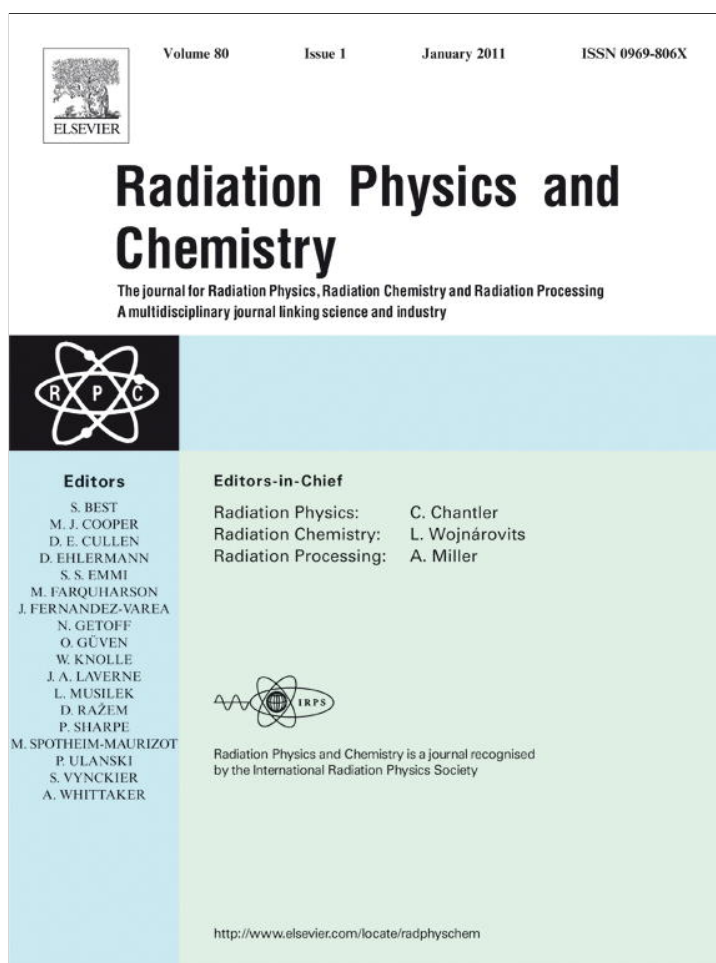


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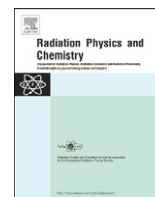
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Solid state radiolysis of amino acids in an astrochemical perspective

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ABSTRACT

The aliphatic amino acids L-alanine and L-leucine and the aromatic amino acids L-phenylalanine, L-tyrosine and L-tryptophan were irradiated in the solid state to a dose of 3.2 MGy. The degree of decomposition was measured by differential scanning calorimetry (DSC). Furthermore the degree of racemization was measured by optical rotatory dispersion (ORD) spectroscopy. From the DSC measurement a radiolysis rate constant k and the half life $T_{1/2}$ for each amino acid have been determined and extrapolated to a dose of 14 MGy, which corresponds to the expected total dose delivered by the decay of radionuclides to the organic molecules present in comets and asteroids in 4.6×10^9 years, the age of the Solar System. It is shown that all the amino acids studied can survive a radiation dose of 14 MGy although they are reduced to 1/4–1/5 of their original value they had at the beginning of the history of the Solar System. Consequently, the amount of alanine or leucine found today in the meteorites known as carbonaceous chondrites is just 1/4–1/5 of the amount originally present at the epoch of the formation of the Solar System 4.6×10^9 years ago. Among the amino acids studied, tyrosine shows the highest radiation resistance while tryptophan does not combine its relatively high radiation resistance with an elevated level of racemization resistance. Apart from the exception of tryptophan, it is shown that the radiolysis rate constants k of all the amino acids studied are in reasonable agreement with the racemization rate constant k_{rac} .

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1. Introduction

In 1955–1956 Nobel laureate Harold C. Urey published a couple of papers on the amount of energy generated by the decay of radionuclides in comets, asteroids, meteorites and larger bodies of the solar system. The results of such calculation were confirmed in more recent times by Draganic et al. (1993). Essentially these calculations show that in comets or asteroids at a depth of 20 m or more, the cosmic rays are completely shielded and the radiations are produced almost exclusively from the radionuclide decay. In a time scale of the age of the Solar System, i.e. 4.6×10^9 years (Unsold and Baschek, 2002), the total radiation produced by radionuclide decay in bulk comets, asteroids and larger bodies of the Solar System is ≈ 14 MGy. The short lived radionuclide ^{26}Al is able to produce ≈ 11 MGy in the first billion years of existence of the Solar System (Kohman, 1997) while the remaining contribution to the total radiation dose of 14 MGy derives from the decay of radionuclide having long and very long decay time, for

instance ^{40}K , ^{232}Th , ^{235}U and ^{238}U (Urey, 1955, 1956; Draganic et al., 1993).

Comets and other bodies of the Solar System especially far away from the Sun in the Kuiper belt or in the Oort cloud are thought to include very primitive organic material embedded in ice and rocks. Such material has not been processed so much during the Solar System formation and remained embedded inside the host bodies. The almost unique source of degradation and processing of the organic material occurring in 4.6×10^9 years at a depth > 20 m in comets or asteroid derives almost exclusively by the radionuclide decay. Indeed, a series of amino acids even in chiral excess (in scalemic mixture) and a plethora of other organic molecules have been found in meteorites (Pizzarello and Cronin, 2000; Goodfriend et al., 2000; Sephton, 2002; Pizzarello et al., 2008). The abiotic synthesis of such molecules occurred before the Solar System formation in the so-called giant molecular clouds, in the envelope of highly evolved stars and in the diffuse interstellar medium and have then been incorporated into comets, asteroids and larger bodies at the epoch of the Solar System formation (Kwok, 2009).

