

Research Article

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Effect of γ -radiation on adenine dissolved in distilled water, saline solutions and artificial seawater resembling that of 4.0 billion years ago

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Abstract

In this work, the effect of γ -radiation on the decomposition of adenine dissolved in distilled water, saline solutions and artificial seawater was studied. As the composition of the major cations and anions of artificial seawater probably better resembles the composition of seawater on the Earth 4.0 billion years ago, this seawater was named artificial seawater 4.0 Ga. The main finding in this work is that artificial seawater 4.0 Ga demonstrated a better protective effect of adenine against γ -radiation. In addition, artificial seawater 4.0 Ga showed that adenine had no changes in pH after radiation exposure and the minor radiation-chemical yield *G*. The radiolysis of adenine promoted modifications in Fourier-transform infrared spectra. The deconvolution of some bands demonstrated the formation of a new frequency at 1713 cm⁻¹. High performance liquid chromatography-mass detected a product of decomposition with 151 atomic units. Using the geometry optimization and simulated vibrational spectra it was possible to show that the main species formed are hydroxyl and oxide modified adenine. The data point to the formation of hydroxyl-adenine and adenine N_x-oxide. These products have biological relevance and could be available for chemical evolution.

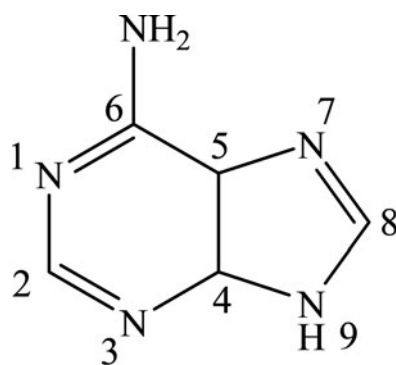
Introduction

From an astrobiology perspective, adenine (Fig. 1) is a purine, one of the nucleic acid bases of the deoxyribonucleic acid/ribonucleic acid, and is an important biomolecule; its abiotic synthesis has been demonstrated under prebiotic chemistry conditions (Oró and Kimball, 1961; Basile *et al.*, 1984; Vergne *et al.*, 2000; Saladino *et al.*, 2001; Roy *et al.*, 2007; Cleaves, 2018). In addition, adenine has been found in meteorites (Hayatsu *et al.*, 1975; Martins *et al.*, 2009; Cleaves, 2018). Thus, it is plausible to suppose that adenine was present in the prebiotic Earth.

In the prebiotic Earth, several energy sources existed such as: UV-radiation, heating from hydrothermal vents or impact meteors or volcanic activity, electric discharge, cosmic rays and radioactivity (Kobayashi *et al.*, 2001). γ -Radiation resulted from the radioactive decay effect from certain radioisotopes (⁴⁰K, ²³²Th, ²³⁵U, ²³⁸U and ²⁴⁴Po); this radiation is classified as ionizing radiation because of its high energy, capable of ionizing (Allen, 1961). To simulate the effects of γ -radiation on prebiotic chemistry experiments, ⁴⁰K and ⁶⁰Co are used as sources (Negrón-Mendoza *et al.*, 2016). Since ionizing radiation and adenine existed in the prebiotic Earth, the interaction between them is an important issue for prebiotic chemistry.

It should be noted that the majority of prebiotic chemistry experiments are performed in distilled water or NaCl solutions (Zaia, 2012). Naturally, neither NaCl solutions nor distilled water are representative of the complex seas of the primitive Earth. Based on the work of Izawa *et al.* (2010), who performed an experiment through leaching of meteorite samples in Tagish Lake, Zaia (2012) suggested a model of artificial seawater. For several years our group has been working with this artificial seawater model, which probably better resembles the major ions of the ocean of the prebiotic Earth (Anizelli *et al.*, 2014, 2015, 2016; Canhisares-Filho *et al.*, 2015; Carneiro *et al.*, 2017; Villafañe-Barajas *et al.*, 2018; Zaia *et al.*, 2018; Baú *et al.*, 2019). Unlike the seawater in the oceans today that have a high concentration of Na⁺ and Cl⁻ (Bearman, 2004), this artificial seawater contains high concentrations of Mg²⁺ and SO₄²⁻ (Zaia, 2012).

The radiolysis of adenine has been the subject of earlier investigations (Conlay, 1963; Ponnampertuma *et al.*, 1963; van Hemmen and Bleichrodt, 1971; Yamamoto, 1980;



Adenine

Fig. 1. Molecular structure of adenine.

Yamamoto and Fuji, 1986; Hartmann *et al.*, 2007; Su *et al.*, 2011). It has been reported that adenine is not easily decomposed by γ -radiation. There are several adenine decomposition products reported in the literature, among them adenine N_x -oxides, hydroxyl-adenine, xanthine and hypoxanthine and species with open rings. In addition, the effects of exposure to ionizing radiation on seawater are not yet fully understood (Draganić, 2005). The radiolysis of seawater is a matter of importance for radiation chemistry, since it may change the number of products from radiolysis of water (Kumagai *et al.*, 2013; Hata *et al.*, 2016a, 2016b).

Therefore, the aim of this research is to quantify and characterize adenine radiolysis products in distilled water, saline solutions and artificial seawater 4.0 Ga, in order to provide a better perspective of the role of salts in radiolysis of this organic molecule. Adenine was measured by spectrophotometric (UV/vis) and high-performance liquid chromatography (HPLC). The products of radiolysis were characterized by high performance liquid chromatography used in combination with mass spectrometry (HPLC-Mass) and infrared spectroscopy (FT-IR). Theoretical calculations were performed to elucidate the possible products of decomposition, through optimization of geometry, simulated vibrational frequencies and relative energy comparison.

Materials and methods

Materials

Adenine

Adenine (Fig. 1), with the highest purity available ($\geq 99\%$), purchased from Sigma Aldrich[®], was used as received.

Glassware

All the glassware for irradiation was cleaned, according to chemical radiation procedures, with a hot mixture of HNO_3 and H_2SO_4 for 4 h, followed by washing with double distilled water and Milli-Q purified water. The glassware was wrapped in aluminium foil and heated at 300 °C overnight for full elimination of organic matter.

Sample preparation

Three different sets of samples were prepared. Adenine (500 $\mu\text{g ml}^{-1}$) was dissolved in distilled water, different saline waters or artificial seawater 4.0 Ga. The solutions were de-aired by bubbling with argon (Ar), sealed and irradiated in a ^{60}Co source.

Seawater and saline solutions

The artificial seawater 4.0 Ga was prepared as described by Zaia (2012). In 1 l of Milli-Q water, several salts were dissolved in the following order: Na_2SO_4 (0.271 g), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (0.500 g), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (2.500 g), KBr (0.050 g), K_2SO_4 (0.400 g) and MgSO_4 (15.00 g). The following salt solutions (0.129 mol l^{-1}) were prepared separately: (1) KCl, (2) K_2SO_4 , (3) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, (4) MgSO_4 and (5) a saline solution containing $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ plus MgSO_4 .

Methods

Radiolysis

The samples were irradiated in a γ ray source (Gammabean 651-PT) at room temperature (298 K). The irradiation dose was determined using a ferrous sulphate-copper sulphate dosimeter. The dose rate used was 197 Gy min^{-1} and the irradiation dose from 0.0 to 94.52 kGy.

UV/vis spectrophotometry

The quantity of adenine was determined by reading the absorbance at 260 nm with a spectrophotometer UV/vis Varian, model Cary 100 Scan (Fig. 2).

HPLC analysis

Adenine was quantified using a Varian 9005 equipped with a UV/vis detector and a column C-18. The liquid used in the mobile phase contained a mixture of 77% A (ammonium acetate 0.1 mol l^{-1} at pH 4.5) and 23% B (250 ml of acetonitrile, 250 ml of methanol and 4 ml of tetrahydrofuran), adopting a flow rate of 0.3 ml min^{-1} . The detection was carried out at 260 nm.

Infrared spectroscopy (FT-IR)

FT-IR spectra were obtained using a reflectance accessory in a spectrometer (PerkinElmer spectrum 400, USA). The spectra were recorded at transmittance modes from 4000 to 650 cm^{-1} and a resolution of 4 cm^{-1} over 10 scans.

Statistical analysis

The Turkey test was performed to analyse the absorption differences, adopting a significance level of $p < 0.05$.

