)$_2$)=8.0 × 10^1 dm^3 mol^{-1} s^{-1}. This rate constant is about 3 orders of magnitude lower than its analog free-radical molecule reaction (·CH$_2$OH + CH$_2$(OH)$_2$), reaction 15 in Table I). The decrease in reactivity might be due to steric effects cause by the presence of an additional hydroxyl group in the radical.

The formation of hydrogen peroxide and molecular hydrogen were studied at low absorbed doses (<0.1 kGy). Hydrogen peroxide was not detected in irradiated solutions in spite of an expected yield of formation of G=0.69; therefore, reaction 13 in Table I is not sufficient to account for its disappearance. An additional reaction must be considered in the mechanism. The most probable fate is its reaction with the radicals (·P$_n$ and ·P$_m$) formed by reactions 16 to 24. Molecular hydrogen was formed with a radiation chemical yield of 0.88 ± 0.04 (Figure 2). Such a value is consistent, within experimental error, with a 83% abstraction of hydrogen atoms

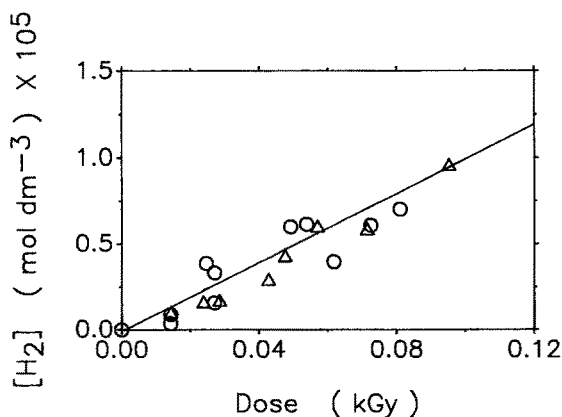Fig. 2. Dose dependance of molecular hydrogen in 1.0 mol dm^{-3} (○) and in ≈0.04 mol dm^{-3} (△) CH$_2$(OH)$_2$ solutions at 298 K. Line was obtained by computer simulation.
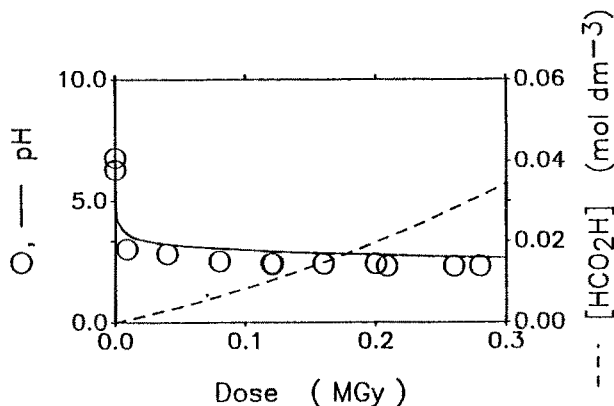
Fig. 3. Dependance of formic acid and pH of irradiated solutions of formaldehyde as a function of dose at 298 K. Lines were computed; solid line shows the trend assuming that the pH is only modified by the dissociation of formic acid.

(reaction 9 in Table I) reported elsewhere (Witter and Neta, 1973). The rate of formation in hydrogen was not affected at lower concentrations of formaldehyde ($\approx$0.04 mol dm^{-3}).

Methanol and formic acid are the expected major products in the radiolysis of formaldehyde. Both of them were identified by HPLC and GC-MS. Their radiation chemical yields were estimated to be: $G(CH_3OH) \approx 2.7$ at 200 kGy and $G(HCO_2H) \leq 3.6$ at 9 kGy. The yield of formation of formic acid was estimated from the change of pH of the irradiated solution. The pH of the solution changed abruptly from 6.7 at 0 kGy to 3 at 9 kGy and then falling steadily to 2.3 at 280 kGy (Figure 3).

The formations of methanol and formic acid account for only $\approx$24% of the destroyed molecules of formaldehyde, indicating that a significant amount of formaldehyde molecules should be also involved in the formation of other molecules, possibly additional products larger than formaldehyde molecules. Analyses of the irradiated samples indicate the lack of formation of stable nonvolatile products after the solutions were evaporated under reduced pressure ($\approx$45 °C) and freeze-dried. The weight of the dry residue from the blanks and the irradiated samples (0.025 g dm^{-3}, due to paraformaldehyde) was unchanged in the dose range from 0 to 200 kGy. Only at extremely high doses of radiation ($\geq$8 MGy), the formation of some oligomeric material was detected. This material is very likely formed by secondary reactions involving the primary products of formaldehyde.