In the present work we report about the decomposition and racemization of a series of selected amino acids that have been irradiated in the solid state at 3.2 MGy, a dose equivalent to 1.05×10^9 years. From the degree of decomposition reached we

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were able to both establish the relative resistance to radiation and extrapolate the initial amount at the epoch of the Solar System formation.

2. Experimental

2.1. Materials and equipment

The amino acids L-phenylalanine, L-tyrosine, L-tryptophan, L-alanine and L-leucine were obtained from Sigma and used as received.

The Differential Scanning Calorimetric (DSC) measurements were made on a DSC-1 Star System from Mettler-Toledo. The Optical Rotatory Dispersion spectra were obtained on a Jasco P-2000 spectropolarimeter with a dedicated monochromator.

2.2. Irradiation procedure with γ rays

The irradiation with γ rays was made in a ^{60}Co Gamma cell from Atomic Energy of Canada at a dose rate of 1.7 kGy/h. A total dose of 3200 kGy = 3.2 MGy was delivered to each sample. The samples were irradiated in the solid state inside tightly closed glass vials.

2.3. Analysis with differential scanning calorimetry

The irradiated samples were tested for purity by Differential Scanning Calorimetry (DSC) at a heating rate of 10 °C/min in static air. As reference the DSC test was applied also on pristine, not irradiated samples under the same conditions. The amount percent of residual sample after the solid state radiolysis N_γ was determined from the ratio of the melting enthalpy after the radiolysis at 3.2 MGy (ΔH_γ) to the enthalpy before radiolysis measured on the pristine sample (ΔH_0):

$$N_\gamma = 100[\Delta H_\gamma / \Delta H_0] \quad (1)$$

The DSC trace on aliphatic amino acids was recorded on conventional Al crucibles with a cap. Instead for the aromatic amino acids use was made of special medium pressure and tightly closed steel crucibles to avoid amino acids sublimation.

2.4. Analysis of the radioracemization degree by Optical Rotatory Dispersion spectroscopy

The degree of radioracemization was measured by Optical Rotatory Dispersion (ORD) spectroscopy. The irradiated amino acid samples were dissolved in water or in 1 M HCl and the optical rotation was measured on the resulting solution using a polarimetric cell of 0.5 dm length in the range between 350 and 600 nm. As reference, the same measurement was also made on standard pristine amino acid dissolved in the same medium at the same concentration. From the ratio of the specific optical rotation after radiolysis $[\alpha]_\gamma$ to that before radiolysis $[\alpha]_0$ the residual optical activity R_γ has been determined:

$$R_\gamma = 100[\alpha]_\gamma / [\alpha]_0 \quad (2)$$

3. Results and discussion

3.1. Alanine and leucine solid state radiolysis

Alanine can be considered as the simplest chiral amino acid and is formed easily in the Miller abiotic synthesis as one of the most abundant amino acid (Miller, 1953, 1955, 2000). Alanine is

formed also in the Sagan synthesis under UV irradiation (Sagan and Khare, 1971). Vacuum UV irradiation of ice analogs produces a mixture of amino acids and can be considered an extension of the Sagan synthesis; alanine is among the most abundant amino acid in such experiments (Muñoz Caro et al., 2002; Nuevo et al., 2008). Irradiation of ice with circularly polarized light produces asymmetric synthesis of a mixture of amino acid precursors, which on hydrolysis yield free amino acids in enantiomeric excess (Takano et al., 2007). Such types of reactions have been indicated by Jorissen and Cerf (2002) as the source of biomolecular homochirality. Notably, alanine has been found in different meteorites (Pizzarello and Cronin, 2000; Sephton, 2002; Pizzarello et al., 2008) together with leucine and other amino acids. As a proof of the abiotic origin of the amino acids present in meteorites it is reported that the distribution of abundances of the different amino acids follows that observed in the laboratory synthesis according to the Miller or the Sagan derived reactions. Leucine is one of the preferred amino acids for the asymmetric photolysis studies since it has been reported that among the amino acids it gives the highest enantiomeric excess in such experiments (Meierhenrich et al., 2005; Meierhenrich, 2008). Solid state radiolysis of aliphatic amino acids has been reviewed by Swallow (1960) and Sagstuen et al. (2004). The alanine radicals (Sagstuen et al., 1997) and the products of leucine radiolysis are well known (Fu and Dean, 1997). Depending on the conditions, a decarboxylation reaction occurs and other products are formed as well (Swallow, 1960). For example, as a result of solid state radiolysis alanine is decarboxylated and gives ethylamine; on being dissolved in water it yields pyruvic acid and ammonia (Swallow, 1960). Similar fate has been reported also for the solid state radiolysis of longer chain amino acids like leucine, although other secondary reactions also appear like the formation of double bonds in the aliphatic chain (Swallow, 1960).

The goal of the present work is not to identify the radiolysis decomposition products of alanine and leucine but to determine their radiation resistance and the amount that can survive a radiation dose equivalent to that produced by the radionuclide decay in 4.6×10^9 years. To determine the amount of alanine and leucine remaining after 3.2 MGy, a DSC study has been done on the irradiated samples in comparison to the reference pristine amino acid. Using Eq. (1) it was possible to determine the amount of amino acid that survive a dose of 3.2 MGy. Figs. 1 and 2 show, respectively, the DSC traces of alanine and leucine before and after the irradiation. As expected the irradiated sample shows a significantly lower onset and peak melting point than the pristine sample and this is in line with the formation of radiolysis products in crystals of the amino acids and the partial decomposition of the pristine amino acid itself. Indeed, irradiated alanine crystals are yellow in color with a disagreeable smell and, similarly, leucine shows yellow-orange crystals with a disagreeable smell while before irradiation the crystals were white in both cases without any odour.

