THE RADIORACEMIZATION OF AMINO ACIDS BY IONIZING RADIATION: GEOCHEMICAL AND COSMOCHEMICAL IMPLICATIONS*

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Abstract. A number of optically active amino acids, both in the solid state and as sodium or hydrochloride salts in aqueous solution, have been exposed to ionizing radiation from a 3000 Ci ^{60}Co γ-ray source to see if radioracemization might accompany their well-known radiolysis. γ-Ray doses causing 55–68% radiolysis of solid amino acids typically engendered 2–5% racemization, while aqueous solutions of the sodium salts of amino acids which underwent 53–66% radiolysis showed 5–11% racemization. Amino acid hydrochloride salts in aqueous solution, on the other hand, showed little or no radioracemization accompanying their radiolysis. Both radiolysis and radioracemization were roughly proportional to γ-ray dose in the range studied ($1-36 \times 10^6$ rads). Mechanisms for the radioracemization of amino acids in the solid state and as aqueous sodium salts are discussed, and the absence of radioracemization for aqueous hydrochloride salts is rationalized. Isovaline, a non-protein amino acid which has been isolated from the Murchison meteorite, contains no α-hydrogen atom and is therefore incapable of racemization *via* the chemical mechanisms by which ordinary amino acids racemize. Nevertheless, isovaline suffers radioracemization in the solid state to an extent comparable to that shown by ordinary amino acids, as do its sodium and hydrochloride salts in the solid state. The sodium salt of isovaline in aqueous solution, however, fails to racemize during its radiolysis. Several implications of the newly described phenomenon of radiomization are pointed out for the fields of geochemistry and cosmochemistry.

1. Introduction

In recent years we have been involved in a variety of experimental investigations (Bonner, 1974; Bonner and Flores, 1975, Bonner *et al.*, 1975, 1976/77, 1978; Noyes *et al.*, 1977) probing the possible validity of the Vester-Ulbricht mechanism (Vester *et al.*, 1959; Ulbricht, 1959; Ulbricht and Vester, 1962) for the origin of optical activity in nature *via* parity violation during the β-decay or radionuclides. In one series of such experiments (Bonner *et al.*, 1978) a number of 17–25 year-old samples of crystalline ^{14}C-labelled amino acids, both racemic and optically active, of high specific radioactivity were examined by gas chromatography (G.C.) for both gross radiolysis and possible stereoselective (asymmetric) degradation. These samples, which had undergone self β-radio-

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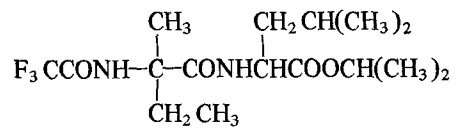
lysis during the several decades since their original preparation and purification (Bernstein *et al.*, 1972), showed as much as 67% gross degradation, but no asymmetric radiolysis. Several of the optically active ^{14}C-labelled amino acids, however, gave G.C. analyses which suggested that radiation induced racemization might also have accompanied their gross radiolysis. Since the possibility of such *radioracemization* had not been considered in any of the above (or other) experiments involving attempted stereoselective β-radiolysis, and since such a possibility had been only scarcely suggested in earlier literature (Feng and Tobey, 1959; Evans, 1966; Evans *et al.*, 1968), we decided to undertake a systematic preliminary investigation of the phenomenon. Our general plan was to subject a number of crystalline or dissolved optically pure D- and L- amino acids to heavy doses of ionizing radiation, then to examine the partially destroyed residue by G.C. for both gross radiolysis and possible radioracemization.

2. Experimental

The samples irradiated consisted of 10–17 mg portions, either solid or dissolved, of the optically pure (as determined by G.C.) amino acids listed in the Tables below. The samples were of the purest quality available from Aldrich Chemical Co., Calbiochem, Mann Research Laboratory, Nutritional Biochemicals, or Sigma Chemical Co. For hydrochloride salt irradiations the weighed amino acid was first dissolved in an equivalent amount of 0.1 *N* aqueous HCl, while for sodium salt irradiations each sample was dissolved in one equivalent volume of 0.1 *N* NaOH. The solid or dissolved samples were placed in 1 x 4 cm glass vials stoppered with Bakelite caps fitted with Teflon gaskets. The vials were placed in a 3000-Ci ^{60}Co γ-ray source at the Lawrence Berkeley Laboratory, a source designed to deliver high dose rates ($4–10 \times 10^6$ rads hr^{-1}) to small samples. Irradiations proceeded for time periods (5–90 hrs.) sufficient to afford the total radiation doses shown in the following Tables and to provide *ca.* 50–70% gross radiolysis.