Computations based on the reaction process shown in Table I suggest the formation of oligomeric radicals ($\cdot P_n$ and $\cdot P_m$) with a maximum size centered at six formaldehyde-subunits. These radicals presumably react by dimerization and/or disproportionation leading to the final products (reaction 25 in Table I). In spite of their mode of reaction, it is predicted that the oligomeric fraction should be abundantly formed (e.g., 0.01 mol at 0.06 MGy) with a maximum size centered between six to twelve formaldehyde-subunits. However, the lack of nonvolatile

products in radiolysed aqueous formaldehyde solutions could suggest that:

(1) The oligomers are hydrolyzed under the acidic conditions produced *in situ* during irradiation.

(2) The oligomers are depolymerized by a shift of equilibria due to the presence of radiolytic methanol (expected to be present in the range of 0.01–0.05 mol dm^{-3} at 0.1–1.0 MGy) in a fashion similar to that suggested for the stabilization of commercial methanol-formaldehyde solutions (Le Botlan, 1987).

(3) The oligomers are volatile and labile, breaking down into smaller molecules during analysis.

Further work needs to be done to search for other products formed in the radiolysis of formaldehyde solutions. These findings would be relevant not only to cometary chemistry but also to terrestrial prebiotic chemistry.

4.2. RADIATION-INDUCED DECOMPOSITION OF FORMALDEHYDE AT 77 K

Table II summarizes the experimental and theoretical data for the radiolysis of formaldehyde at 298 K. In addition, it includes our predicted data at 77 K since this temperature is of interest to cometary environments. We have considered two extreme situations in which oligomerization of the radical $\cdot CH(OH)_2$ with formaldehyde could (case 1) or could not (case 2) take place. Preliminary examinations at low temperatures (77 K) indicate that $G(-CH_2(OH)_2) \leq 0.48$: Less than one percent decomposed in the dose range of 200–400 kGy.

A previous examination of the radiolysis of frozen anhydrous formaldehyde has revealed that formaldehyde undergoes intense degree of polymerization even at temperature as low as 4 K (Goldanskii *et al.*, 1973). Such phenomenon was interpreted as a tunneling effect. The role of radiation was restricted to the formation of primary

TABLE II

Initial radiation chemical yields (G) for γ-radiolyzed solutions of formaldehyde

Compound	Experimental	Predicted		
	298 K	298 K	77 K	
			Case 1[a]	Case 2[b]
$CH_2(OH)_2$[c]	26.3 ± 1.2	23.31	4.63	0.35[d]
H_2	0.88 ± 0.04	0.96	0.35	0.35
H_2O_2	0.0	0.69	0.10	0.10
CH_3OH	≈2.7[e]	2.61	0.05	0.05
HCO_2H	≤3.6[f]	0.67	0.01	0.30[g]

[a] Case 1 assumes that oligomerization takes place.
[b] Case 2 assumes that no oligomerization occurs.
[c] Decomposition.
[d] Experimental value is estimated to be ≤0.48 in the dose range 200–400 kGy.
[e] Estimated at 200 kGy.
[f] Estimated at 9 kGy.
[g] Experimental value is estimated to be about 0.20.

active centers which led to initiation of the polymer (endothermic process). Once the chain started, the formation of each new link was an exothermic process which proceeds spontaneously. In contrast, the radiation-induced oligomerization of formaldehyde is inhibited when it is embedded in a water-icy environment. The most likely explanation is that the radical $\cdot CH(OH)_2$ has a very low mobility at low temperature in a water-icy matrix. Consequently it can not react with formaldehyde molecules to initiate the oligomerization process.