Table 1 reports the onset and peak of the endothermal melting transitions before and after the radiation treatment. For alanine the melting peak is lowered by 11 °C after the radiolysis and for leucine the shift to lower temperatures after radiolysis is even more dramatic: 21.8 °C. Furthermore, also the melting enthalpy is dramatically reduced after 3.2 MGy radiolysis. This can be observed in Figs. 1 and 2 by the reduction in area of the endothermal transitions after radiolysis; the melting enthalpy values are reported in Table 1. By applying Eq. (1), from the melting enthalpy it is possible to know the amount of residual alanine and leucine after 3.2 MGy. Table 1 shows that the N_γ values are 67.7% for alanine and 72.3% for leucine. In other words this means that only 67.7% of the original amount of alanine survived a dose of 3.2 MGy and only 72.3% of the original leucine.

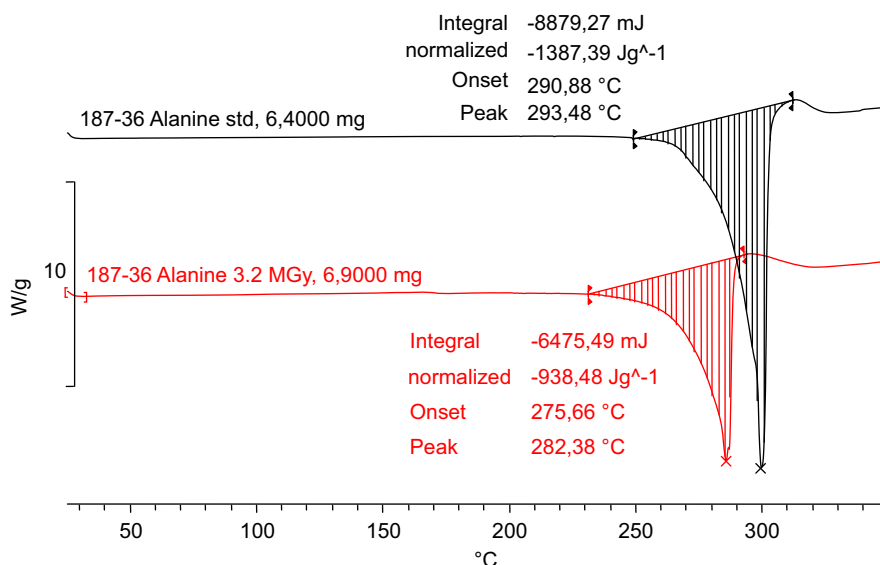


Fig. 1. DSC of alanine in an Al crucible at the heating rate of 10 °C/min. The upper trace is due to standard pristine alanine and the lower trace is due to 3.2 MGy treated sample.

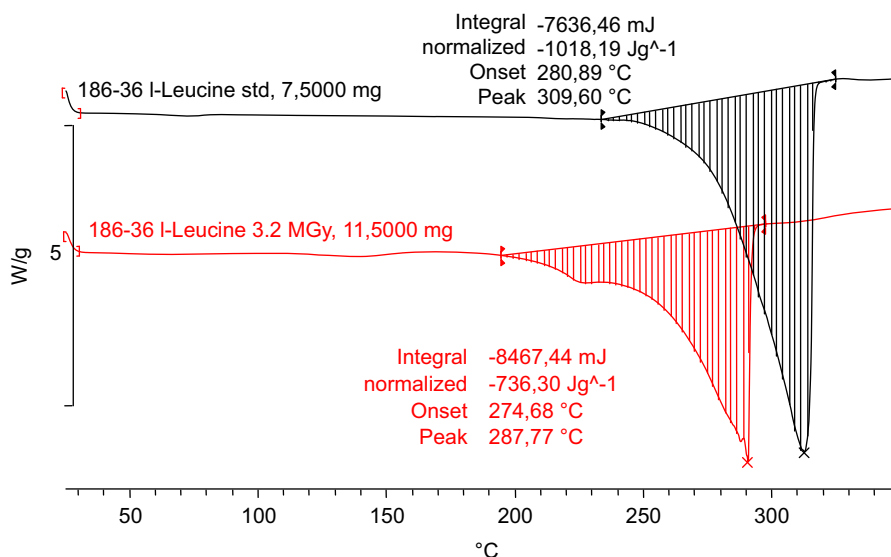


Fig. 2. DSC of leucine in an Al crucible at the heating rate of 10 °C/min. The upper trace is due to standard pristine leucine and the lower trace is due to 3.2 MGy treated sample.

Table 1
Alanine and leucine before and after solid state radiolysis.

	l-alanine	l-alanine 3.2 MGy	l-leucine	l-leucine 3.2 MGy
Melting point, onset (°C)	290.9	275.7	280.9	274.7
Melting point, peak (°C)	293.5	282.4	309.6	287.8
Melting enthalpy (J/g)	-1387.4	-938.5	-1018.2	-736.3
Residual product after 3.2 MGy (DSC, N_γ) (Eq. (1))		67.7		72.3
Residual optical activity after 3.2 MGy (ORD, R_γ) (Eq. (2))		75.8		82.6

The amino acids under study were subjected also to ORD measurements with the purpose to study the radioracemization degree. To avoid artificially induced racemization, the pristine and solid state irradiated amino acids were dissolved in acidic or neutral solution (Djerassi, 1960; Jirgensons, 1973) before the ORD

measurement. Thus, the pristine and the irradiated amino acid samples were dissolved in water or in 1 M HCl at the same concentration and the ORD curve was measured with a spectropolarimeter. It is well known that high energy radiation plays against preservation of chirality and the phenomenon occurring in these conditions is called radioracemization (Cataldo, 2007a, 2007b; Cataldo et al., 2008). Only in rare cases the radiation may play a chiral amplification role (Cataldo et al., 2007, 2009a, 2009b).