Computational details

The molecular geometries were optimized, and the frequencies and relative energy (E_{rel}) determined using the density functional theory method with B3LYP functional (Becke, 1988, 1993; Lee *et al.*, 1988), basis set aug-cc-pVDZ level (Dunning, 1989), using the Gaussian 03 program (Frisch *et al.*, 2004). The aug-cc-pVDZ basis set was chosen for the correct description of oxygen and nitrogen atoms. This basis set includes additional diffuse functions (prefix aug-), which were used to take into account the relatively diffuse nature of the lone pairs.

Results

Aqueous adenine exposure to γ -irradiation

Several experiments were performed to better understand the behaviour of adenine exposed to γ -irradiation at different doses. Solutions of adenine dissolved in distilled water, with and without O_2 , were γ irradiated. In addition, adenine dissolved in salt

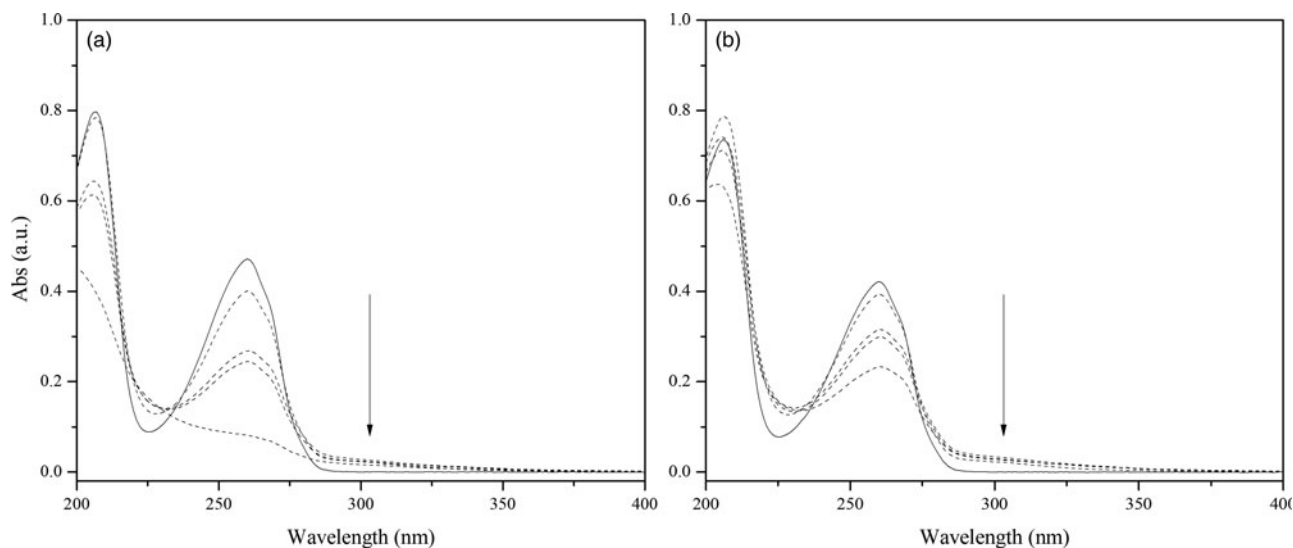


Fig. 2. UV/Vis spectra of adenine in: (a) distilled water and (b) seawater. Spectra of patterns not irradiated (*solid line*) and irradiated samples (*dashed line*). For all experiments, the adenine concentration was $500 \mu\text{g ml}^{-1}$. Seawater was prepared as described by Zaia (2012). The following irradiation doses were used: 23.71, 47.26, 71.12 and 94.52 kGy.

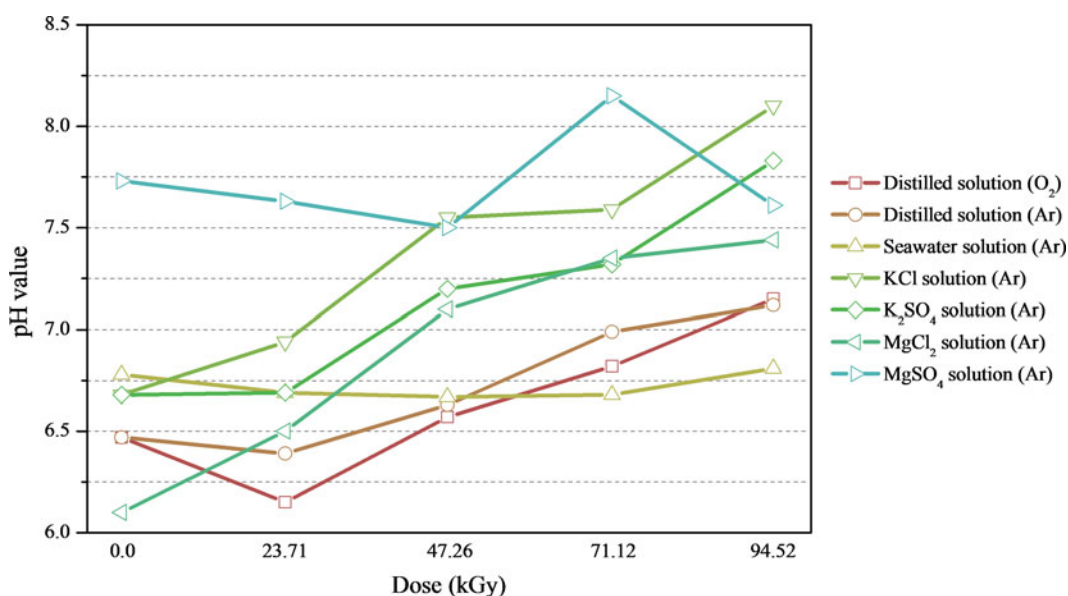
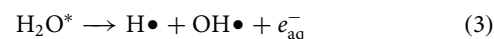
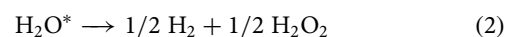


Fig. 3. pH values of the solutions of adenine after irradiation. For all experiments, the adenine concentration was $500 \mu\text{g ml}^{-1}$. Seawater was prepared as described by Zaia (2012). The concentration of all saline solutions was 0.129 mol l^{-1} .

solutions (KCl, K_2SO_4 , MgCl_2 and MgSO_4), in a salt mixture ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ plus MgSO_4) and in artificial seawater 4.0 Ga was also γ irradiated; in all these latter cases the solutions were oxygen free as O_2 was removed by bubbling Ar into the sample.

OH^\bullet is the main oxidizing substance formed after water radiolysis through ionizing radiation (Equations (1–3)) (Samuel and Magee, 1953; Allen, 1961; Draganić and Draganić, 1971). Dissolved oxygen (O_2) should be withdrawn from the solution since it can switch the main oxidizing species formed by removing the hydrated electron (e_{aq}^-) (Equation (4)) (Draganić and Draganić, 1971).



The pH of the samples increased after irradiation, with two exceptions, adenine dissolved in MgSO_4 and adenine dissolved in artificial seawater 4.0 Ga (Fig. 3). Changes in pH are an indication of the occurrence of chemical reactions. In addition, the irradiated solutions showed a yellowish colour, another indication of

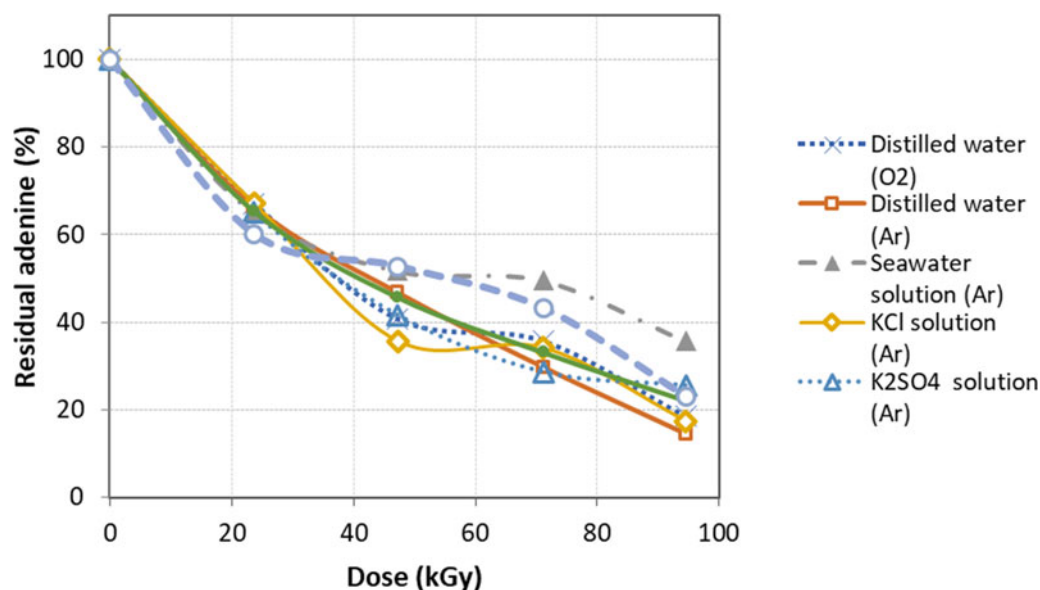


Fig. 4. Residual adenine% at different irradiation doses.