4.3. IMPLICATIONS TO COMETARY NUCLEI

The spatial distribution of radicals produced by the radiolysis of water as well as the efficiency of radical-radical and radical-solute reactions depend on the type of radiation and its energy, more specifically on the radiation linear energy transfer (LET) (Draganić and Draganić, 1971). Our calculations and experiments are for gamma rays which have a low LET, 0.23 keV μm^{-1}. Cometary nuclei have been mainly exposed to cosmic rays flux (Ryan and Draganić, 1986). The cosmic ray-protons are the dominating ionizing particles in the interstellar medium, about 95% of the cosmic ray flux. Most abundant are the protons which have energies
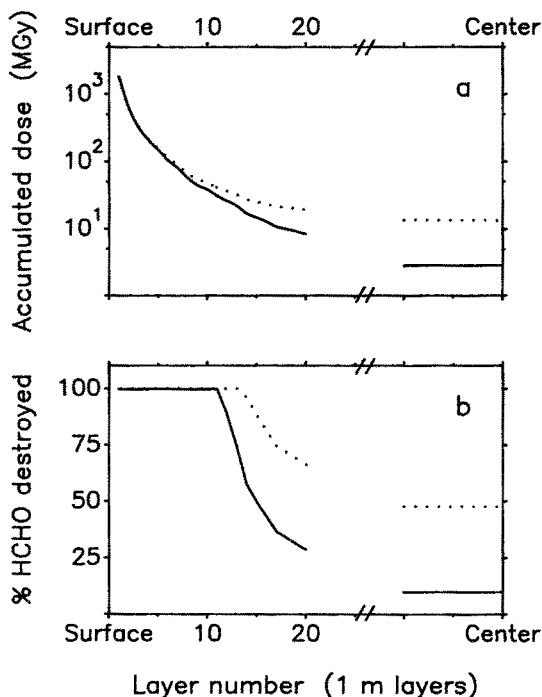

Fig. 4. (a) Dose-depth curve for contributions of cosmic rays-protons with energies ranging from 0.001 GeV to 10^{10} GeV and of radionuclides (Adapted from Draganić et al, 1984, 1987; Ryan and Draganić, 1986). (b) Radiation damage-depth curve of formaldehyde in comets: Case 2 at 77 K. Solid lines: Cosmic rays-protons and ^{40}K, ^{235}U, ^{238}U, ^{232}Th, ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be, and ^{237}Np; Dotted lines: ^{26}Al and those included for the case of solid lines.

of about 2 GeV (Draganić and Draganić, 1988) and a LET similar to gamma rays (Draganić *et al.*, 1984). Therefore, gamma ray irradiation could be a suitable energy source in the laboratory for the simulation of 2 GeV proton irradiation of cometary nuclei (Draganić *et al.*, 1984).

To evaluate the role of ionizing radiation on cometary chemistry, we have used the calculations of Ryan and Draganić (1986) and Draganić *et al.* (1987) for the dosimetry of cosmic-ray protons with energies ranging from 0.001 GeV to 10^{10} GeV as well as the estimates of Draganić *et al.* (1984) for the contributions of imbedded radionuclides (^{40}K, ^{235}U, ^{238}U, ^{232}Th, ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be, and ^{237}Np) to total the absorbed dose. Figure 4a shows the variation of dose as a function of depth from the comet surface accumulated over 4.6 billion years. Figure 4b shows the predicted alteration of formaldehyde according to such radiation doses for case 2 at 77 K. Within the first 10 to 20 m layers of the comet surface, there is a heavy radiation-processing. However, this rapidly diminishes down to about 10%. If we consider the early existence of ^{26}Al, although this is still disputed, then the amount of radiation-processing of comet nuclei could be increased as much as about 50% in the interior layers.

According to available estimates comet Halley has made about 1000 passages near the Sun and lost in each passage an equivalent of a matter layer of about 1 m (Mukhin *et al.*, 1989) to 10 m (Mitchell *et al.*, 1989). Since the surface temperature of a comet may be increased as the comet approaches the Sun, the result may be that some of the outer layer may be burned off but some radiation damage may migrate inwards as the comet leaves the Sun. Therefore, a minimum of 10% of radiation-induced decomposition of formaldehyde could be expected for the surface of comet Halley.

5. Concluding remarks

Our work allows us to estimate the possible role of ionizing radiation in chemically altering the pristine nature of comets. The data indicate that massive radiation-processing has taken placed in the outer layers (10–20 m) of comets due to cosmic radiation. The internal contribution of radionuclides (^{40}K, ^{235}U, ^{238}U, ^{232}Th, ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be, and ^{237}Np) to the radiation-processing of comet nuclei seems to be modest. These results imply that the original composition of cometary nuclei have not been significantly altered since their formation, and the study of the chemical composition of comets will provide information about the composition of the presolar nebula.

Acknowledgements

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