Fig. 3 shows the ORD curves of alanine and leucine before and after the irradiation at 3.2 MGy. In both cases the irradiation has caused a shift of the ORD curve toward the abscissa axis. Such shift is due to a reduction in the specific optical rotation of the irradiated amino acid so that $[\alpha]_\gamma < [\alpha]_0$ (see Eq. (2)). In both cases the ORD curve shift due to radioracemization is uniform in the entire range of wavelengths employed. Using Eq. (2) it is possible to measure R_γ to evaluate the amount of residual specific optical rotation of the radiation-treated amino acid. In Table 1 the value of R_γ is reported,

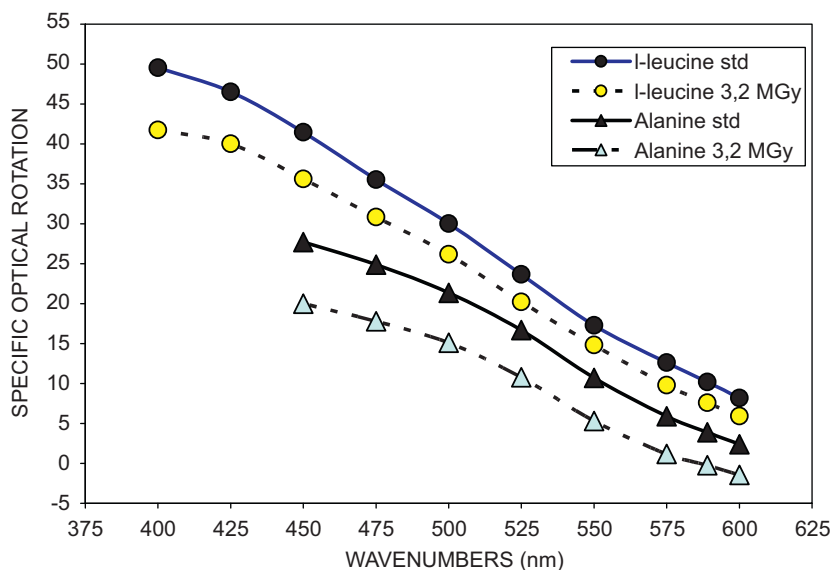


Fig. 3. Optical rotatory dispersion (ORD) of leucine and alanine before and after solid state radiolysis at 3.2 MGy. The extent of radioracemization can be appreciated by the shift of the ORD curve toward the abscissa after the radiolysis. Concentration in 1 M HCl (pristine and irradiated): alanine 4.1 mg/ml and leucine 5.2 mg/ml.

i.e. the residual product after radioracemization as measured by the residual specific optical rotation. In the case of alanine $R_r=75.8\%$ while for leucine such value is 82.6%. The radioracemization degree is in reasonable agreement with N_r , the DSC measurement of the residual amount of amino acid after 3.2 MGy. It can be noticed that the value of R_r is generally higher than the value of N_r . Evidently the radioracemization rate constant is lower than that of real radiolysis as measured by changes occurring in melting enthalpy. This may imply that although the given amino acid is destroyed by the radiation, the resulting products in part may still preserve the chiral centers and give a positive contribution to the total chirality. Such a discrepancy between the polarimetric measurements of radioracemization and the degree of radiolysis of the organic substrate was also reported by Bonner et al. (1979).

The term “radioracemization” *stricto sensu* means that the given enantiomer survived the radiolysis but was converted into its opposite isomer by an inversion of the chiral center. In the present work the term “radioracemization” has been used in a broader way indicating only the shift toward the abscissa axis of the ORD curve after radiolysis. Such a shift involves the real radioracemization phenomenon, i.e. the trend induced by high energy radiation to form a racemic mixture starting from a scalemic mixture or from a pure enantiomer by the inversion of the chiral center. In fact it involves also the preservation of the chiral center in the radiolysis products, which have different specific optical rotation than that of the mother molecule. Thus, it is necessary to distinguish between true and apparent radioracemization but in our ORD measurements we cannot do such a distinction and hence we are talking about a radioracemization but in a broader sense.

3.2. Phenylalanine, tyrosine and tryptophan solid state radiolysis

Phenylalanine, tyrosine and tryptophan are all aromatic amino acids and are in general less commonly found in meteorites. For instance, only phenylalanine and tyrosine have been found in the Murchinson meteorite (Meierhenrich, 2008). In addition, the aromatic amino acids are not found in the Miller and in the Sagan synthesis (Miller, 1955, 2000), so that in the prebiotic chemistry they are considered “less primitive” than the aliphatic amino

acids, which instead are formed quite easily. Even the irradiation of interstellar ice analogs produces only extremely low trace amounts of aromatic amino acids (Nuevo et al., 2008). Thus, the formation of aromatic amino acids may involve other reactions, like for instance the photochemical alkylation of glycine containing polypeptides with toluene (Sperling and Elad, 1971) to form a phenylalanine residue. On the other hand irradiation of phenylalanine in aqueous solution produces tyrosines (Taguchi et al., 2001). Large part of the studies on aromatic amino acid radiolysis have been conducted in aqueous solutions (Rowbottom, 1955; Swallow, 1960; Chrysochoos, 1968; Armstrong and Swallow, 1969). However solid state irradiation leads to decarboxylation and formation of free amine (Swallow, 1960). Furthermore, solid state irradiation of aromatic amino acid leads also to the formation of complex products like dipeptides or oligopeptides (Wang et al., 2007).

As reported for the aliphatic amino acids alanine and leucine, the aromatic amino acids phenylalanine, tyrosine and tryptophan were also subjected to solid state irradiation at 3.2 MGy. The resulting irradiated crystals were analyzed by DSC and Figs. 4–6 report a comparison between the DSC traces of the pristine amino acids and those of the irradiated samples. Table 2 reports a summary of the DSC analysis.