Table 1. Survival of adenine by dose of γ -radiation

Dose (kGy)	Distilled water (O ₂)	Distilled water (Ar)	Seawater solution (Ar)	KCl solution (Ar)	K ₂ SO ₄ solution (Ar)	MgCl ₂ solution (Ar)	MgSO ₄ solution (Ar)	Saline mixture (Ar)
0	506.00 ± 9.17 a, A	506.33 ± 4.72 a, A	506.00 ± 9.17 a, A	505.33 ± 1.15 a, A	502.00 ± 10.58 a, A	505.33 ± 2.31 a, A	497.33 ± 0.58 a, A	–
23.71	339.68 ± 26.11 a, B	335.39 ± 33.86 a, B	328.13 ± 9.26 a, B	338.71 ± 26.44 a, B	326.24 ± 30.59 a, B	329.94 ± 56.59 a, B	299.13 ± 16.45 a, B	–
47.26	206.43 ± 19.42 a,b, C	236.47 ± 59.17 a,b, C	261.46 ± 11.63 a, C	180.02 ± 16.33 b, C	209.07 ± 16.91 a,b, C	230.84 ± 2.49 a,b, C	262.26 ± 22.34 a, B,C	–
71.12	180.96 ± 18.12 b,c, C	150.32 ± 27.94 c, D	250.36 ± 15.27 a, C	172.38 ± 21.46 b,c, C	143.97 ± 1.20 c, D	167.38 ± 22.28 b,c, D	214.87 ± 24.56 a,b, C	–
94.52	93.77 ± 38.11 b, D	73.27 ± 14.22 b, E	180.67 ± 15.79 a, D	87.70 ± 32.10 b, D	128.44 ± 1.67 a,b, D	111.71 ± 1.91 a,b, D	114.54 ± 34.62 a,b, D	103.29 ± 8.11 b

The results are present as mean ± standard error. The number of sets was one with three samples each set. It was irradiated 5 mL of adenine solution at a concentration of 500 $\mu\text{g mL}^{-1}$, at different doses of γ -radiation exposure. Capital letters in columns were statistically different from each other by Tukey's test ($p < 0.05$). Lowercase letters in lines were statistically different from each other by Tukey's test ($p < 0.05$). For all saline solutions 0.129 mol l^{-1} of each salt was used. Saline mixture contained MgCl₂·6H₂O and MgSO₄ (1/1). Artificial seawater 4.0 Ga were prepared as described by Zaia (2012).

a chemical reaction (Fig. 2). The UV/vis spectra of samples showed that as the dose increased, the absorption of the characteristic band of adenine at 260 nm (Fig. 2) decreased. In general, the decomposition was minor in the case of the system containing the adenine dissolved in artificial seawater 4.0 Ga.

After irradiation, for the salt and artificial seawater solutions, the quantity of adenine was quantified by HPLC, the cations were first removed using a cation exchange resin before injection. Figure 4 shows the decomposition pattern of adenine as a function of dose. As dose increased, decomposition also increased in all the experiments. Solutions containing different cations and anions were prepared in order to understand the contribution of each species to decompositions. However, this effect could not be fully tracked, since the behaviour did not show a clear tendency. Nonetheless, some points should be highlighted. The decomposition at 23.71 kGy of adenine was very likely for all samples. However, as irradiation continued, differences were more evident. For example, at 47.26 kGy the sample of adenine

dissolved in KCl solution presented the highest degradation (64.38%), while both the sample of adenine dissolved in MgSO₄ solution and the one dissolved in artificial seawater 4.0 Ga showed the lowest degradation, 47.27 and 48.33% respectively. At 71.12 kGy, decomposition was higher for adenine dissolved in distilled water (70.31%) and lower for adenine dissolved in seawater solution (50.52%). Finally, at the highest radiation dose, the distilled water system presented the highest decomposition (85%) and the seawater solution showed the lowest decomposition (64%). Even though the degradation of adenine at the highest dose was not statistically different in the solutions (Table 1), a tendency for better protection of adenine was observed in the case of the seawater model experiment.

Vibrational analysis

For the samples of adenine dissolved in distilled water, the FT-IR spectra demonstrated that an increase in irradiation doses

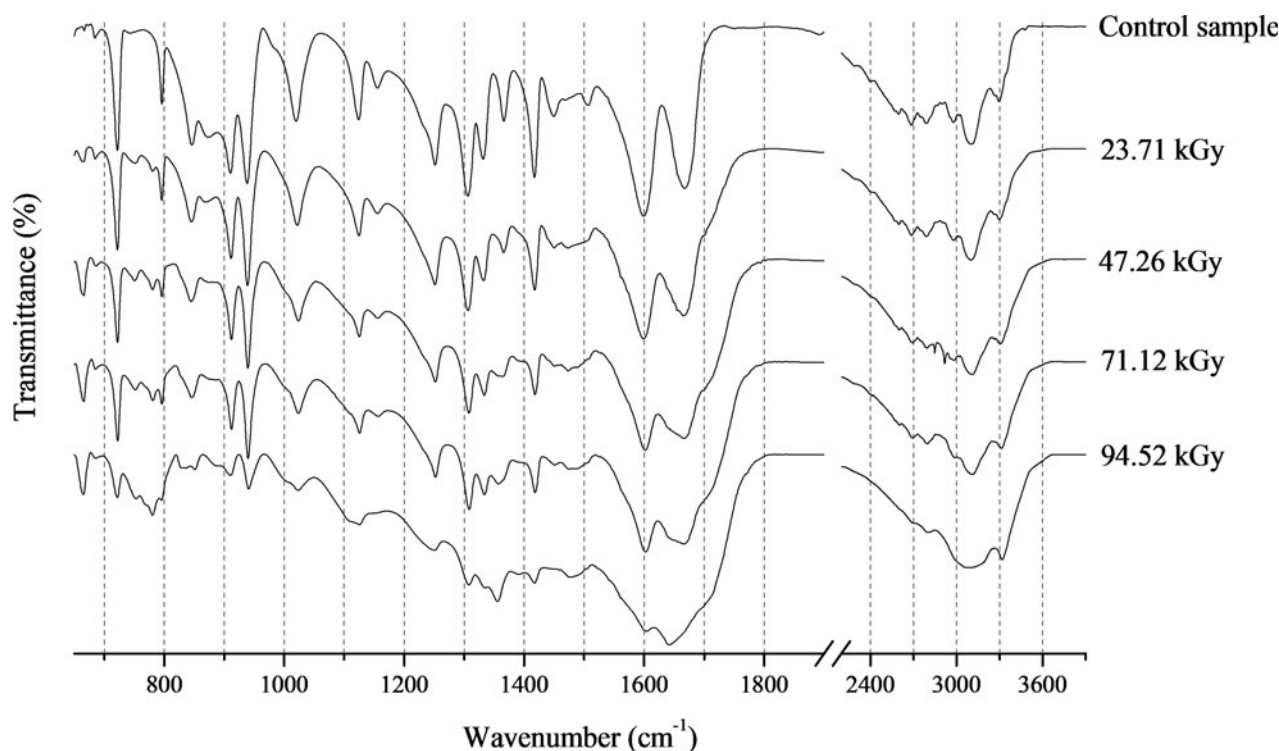


Fig. 5. FT-IR spectra of adenine after irradiated at different doses. Adenine was dissolved in distilled water ($500 \mu\text{g ml}^{-1}$), after the samples were irradiated and solutions were lyophilized. Before the irradiation, O_2 was removed by fluxing Ar into the sample.