Because of the sublimation tendency of the aromatic amino acids, their DSC traces were recorded in sealed steel crucibles, in contrast with the aliphatic amino acids, whose melting points were measured in common aluminum crucibles. This was necessary to get a sharp endothermic transition; otherwise due to sublimation an irregular DSC trace should have been obtained.

As observed for the aliphatic amino acids, also the irradiated aromatic amino acids display a reduction in the melting point peak and area of the endothermic transition, which is linked to the purity of the samples. As shown in Figs. 4–6 and in Table 1, the melting point peak of phenylalanine undergoes a shift to lower temperatures of about 15 °C; such a shift in the melting peak is less pronounced in the case of tryptophan, about 8 °C shift, and practically negligible in the case of tyrosine. The reduction in the melting point peak (and consequently in the onset) is due to the formation of non-volatile radiolysis products, which remain trapped in the crystals of the amino acid. After the solid state irradiation at 3.2 MGy the phenylalanine crystal appears light brown and emits a sweet and fishy characteristic smell, which

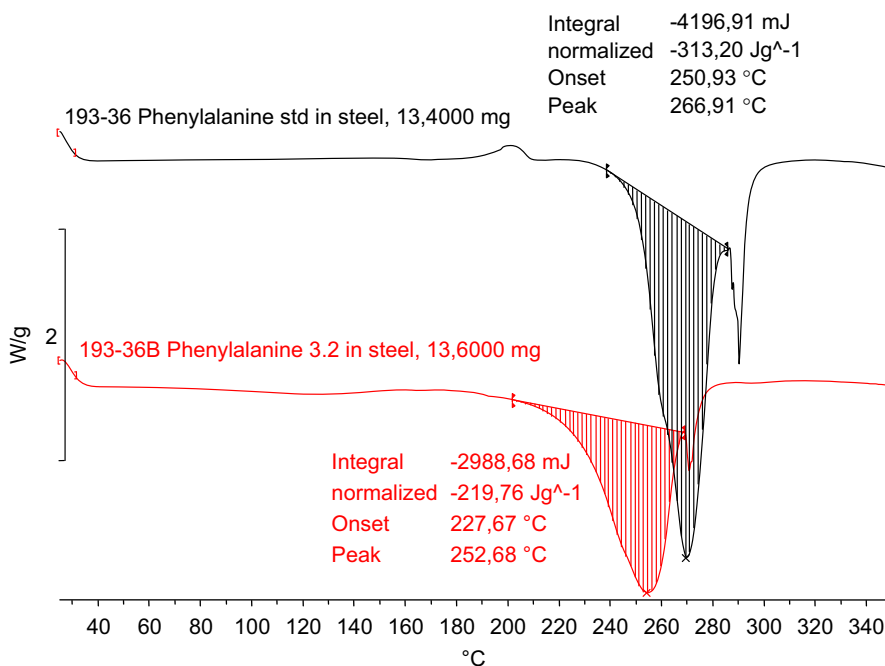


Fig. 4. DSC of phenylalanine in a sealed steel crucible at the heating rate of 10 °C/min. The upper trace is due to standard, pristine phenylalanine and the lower trace is due irradiated phenylalanine at 3.2 MGy.

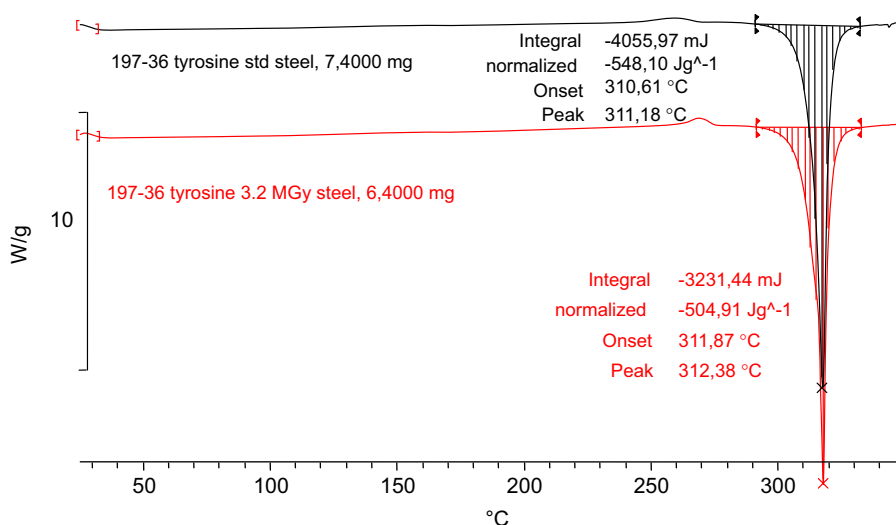


Fig. 5. DSC of tyrosine in a sealed steel crucible at the heating rate of 10 °C/min. The upper trace is due to standard, pristine tyrosine and the lower trace is due to irradiated tyrosine at 3.2 MGy.

recalls that of the decarboxylation product phenethylamine (1-amino-2-phenylethane). This is not the only product present, in fact when the irradiated crystals of phenylalanine are dissolved in water at pH=0, they release a brown insoluble fraction, evidently another oligomeric product derived from phenylalanine radiolysis. The irradiated tryptophan crystals appear light brown and shiny while surprisingly the irradiated tyrosine crystal are white like the pristine non-irradiated sample.

Because of the presence of such products, the melting enthalpy is also reduced accordingly and by using Eq. (1) it is possible to calculate the value of N_r , i.e. the amount of residual amino acid surviving to the radiolysis. As shown in Table 2, the amount of residual phenylalanine after 3.2 MGy is 70.2%, in line with the residual amount of irradiated alanine and leucine (see Table 1),

instead both tyrosine and tryptophan show a higher level of radiation resistance since at 3.2 MGy the residual amount found by DSC is 92% in both cases.

In order to measure the extent of radoracemization of the irradiated aromatic amino acids, an ORD measurement was conducted on both pristine and irradiated samples dissolved in 1 M HCl. The results of such measurements are shown in Fig. 7. As expected, in all cases a reduction in specific optical rotation at any wavelength was observed with the consequent shift of the entire ORD curve toward the zero axis in the case of the irradiated samples. As shown in Table 2, the residual specific optical rotation for both phenylalanine and tryptophan after solid state irradiation is around 82.5% and 79.1%, respectively. Thus, after 3.2 MGy about 80% of the pristine ORD values are maintained by these two amino

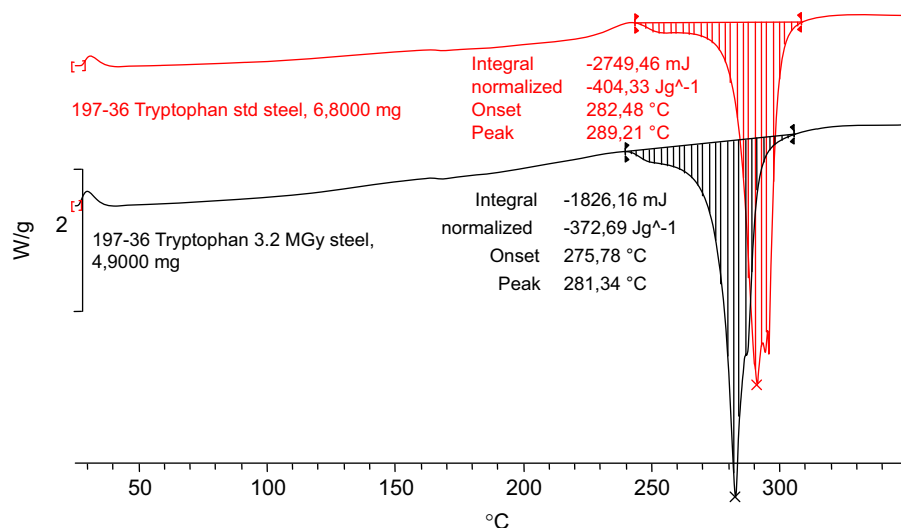


Fig. 6. DSC of tryptophan in a sealed steel crucible at the heating rate of 10 °C/min. The upper trace is due to standard, pristine tryptophan and the lower trace is due to irradiated tryptophan at 3.2 MGy.

Table 2
Phenylalanine, tyrosine and tryptophan before and after solid state radiolysis.

	L-phenylalanine	L-phenylalanine 3.2 MGy	L-tyrosine	L-tyrosine 3.2 MGy	L-tryptophan	L-tryptophan 3.2 MGy
Melting point, onset (°C)	250.9	227.7	310.6	311.9	282.5	275.8
Melting point, peak (°C)	266.9	252.7	311.2	312.4	289.2	281.3
Melting enthalpy (J/g)	-313.2	-219.8	-548.1	-504.9	-404.3	-372.7
Residual product after 3.2 MGy (DSC, N_γ) (Eq. (1))		70.2		92.1		92.2
Residual optical activity after 3.2 MGy (ORD, R_γ) (Eq. (2))		82.5		86.7		79.1

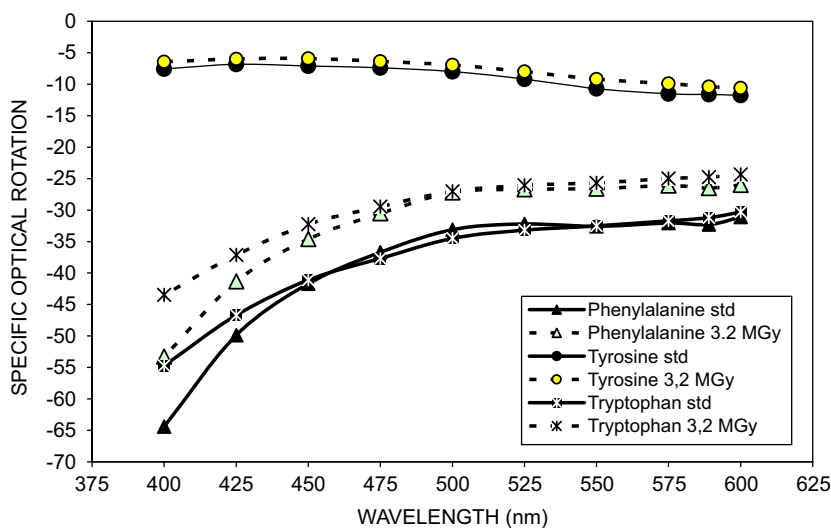


Fig. 7. Optical rotatory dispersion (ORD) of phenylalanine, tyrosine and tryptophan before and after solid state radiolysis at 3.2 MGy. The extent of radioracemization can be appreciated by the shift of the ORD curve toward the zero axis after radiolysis. The radioracemization is minimal in the case of tyrosine and appreciable. Concentration in 1 M HCl (pristine and irradiated): phenylalanine 5.0 mg/ml; tyrosine 10.0 mg/ml and tryptophan 8.0 mg/ml.

acids. Tyrosine shows the best radiation resistance not only in DSC but also in terms of radioracemization because after 3.2 MGy the residual specific optical rotation (R_γ) is 86.7%. By comparing the N_γ values of Table 2, which refer to the residual amount of amino acid that survived the radiolysis as determined by DSC with R_γ , i.e. residual optical activity, it is possible to observe once

again a reasonable agreement between the two values so that with two different analytical techniques the residual amount of amino acid after 3.2 MGy has been determined. In Table 2 in some cases the N_γ value exceeds R_γ and in other cases the opposite condition occurs. As discussed in Section 3.1, if $R_\gamma/N_\gamma > 1$ the radiolysis products still possess a chiral center and give a positive

contribution to the residual optical activity with respect to the actual residual amount of the given amino acid. Instead if $R_\gamma/N_\gamma < 1$, the radiolysis products do not have a chiral center or, if they have, it gives a negative contribution to the total optical activity.