increased adenine decomposition (Fig. 5). The major changes in the FT-IR spectra occurred at 1598 and 1668 cm^{-1} and these bands are attributed to the $\nu(\text{C}=\text{C})$ stretching and $\beta(\text{NH}_2)$ in-plane bending, respectively (Fig. 4) (Matholouthi *et al.*, 1984; Bertoluzza *et al.*, 1987; Mohamed *et al.*, 2009; Anizelli *et al.*, 2014). In addition, in this region, shifts occurred in the bands and a new band appeared. The intensity of the bands at 911 , 938 , 1019 , 1123 , 1251 and 1415 cm^{-1} decreased (Fig. 4); these bands are attributed to $\delta(\text{C}-\text{N}-\text{C})_{\text{py}}$ deformation of the pyrimidine ring, $\delta(\text{N}-\text{C}=\text{N})_{\text{im}}$ deformation of the imidazole ring, $\rho(\text{NH}_2)$ rocking, $\delta(\text{C}-\text{H})_{\text{im}}$ deformation, $\nu(\text{C}-\text{NH}_2)$ stretching and $\nu(\text{C}=\text{N})_{\text{py}}$ stretching, respectively (Matholouthi *et al.*, 1984; Bertoluzza *et al.*, 1987; Mohamed *et al.*, 2009; Anizelli *et al.*, 2014). Thus, it can be inferred that irradiation has an effect on the pyrimidine and imidazole rings of adenine.

To better understand these band shifts and new band formation, in the region from 1550 to 1750 cm^{-1} , a deconvolution of the FT-IR spectra was performed (Fig. 6). The deconvolution of adenine control bands showed four bands at $1572/1603$, 1650 and 1674 cm^{-1} (Fig. 6(a)). These bands could be attributed to $\nu(\text{C}=\text{C})$ stretching, $\nu(\text{C}=\text{N})$ stretching and $\beta(\text{NH}_2)$ in-plane bending, respectively (Matholouthi *et al.*, 1984; Bertoluzza *et al.*, 1987; Mohamed *et al.*, 2009; Anizelli *et al.*, 2014). For the adenine irradiated sample (71.12 kGy) the bands shifted from $1572/1603$, 1650 and 1674 cm^{-1} to $1600/1602$, 1640 and 1668 cm^{-1} (Fig. 5(b)). In addition, Fig. 5(b) presents a new band at 1713 cm^{-1} , which could be due to the formation of a new compound. For adenine dissolved in KCl and MgCl_2 solutions, the FT-IR spectra of irradiated samples demonstrated the same behaviour as in distilled water (figure not shown). However, for the samples of adenine dissolved in artificial seawater 4.0 Ga, K_2SO_4 and MgSO_4 solutions, the FT-IR spectra of the irradiated samples only demonstrated bands due to SO_4^{2-} (figure not shown).

Characterization of the product

The FT-IR spectra of irradiated adenine samples showed a new band at 1713 cm^{-1} , which may be due to the production of a new compound (Figs. 5 and 6(b)). This compound could be xanthine or hypoxanthine (similar bases to adenine). However, HPLC chromatograms of standards showed that xanthine and hypoxanthine had different retention times to the unknown compound (figure not shown). The peak of the unknown compound, for both irradiated samples of adenine (distilled water and artificial seawater 4.0 Ga), appears close to the adenine peak, with a difference of less than 0.5 min (Fig. 7). This behaviour suggests that the unknown compound has a similar structure to adenine. The quantity of the unidentified compound formed increased until 71.12 kGy dose and decreased at 94.52 kGy dose (Fig. 7).

After irradiation of the samples in distilled water and artificial seawater 4.0 Ga, using HPLC-MS, the peaks at $136 m/z$ and $137 m/z$ showed a retention time of 1.83 min . A standard of adenine showed the same m/z peaks and retention time. The unknown compound detected previously in HPLC chromatograms (Fig. 7) showed peaks at 152 and $153 m/z$ with a retention time varying from 2.01 to 2.07 min (figure not shown). Xanthine has a peak at $152.1 m/z$, however its retention time is 1.83 min . The standard of hypoxanthine showed retention times of $137 m/z$ and 1.84 min which did not match the retention time of the unknown compound. Thus, it is very likely that the unknown compound is not xanthine or hypoxanthine. The formation of isoguanine (molar mass = 151.1261) has been reported in radiolysis experiments of oxygenated adenine, and it probably formed in the current experiments; this result was not corroborated due to the lack of a standard. Although different conditions have been used in several experiments, the most common product detected in adenine radiolysis experiments is 8-hydroxy-adenine; in fact, according to Conlay

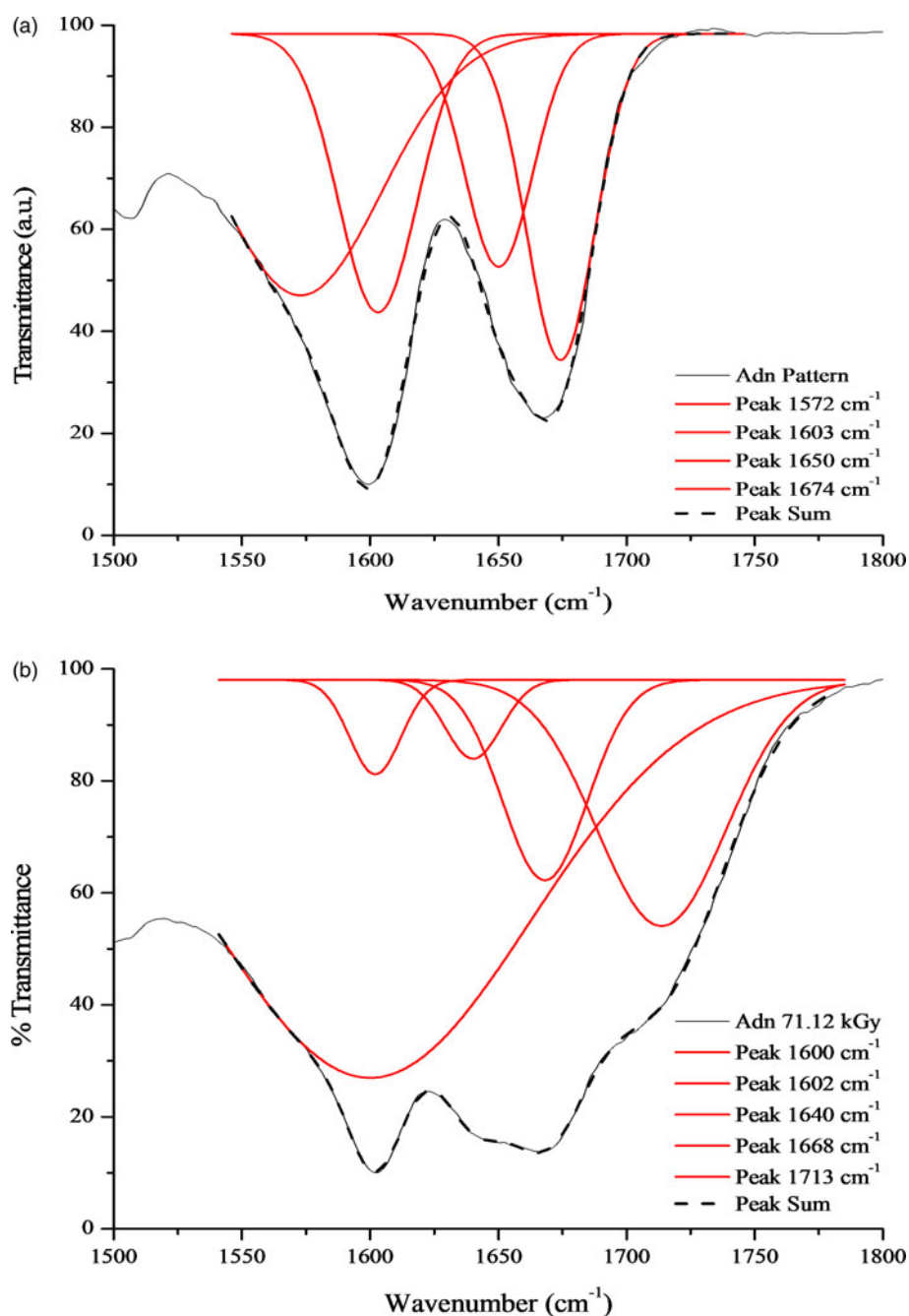


Fig. 6. Deconvolution bands of FT-IR spectra in the region of 1550 to 1750 cm⁻¹ of adenine. (a) Control sample. The best regression was obtained with four bands ($r^2=0.998$). (b) Irradiated sample at 71.12 kGy. The best regression was obtained with five bands ($r^2=0.999$). Adenine was dissolved in distilled water (500 $\mu\text{g mL}^{-1}$), after the sample was irradiated and solution was lyophilized. Before the irradiation, O₂ was removed by fluxing Ar into the sample.