3.3. Solid state radiolysis of amino acids in an astrochemical perspective

Different types of organic molecules may survive in the harsh conditions occurring in the interstellar medium and in certain bodies of the solar system for very long intervals of time (Draganic et al., 1993; Sephton, 2002; Pizzarello and Cronin, 2000; Kminek and Bada, 2006; Cataldo, 2007b, Cataldo et al. 2008; Pizzarello et al., 2008; Meierhenrich, 2008; Izumi et al., 2008).

Simple organic molecules are formed in different environments in space, ranging from dense molecular clouds to the circumstellar envelopes of evolved stars as well as in the diffuse interstellar medium (Kwok, 2009). Such molecules, which include amino acids, sugars, lipids and many others, are then incorporated inside comets, asteroids and in ice and rocks of larger bodies at the age of formation of the Solar System 4.6×10^9 years ago (Draganic et al., 1993; Kwok, 2009). More precisely, amino acids, sugars and lipids have not been detected in a definitive way in the interstellar medium but have been found in meteorites (Hayatsu and Anders, 1981) and are thought to be present in comets and asteroids and their presence suggests that they were formed before the formation of the Solar System, otherwise inside comets and asteroids the primitive molecules may undergo further processing or may remain in their pristine state (Yabushita, 1993). Biochemically important molecules like for instance amino acids have been found in carbonaceous chondrites after 4.6×10^9 years (Pizzarello and Cronin, 2000; Pizzarello et al., 2008); it is evident that they were able to resist the cosmic rays bombardment and radiations derived from the radionuclide decay. It has been calculated that the surface of comets and asteroids receives from cosmic rays a total dose of 300 MGy in 4.6×10^9 years (Draganic et al., 1993). Other authors (Kminek and Bada, 2006) reported even higher dose derived from cosmic rays bombardment for Martian regolith: for the first few meters from the surface a dose of 200–800 MGy has been calculated for the last 3 billion years. Considering these extremely high doses and the experiment on amorphization of C_{60} and C_{70} fullerenes with simulated cosmic rays at 250 MGy (Cataldo et al., 2009a, 2009b),

it is commonly accepted that the surfaces of comets and asteroids are covered with a layer of highly refractory organics resembling in some way coal and called kerogen. Cometary missions, like the Giotto Mission to the Halley comet, have shown that indeed the surface of such bodies is extremely dark and characterized by very low albedo (Crovisier and Encrenaz, 2000). Thus, the primitive organic molecules must be found at a depth of several meters, where they are shielded from cosmic rays and are subjected only to the radiation derived from radionuclide decay. Such a dose is only 14 MGy in 4.6×10^9 years as calculated by Urey (1955, 1956) and Draganic et al. (1993). To reach this dose it is necessary to consider the decay of radionuclide ^{26}Al (Kohman, 1997) in the first billion years of the Solar System as Urey (1955, 1956) and Draganic et al. (1993) do correctly; otherwise relatively smaller doses can be calculated.

Assuming a first order kinetics in the solid state radiolysis of the amino acids we may calculate both the rate constant k and the half-life period $T_{1/2}$ according to the following equations (Yeremin, 1979):

$$N_\gamma = N_0 e^{-kt} \quad (3)$$

$$\ln(N_0/N_\gamma) = kt \quad (4)$$

$$T_{1/2} = (\ln 2)/k = 0.963k^{-1} \quad (5)$$

where N_γ is the amino acid concentration at any time of radiolysis and N_0 the concentration at the beginning of the radiolysis, assuming also a linear relationship between the radiation dose 14 MGy and the age of the Solar System 4.6×10^9 years. Thus, 3.2 MGy correspond to 1.05×10^9 years. Since $N_0=100$ and N_γ are known by the DSC analysis at 3.2 MGy, i.e. at 1.05×10^9 years, it is possible to derive Eq. (3) from the graphs reported in Fig. 8.

From Eq. (3) the rate constant k can be easily derived and expressed in year^{-1} (y^{-1}). Using Eq. (5) it is possible to derive the half life $T_{1/2}$ (in year, y) of the irradiated amino acid. These results are reported in Table 3 and it can be easily observed that the shortest $T_{1/2}$ is displayed by alanine (1.87×10^9 y) followed by phenylalanine (2.06×10^9 y) and by leucine (2.25×10^9 y). Tyrosine and tryptophan are much more radiostable and their $T_{1/2} \sim 8.9 \times 10^9$ y. Consequently, we can find today in comets and asteroids that only 18% of the original amount of alanine present at the beginning of the Solar Systems 4.6×10^9 years ago, 21% of the original phenylalanine and 24% of the original leucine. In other words, the amount of amino acids found today in the meteorites known as carbonaceous

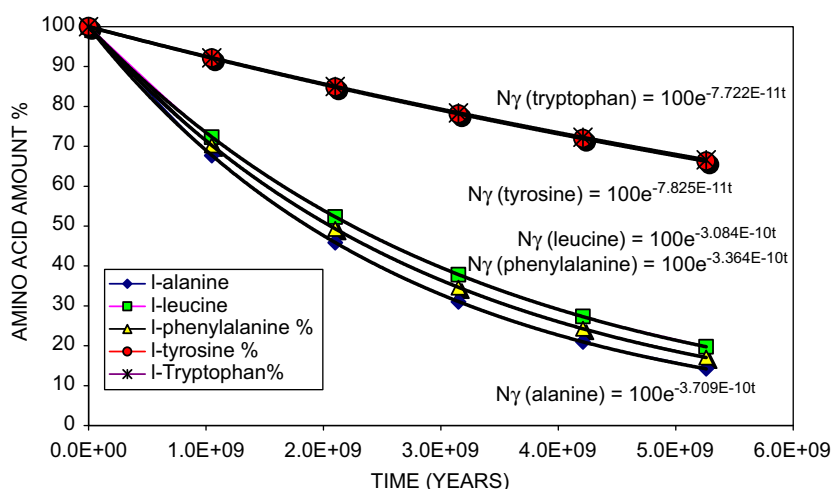


Fig. 8. Radiolysis of amino acids in the solid state. The radiolysis rate constants k (in year^{-1}) have been determined assuming first order kinetics, knowing that 3.2 MGy correspond to 1.05×10^9 years and knowing N_γ from the DSC analysis of the amino acids. $k(\text{ala})=3.7 \times 10^{-10} \text{y}^{-1}$, $k(\text{leu})=3.1 \times 10^{-10} \text{y}^{-1}$, $k(\text{phe})=3.4 \times 10^{-10} \text{y}^{-1}$, $k(\text{tyr})=7.8 \times 10^{-11} \text{y}^{-1}$ and $k(\text{try})=7.7 \times 10^{-11} \text{y}^{-1}$.

Table 3
Radiolysis and radioracemization rate constants and half life as determined by DSC and ORD.

	L-alanine	L-leucine	L-phenylalanine	L-tyrosine	L-tryptophan
N_γ after 4.6×10^9 years (%)	18.1	24.2	21.3	69.8	70.1
R_γ after 4.6×10^9 years (%)	29.7	43.3	43.1	95.3	35.8
Radiolysis (DSC) k (y^{-1})	3.7×10^{-10}	3.1×10^{-10}	3.4×10^{-10}	7.8×10^{-11}	7.7×10^{-11}
Radioracemization (ORD) k_{rac} (y^{-1})	2.6×10^{-10}	1.8×10^{-10}	1.8×10^{-10}	1.05×10^{-11}	2.23×10^{-10}
Radiolysis (DSC) $T_{1/2}$ (y)	1.87×10^9	2.25×10^9	2.06×10^9	8.85×10^9	8.97×10^9
Radioracemization ORD $T_{1/2rac}$ (y)	2.63×10^9	3.81×10^9	3.79×10^9	6.59×10^{10}	3.11×10^9

chondrites is only 1/5–1/4 of that originally present in the body from where the meteorite was originated. Instead tyrosine and tryptophan can be better preserved because of their higher radiation resistance and can be found in amounts more closer to their original value. However, normally these two amino acids are not found in meteorites because as discussed previously they are less “primitive” than alanine and leucine and may have been formed in later times through other processes.

One study here is radiolysis of a given amino acid without caring about its optical activity and its enantiomeric excess and another one is instead evaluation of residual optical activity after radiolysis at 3.2 MGy. Using the residual optical activity R_γ derived from the ORD curve, and making the same mathematical treatment reserved for N_γ , it is possible to derive the analogous equations:

$$R_\gamma = R_0 e^{-kt} \quad (6)$$

$$\ln(R_0/R_\gamma) = k_{rac} t \quad (7)$$

$$T_{1/2rac} = (\ln 2)/k_{rac} = 0.963 k_{rac}^{-1} \quad (8)$$

from where both radioracemization rate constant k_{rac} and the half life of optical activity $T_{1/2rac}$ can be derived. The data obtained are reported in Table 3 and show that the radioracemization rate constant and the consequent half life $T_{1/2rac}$ are in reasonable agreement with the $T_{1/2}$ values of aliphatic amino acids and aromatic amino acids. Only for tyrosine a larger discrepancy can be observed with $T_{1/2rac} \gg T_{1/2}$, suggesting that this amino acid is more prone to radiolytic decomposition than the radioracemization. However one has to keep in mind that with spectropolarimetric measurements we do not distinguish among the radiolysis products formed. Whether or not the radiolysis products are still optically active and what contribution they give to the total specific optical rotation and to the residual amino acid remain unknown. Therefore, we may conclude that we may trust our DSC measurements more, which in general are also supported by ORD results.

To show the validity of our approach, we should compare our k and $T_{1/2}$ results derived by calorimetric measurements with those of Kminek and Bada (2006). These authors have irradiated alanine in the solid state with γ radiation and have measured the N_γ by HPLC analysis instead of DSC used by us. They have found a radiolysis rate constant $k = 3.43 \times 10^{-10} y^{-1}$, which corresponds to $T_{1/2} = 2.02 \times 10^9 y$. These values are in good agreement with our results (Table 3), where we have found $k = 3.71 \times 10^{-10} y^{-1}$, which corresponds to $T_{1/2} = 1.87 \times 10^9 y$ for alanine.

4. Conclusions

The extrapolation of the radiolysis data obtained at 3.2 MGy suggests that all the amino acids studied can survive a radiation dose of 14 MGy, which is the dose delivered to all organic molecules present for instance in comets or asteroid at a depth of 20 m or more in 4.6×10^9 years—the age of the Solar System. The dose of 14 MGy is due to the decay of all major radionuclides in

4.6×10^9 years and because the depth is > 20 m, the contribution from cosmic rays to this total dose is negligible because of the shielding.

The study shows that the amino acids are reduced to 1/4–1/5 of their original value they had at the beginning of the Solar System. Consequently, the amount of alanine or leucine found today in the meteorites known as carbonaceous chondrites is just 1/4–1/5 of the amount originally present at the epoch of the formation of the Solar System 4.6×10^9 years ago. Among the amino acids studied, tyrosine shows the highest radiation resistance while tryptophan does not have a combination of its relatively high radiation resistance with an elevated level of radioracemization resistance. In general it is shown that the radiolysis rate constants k of all amino acids studied are in reasonable agreement with the radioracemization rate constant k_{rac} .

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