(1963), the main product of adenine irradiation both in oxygen free and oxygen saturated solutions is 8-hydroxyadenine. In addition, in adenine radiolysis experiments, other products have also been detected: hypoxanthine, 4,6-diamino-5-formamido-pyrimidine, 6-amino-8-hydroxy-7,8-dihydropurine, adenine-7-N-oxide and 6-amino-8-hydroxy-7,8-dihydropurine (van Hemmen and Bleichrodt, 1971; Gorin *et al.*, 1977; Yamamoto, 1980; Yamamoto and Fuji, 1986; Hartmann *et al.*, 2007; Agnihotri and Mishra, 2011).

Radiation-chemical yield

The radiation-chemical yield is defined as the number of species produced or disappeared by 100 eV of radiation absorbed (Allen, 1961; Draganić and Draganić, 1971). Radiation-chemical yield G

is the number of disappeared moles of adenine (n) multiplied by Avogadro's number, divided by the absorbed dose (Gy), multiplied by a conversion factor from Gy to eV (Equation (5)).

$$G = 100 \left(\frac{n \times (6.023 \times 10^{23})}{\text{Gy} \times (6.245 \times 10^{18})} \right) \quad (5)$$

After plotting the G values (Fig. 8) for each dose and system, the $G_{(-A)}$ value was estimated (Table 2). In all cases, the $G_{(-A)}$ values were ≤ 1 . The low $G_{(-A)}$ values for the decomposition of adenine suggest its resilience to decomposition in solution, and may be due to reactions of reconstitution with adenine as a product (van Hemmen and Bleichrodt, 1971). The highest $G_{(-A)}$ value was the one estimated for adenine irradiated in

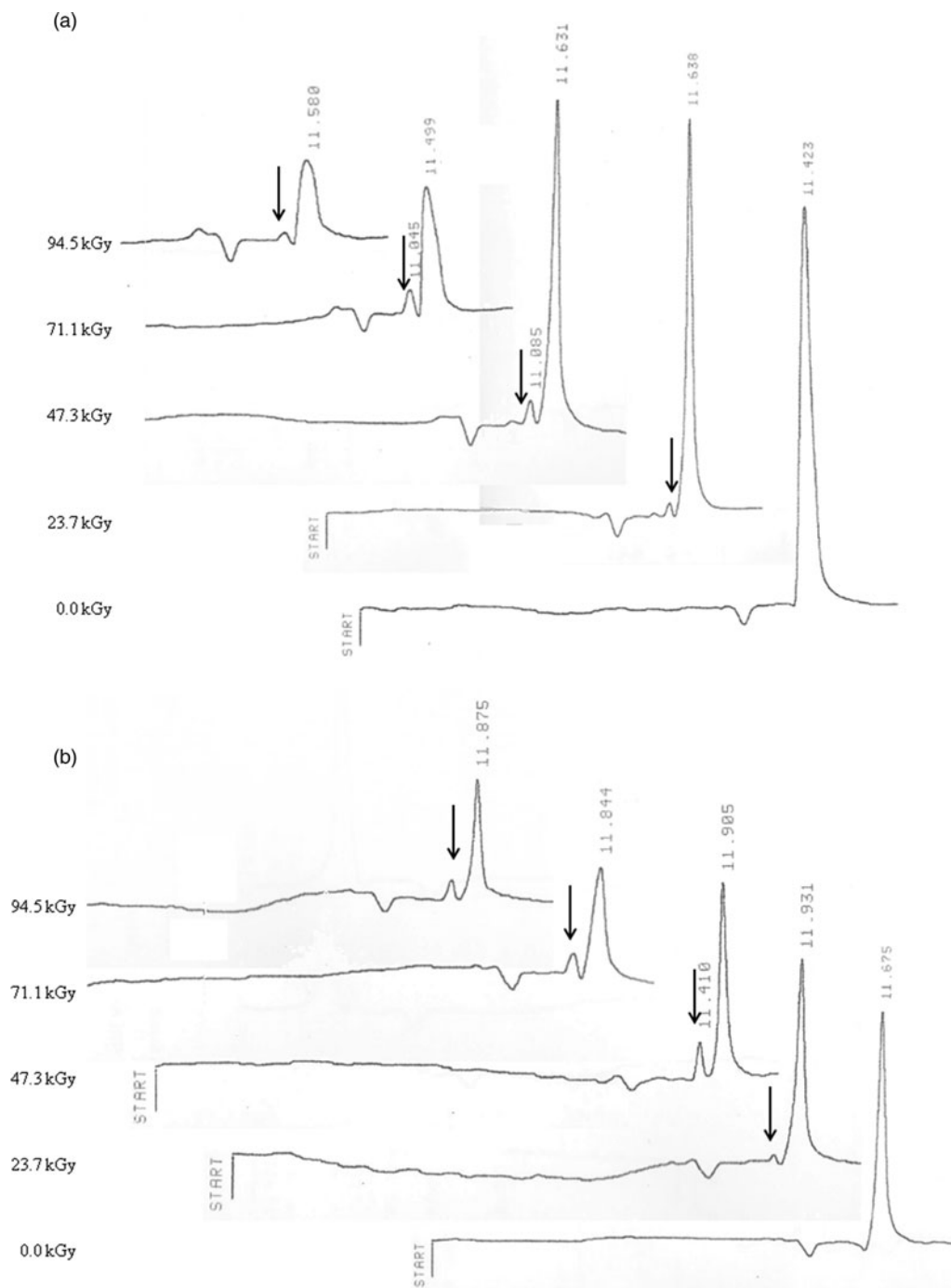


Fig. 7. HPLC chromatograms of adenine radiolysis in: (a) distilled water solution and (b) seawater solution. Adenine was dissolved in distilled water ($500 \mu\text{g ml}^{-1}$) or artificial seawater ($500 \mu\text{g ml}^{-1}$), after the sample was irradiated. Before the irradiation, O_2 was removed by fluxing Ar into the sample. Seawater was prepared as described by Zaia (2012). The adenine peak is showed around 11.4 min, the arrow corresponds to.

MgSO_4 (0.95) solutions, and the lowest for the adenine-KCl system (0.57). The presence of oxygen also affects the decomposition of adenine solution; decomposition of de-aerated solutions is $G_{(-A)} = 0.65$ and of oxygen containing solutions is $G_{(-A)} = 0.61$.

Theoretical calculations

Theoretical calculations were performed to investigate the possible products of decomposition of irradiated adenine. The

following adenine-related compounds were used in the theoretical calculations: the three adenine N_x -oxides (N_1 , N_3 and N_7 -oxides), 2-hydroxy-adenine (enol-amino and keto-amino), 8-hydroxy-adenine (enol-amino and keto-amino) and N-hydroxy-adenine (6-N-hydroxyl-aminopurine) (Fig. 9). It should be pointed out that some of these species are detected in experiments with adenine exposed to γ -radiation (Conlay, 1963; Ponnampereuma *et al.*, 1963; van Hemmen and Bleichrodt, 1971; Yamamoto, 1980; Yamamoto and Fuji, 1986). It should be noted that these molecules have the same molecular mass

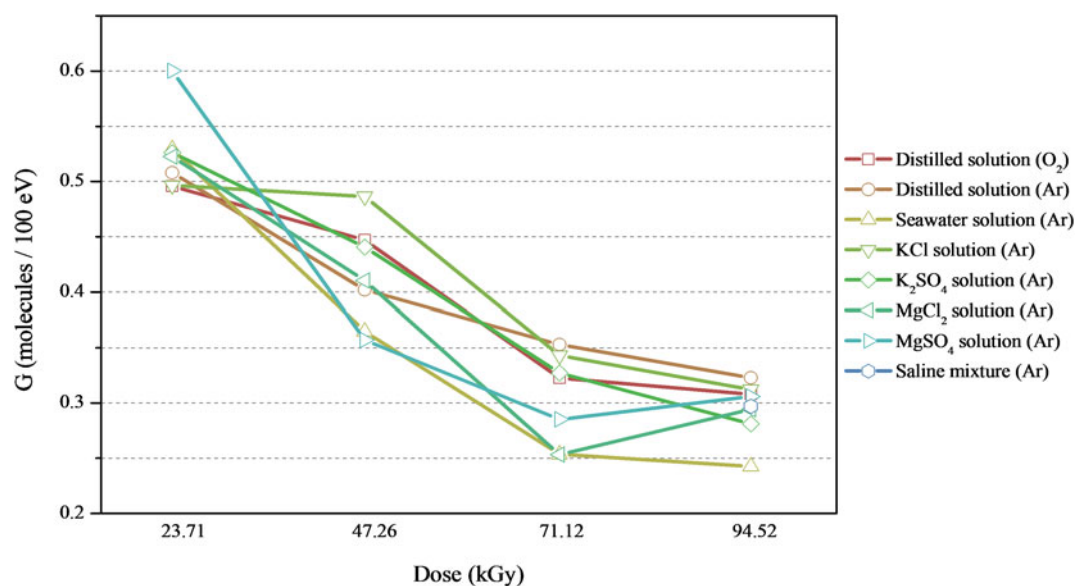


Fig. 8. Radiation-chemical yield in function of the dose. G is defined as the number of molecules of adenine disappeared by 100 eV of absorbed radiation. For all experiments, the adenine concentration was $500 \mu\text{g ml}^{-1}$. Seawater was prepared as described by Zaia (2012). The concentration of all saline solutions was 0.129 mol l^{-1} .

Table 2. $G_{(-A)}$ values calculated for adenine decomposition in each system

System	$G_{(-A)}$
Distilled water (O_2)	0.61
Distilled water (Ar)	0.65
Seawater solution (Ar)	0.78
KCl solution (Ar)	0.57
K_2SO_4 solution (Ar)	0.61
MgCl_2 solution (Ar)	0.58
MgSO_4	0.9

$G_{(-A)}$ refers to G values for adenine degradation.

(151 a.u.) detected by the HPLC-Mass analysis. The geometry of the molecules was optimized by the functional B3LYP and aug-cc-pvdz bases set, and the simulated vibrational spectra. There are several possible adenine N_x -oxides, but only three are common, with oxygen bonded to N_1 , N_3 and N_7 of adenine (Stevens and Brown, 1958). For the hydroxyl adenine species, although there are several tautomers, amino, imino, enol and keto, only those with the lowest relative energy were chosen for the investigations (Cysewski *et al.*, 1995).

For adenine, the main simulated frequencies were 1513, 1600, 1636 and 1660 cm^{-1} , and these were attributed to $\nu(\text{C}=\text{N})_{\text{im}}$ stretching, $\nu(\text{C}=\text{C})$ stretching, $\nu(\text{C}=\text{N})$ stretching and $\beta(\text{NH}_2)$ in plane bending, respectively (Anizelli *et al.*, 2014). The attributions of the frequencies for the adenine N_x -oxides and the hydroxy-adenine were performed according to the theoretical calculations (Table 3). It is important to notice that adenine N_1 -oxide shows a frequency at 1702 cm^{-1} (Table 3). This frequency has a value close to the new band observed in the deconvolution of the FT-IR spectra of the irradiated adenine (Fig. 6(b)). However, adenine N_3 and N_7 -oxide show this frequency at 1673

and 1687 cm^{-1} , respectively (Table 3). The keto-amino species present frequencies at 1746 and 1811 cm^{-1} for 2-hydroxy-adenine and 8-hydroxy-adenine, respectively, attributed to stretching $\nu(\text{C}=\text{O})$. However, these frequencies were not observed experimentally. Thus, the formation of the keto-amino tautomers cannot be assumed.

The hydroxyl and oxide derivatives have lower relative energy than adenine molecules (Fig. 10). Among the N_x -oxides, adenine N_1 -oxide has the lowest E_{rel} , with a difference of a few kcal mol^{-1} , following the sequence $\text{N}_1 < \text{N}_7 < \text{N}_3$. The calculations for the hydroxyl adenine presented a lower value of E_{rel} than N_x -oxides. The relative energies of the keto-amino species are lower than the enol-amino species (Fig. 10). However, as the calculated vibrational frequencies do not point to its formation, it may be concluded that enol-amino could be the formed species.

Discussion

Adenine radiolysis under different conditions has been widely studied (Conlay, 1963; Ponnampertuma *et al.*, 1963; Rhaese, 1968; van Hemmen and Bleichrodt, 1971; Yamamoto, 1980; Yamamoto and Fuji, 1986). Reported G values for adenine decomposition range from 0.35 to 1.2 for adenine concentrations from 2×10^{-5} to $8 \times 10^{-3} \text{ mol l}^{-1}$ (Scholes *et al.*, 1960; Conlay, 1963; Mannan, 1972; and reference therein). In these experiments, the calculated values are always between $0.5 \geq 1.00$. The G value seems to be higher in systems containing oxygen, compared to de-aerated solutions. Conlay (1963) obtained a $G_{(-A)} = 0.86$ for an oxygen containing solution, and $G_{(-A)} = 0.35$ for a non-aerated solution. In this study, both values are very close (Table 2). The relevance of the presence of oxygen is that oxygen can react with adenine molecules or compete with the organic molecule, adenine in this case, to react with water radicals. If oxygen is not continuously supplied into the system it is easily consumed (Mannan, 1972); this behaviour could explain the G values in these experiments, since the aerated solutions were not saturated with oxygen.

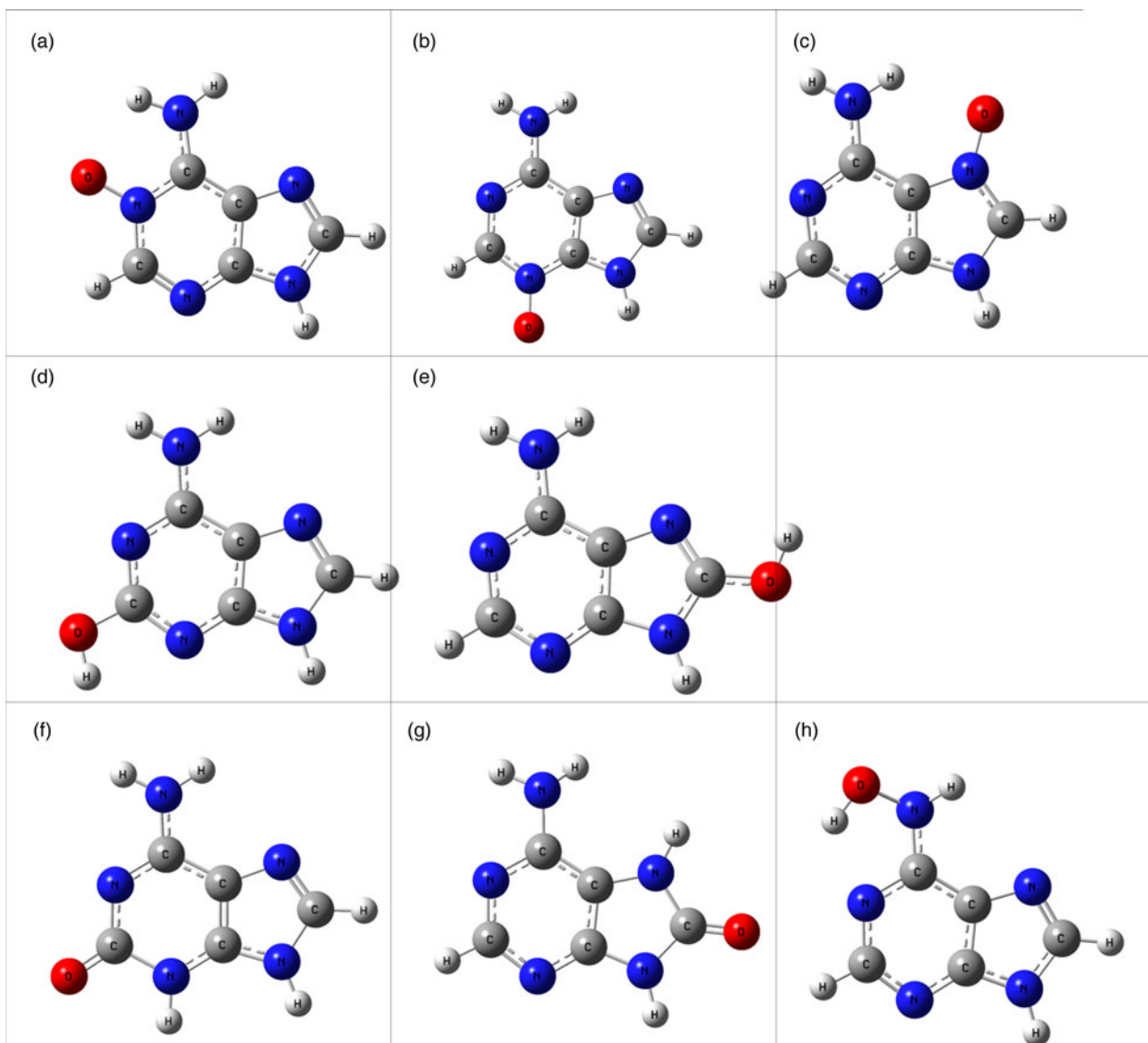


Fig. 9. Structure of optimized geometry of the simulated molecules of: (a) adenine N_1 -oxide; (b) adenine N_3 -oxide; (c) adenine N_7 -oxide; (d) 2-hydroxyl-adenine (enol-amino); (e) 8-hydroxyl-adenine (enol-amino); (f) 2-hydroxyl-adenine (keto-amino); (g) 8-hydroxyl-adenine (keto-amino) and (h) N-hydroxy-adenine.

In radiation chemistry experiments, the ions in the solution strongly influence the radiolysis experiments. In general, halide ions (i.e. Cl^- and Br^-) react with the OH radical (Draganić and Draganić, 1971), the main factor responsible for attacking adenine. In the experiments shown here, the presence of both Cl^- and Br^- in the seawater model produced lower degradation of the organic molecule.

Radical modified adenine derivatives

Adenine in aqueous solution submitted to ionizing radiation generates a variety of substances, such as hypoxanthine, xanthine, 2-hydroxy-adenine (isoguanine), 8-hydroxy-adenine, 6-N-hydroxy-adenine, adenine N_x -oxides and adenine itself, as well as other species with open rings (Conlay, 1963; Ponnampereuma *et al.*, 1963; Rhaese, 1968; van Hemmen and Bleichrodt, 1971; Yamamoto, 1980; Yamamoto and Fuji, 1986). Equations (6), (7) and (8) show the adenine N_1 -oxide and adenine N_7 -oxide synthesis from adenine (Fig. 11). The theoretical calculations indicate a lower relative energy for adenine

N_1 -oxide, suggesting its formation (Fig. 10). Previously published works did not detect the formation of adenine N_3 -oxide, probably because among adenine N_x -oxides, adenine N_3 -oxide has the highest energy (Fig. 10). Yamamoto (1980) suggested the formation of adenine N_7 -oxide and its conversion to adenine N_1 -oxide (equation (8)). Adenine N_x -oxide is stable in aqueous solution and no conversion to adenine was observed through the loss of oxygen atom (Stevens *et al.*, 1958).

Equations (9) to (11) show the formation of 2-hydroxy-adenine, 8-hydroxyl-adenine and N-hydroxy-adenine (Fig. 11). 8-Hydroxy-adenine was the major product formed from irradiation of a de-aerated solution of adenine, followed by hypoxanthine (Conlay, 1963). However, adenine N_x -oxides were not observed (Conlay, 1963). After irradiation of adenine, Ponnampereuma *et al.* (1963) observed the formation of 8-hydroxy-adenine and 4,6-diamino-5-formamidopyrimidine with traces of hypoxanthine and 4-amino-5-formamido-6-hydroxypyrimidine. Submitting aqueous adenine (de-aerated solution) to γ -irradiation, van Hemmen and Bleichrodt (1971) observed the formation of six compounds, with 8-hydroxy-adenine as the major compound. The X-ray irradiation

Table 3. Assignments of the frequencies observed in adenine-related compounds

Pattern		N _x -oxides				
Adenine	Assignments	Adenine N ₁ -oxide	Adenine N ₃ -oxide	Adenine N ₇ -oxide	Assignments	
1660	β(NH ₂)	1702	1673	1687	β(NH ₂)	
1636	ν(C = N)	1627	1643	1632	ν(C = N)	
1605	ν(C = C)	1565	1612	1600	ν(C = C)	
1513	ν(C = N) _{im}	1525	1509	1550	ν(C = N) _{im}	
-	-	1294	1301	1266	ν(N-O)	
Enol-amino		Keto-amino			Hydroxyl-aminopurine	
2-Hydroxy-adenine	8-Hydroxy-adenine	2-Hydroxy-adenine	8-Hydroxy-adenine	Assignments	N-Hydroxy-adenine	Assignments
-	-	1746	1811	ν(C = O)	-	-
1664	1666	1683	1667	β(NH ₂)	1650	ν(C = N)
1653	1648	1633	1644	ν(C = N)	1629	ν(C = C)
1614	1612	1596	1619	ν(C = C)	1554	β(HNOH)
1523	1590	1524	1492	ν(C = N) _{im}	1506	ν(C = N) _{im}
1470	1534	-	-	β(C-O-H)	1145	ν(N-O)

ν-stretching; β-in-plane bending; im-imidazole ring. The assignments of the oxide and hydroxyl-modified adenine derivatives were attributed according to the theoretical calculations.

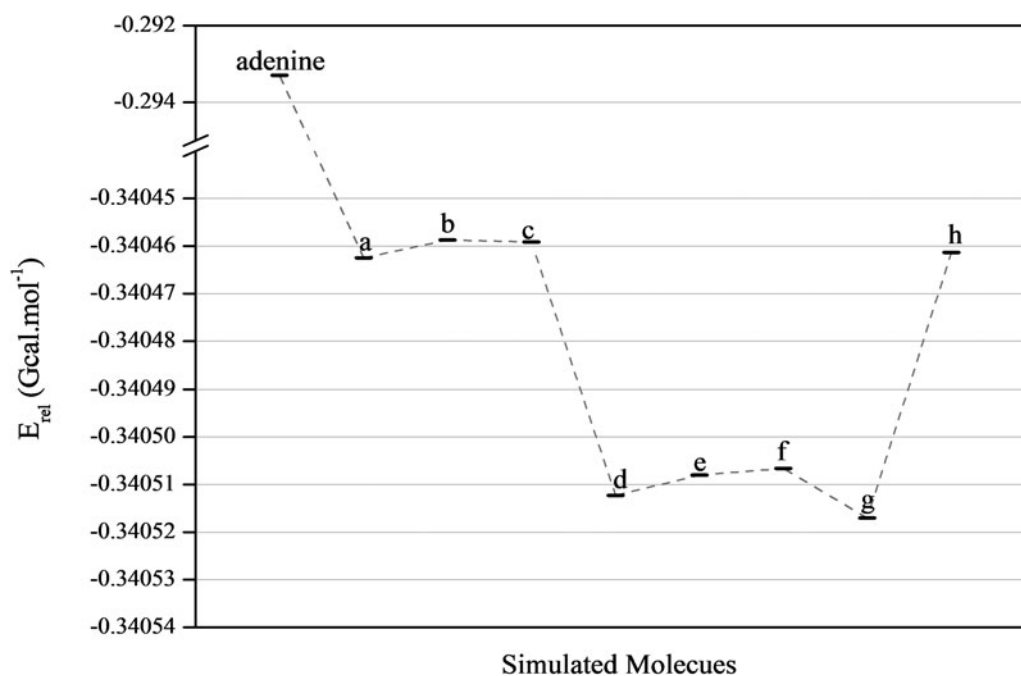


Fig. 10. Relative energies (Gcal mol⁻¹) of the simulate molecules: (a) adenine N₁-oxide; (b) adenine N₃-oxide; (c) adenine N₇-oxide; (d) 2-hydroxyl-adenine (enol-amino); (e) 8-hydroxyl-adenine (enol-amino); (f) 2-hydroxyl-adenine (keto-amino); (g) 8-hydroxyl-adenine (keto-amino) and (h) N-hydroxyl-adenine.

of aqueous adenine led to the formation of several products, such as adenine N₁-oxide, adenine N₇-oxide, 8-hydroxy-adenine and 2-hydroxy-adenine, among others (Rhaese, 1968). The γ-irradiation of aqueous adenine produced several compounds such as: adenine N₇-oxide, adenine N₁-oxide, 2-hydroxy-adenine (isoguanine) and isoguanine-7-N-oxide (Yamamoto, 1980).

The γ-irradiation of adenine in aqueous solution produced 8-hydroxy-adenine, and the chromatographic profile was similar to the present work (Hartmann *et al.*, 2007). Using gas discharges for radiolysis of adenine in aqueous solution, Su *et al.* (2011) observed the formation of 4,6-diamino-5-formamidopyrimidine, 8-hydroxy-adenine and 2-hydroxy-adenine.

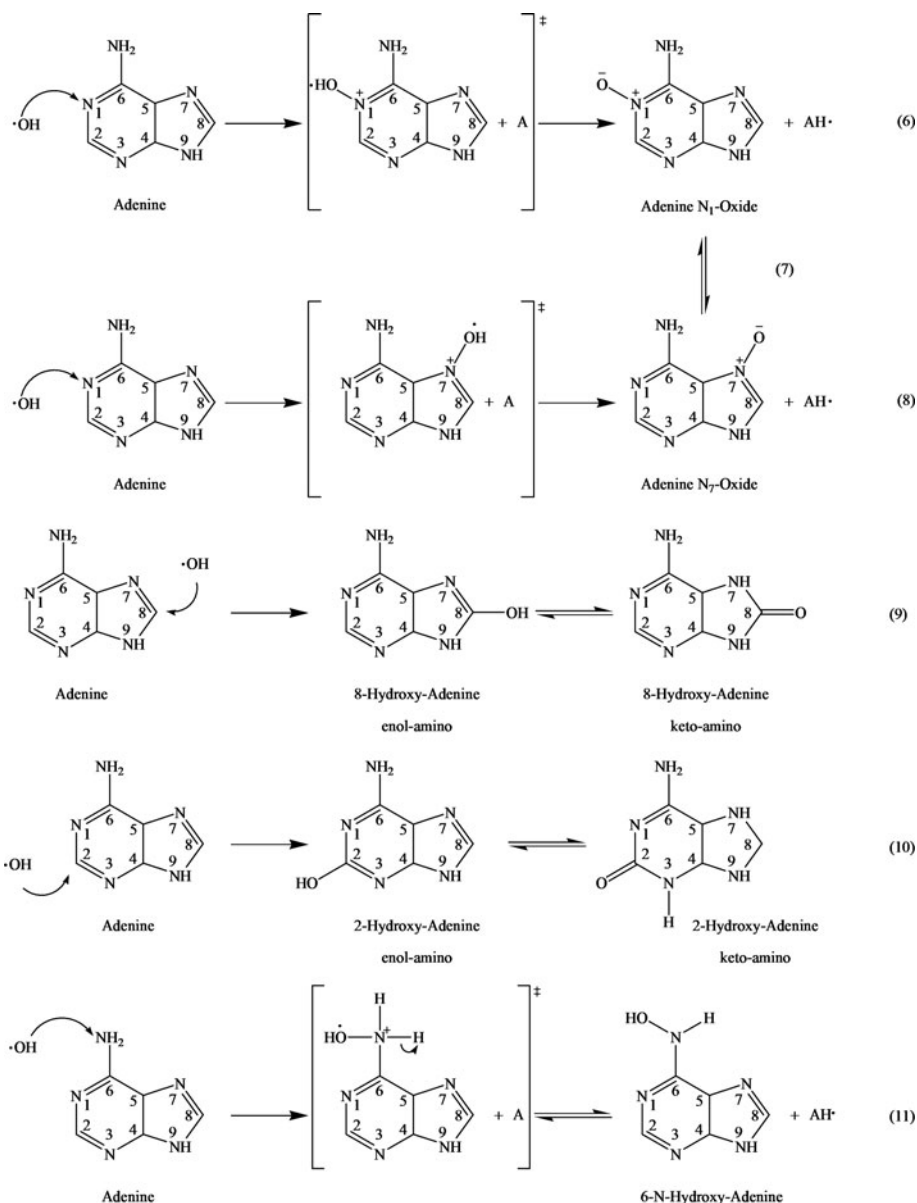


Fig. 11. Reaction mechanisms for the irradiation of aqueous adenine. Steps in brackets refer to transitional states (A Adenine; radical) (Conlay, 1963; Ponnampereuma *et al.*, 1963; Rhaese, 1968; van Hemmen and Bleichrodt, 1971; Yamamoto, 1980; Yamamoto and Fuji, 1986).

Prebiotic seawater relevance

Izawa *et al.* (2010) performed an experiment by leaching meteorite samples from the Tagish lake, and obtained the following order of cations: $\text{Mg}^{2+} > \text{Ca}^{2+} \gg \text{Na}^+ \approx \text{K}^+$ and anions: $\text{SO}_4^{2-} \gg \text{Cl}^-$. It should be noted that the meteorite samples from the Tagish lake are among the oldest rocks from the solar system (Brown *et al.*, 2000). The artificial seawater 4.0 Ga, used in this research, better resembles the major cations and anions of seawater on the Earth of 4.0 billion years ago (Zaia, 2012). Thus, the experiments carried out in this work may better represent what could have occurred in the prebiotic Earth 4.0 billion years ago. Of course, control experiments (in distilled water) are necessary to provide an idea of the effect of the ions. We observed that this seawater influences the stability of minerals and the adsorption of nucleic acid bases (Anizelli *et al.*, 2015, 2016; Canhisares-Filho *et al.*, 2015; Carneiro *et al.*, 2017; Villafañe-Barajas *et al.*, 2018; Zaia *et al.*, 2018). In addition, the interaction of cations of seawater (Ca^{2+} , Mg^{2+} , Sr^{2+} and Na^+) with nucleic acid bases changed

their reactivity (Anizelli *et al.*, 2014; Baú *et al.*, 2019). It should be noted that Mg^{2+} , the highest cation concentration in seawater, could be important in nucleoside formation (Sheng *et al.*, 2009). However, Ferris and Ertem (1993) observed that Mg^{2+} adsorbed onto montmorillonite did not have a catalytic effect on the formation of adenylic acid. K^+ , one of the cations of the seawater, has an effect on the formation of peptides (Dubina *et al.*, 2013).

In general, saline solutions present better adenine protective effects against γ -gamma radiation than distilled water because Br^- , Cl^- and SO_4^{2-} act as scavengers for hydroxyl radicals (Draganić and Draganić, 1971; Kumagai *et al.*, 2013; Hata *et al.*, 2016a, 2016b). It is probable that as the artificial seawater 4.0 Ga contains both Cl^- and Br^- a better protective effect of adenine was achieved (Table 1, Fig. 4) (Hata *et al.*, 2016b).

The results obtained in several works suggested that adenine irradiation produced a large variety of species (Conlay, 1963; Ponnampereuma *et al.*, 1963; Rhaese, 1968; van Hemmen and Bleichrodt, 1971; Yamamoto, 1980; Yamamoto and Fuji, 1986).

The synthesis of different species during irradiation of the adenine samples could be a double-edged sword for prebiotic chemistry. On the one side, a large variety of species could mean much more complex prebiotic chemistry, with more possibilities for the formation of different and more complex molecules. On the other hand, this could represent the production of a mixture which could not further produce any important molecules. This subject, intractable mixture-‘gunk’, has already been addressed by one researcher (Schwartz, 2007).

In the current work, two important results were found. First, the radiolysis of adenine is affected by the presence of ions in the milieu. Second, artificial seawater 4.0 Ga protected adenine against degradation by γ -radiation. In a context of chemical evolution, it is fundamental to take into account the possible composition of primitive seas, in order to understand the fate of organic molecules.

Remarks

The radiolysis of aqueous adenine leads to hydroxyl and oxide radical modified adenine derivatives that could be available for chemical evolution steps. Furthermore, it was demonstrated that the artificial seawater 4.0 Ga, which resembles the early ocean (from 4.0 billion years ago), was able to decrease the decomposition of aqueous adenine through γ -radiation exposure. These results reaffirm the importance of using seawater analogues in prebiotic chemistry experiments, since differences in adenine decomposition were observed only for the seawater solution, which may give rise to results of prebiotic relevance.

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