After irradiation, each solid sample was dissolved and each liquid sample diluted to a volume of 5.0 ml with water or dilute HCl, then was quantitatively divided in half volumetrically, and all solutions were finally rotary-evaporated to dryness under vacuum. One of the 50% aliquots of each sample was then treated with a weighed quantity of the corresponding enantiomeric (or racemic) amino acid, so as to permit determination of the percent degradation of the sample by the 'enantiomeric marker' technique (Bonner, 1973). The amino acid samples were then converted into their *N*-trifluoroacetyl (*N*-TFA) isopropyl ester derivatives (I) for G.C. analysis (Bonner *et al.*, 1974), first by esterifying with 2-PrOH/HCl, the acylating with trifluoroacetic anhydride. In the case of the G.C. analyses of irradiated isovaline samples, however, enantiomeric derivatives of the type I

I



II

proved unsatisfactory in their resolvability characteristics. Suitable quantitative analyses (i.e. baseline resolution) could be achieved, however, by converting the isovaline first into its diastereomeric *N*-TFA-isovalyl-D(or -L)-leucine isopropyl ester derivatives (II) (Flores *et al.*, 1977; Bonner *et al.*, 1979b).

Each derivatized sample was then quantitatively analyzed by G.C. for its enantiomeric composition, using 46 m x 0.5 mm stainless steel capillary columns coated with one or the other of the two optically active enantiomeric G.C. phases, *N*-docosanoyl-D(or -L)-valine *tert*-butylamide (Bonner and Blair, 1979). The columns were installed in a Hewlett-Packard 5700A gas chromatograph and peak area integration was accomplished with the aid of a Hewlett-Packard 3380A digital electronic integrator-recorder, affording the analytical reproducibility and precision previously described (Bonner *et al.*, 1974).

In order to assess the effect of increasing radiation dosage on the extents of both gross radiolysis and racemization, a number of D- or L- leucine samples (15–17 mg) were dissolved in the equivalent volumes of 0.1 *N* HCl or NaOH, and the solutions were irradiated in the above γ-ray source for increasing time periods, so as to achieve the increasing dosages shown in Table IV. The data in the Tables below have been previously presented separately in several publications (Bonner and Lemmon, 1978a, 1978b; Bonner *et al.*, 1979a, 1979b).

3. Results

Tables I and II indicate that γ-radiation causes not only the previously documented radiolysis of amino acids (Garrison, 1968, 1972), but also engenders significant radioracemization as well – both in the solid state and as sodium salts in aqueous solution. Extensive radiolysis also occurs with the dissolved hydrochloride salts of amino acids (Table III) but, in contrast to the sodium salts (Table II), little or no concomittant

TABLE I
γ-Radiolysis and radioracemization of solid amino acids

No. Amino acid	Radiation dose (Rads x 10^{-8})	Decomposition, %	Residual amino acid		
			%D[a]	%L[a]	Racemization, %[b]
1. L-Alanine	8.1	38.6	1.9	98.1	3.8
2. D-2-Aminobutyric acid	8.1	55.8	99.2	0.8	1.6
3. L-Norvaline	8.1	66.1	1.6	98.4	3.2
4. L-Norleucine	8.1	63.1	1.3	98.7	2.6
5. D-Leucine	8.1	67.9	97.2	2.8	5.6
6. L-Leucine	8.1	68.0	2.5	97.5	5.0
7. D-Leucine	10.2	96.1	96.2	3.8	7.6
8. L-Leucine	10.2	93.2	6.8	93.2	13.6

[a]Standard deviations for averages of 2–4 G.C. analyses were generally ± 0.1–0.3%. Same in other Tables.
[b]2-Times the percent of inverted enantiomer.

TABLE II

γ-Radiolysis and radioracemization of amino acid sodium salts (0.10 M aqueous solution)

No. Amino acid	Radiation dose (Rads x 10^{-7})	Decomposition, %	Residual amino acid		
			%D	%L	Racemization, %
1. L-Alanine	1.7	65.8	5.8	94.2	11.6
2. D-2-Aminobutyric acid	1.8	58.0	96.0	4.0	8.0
3. D-2-Aminobutyric acid	1.8	59.4	95.8	4.2	8.4
4. L-Norvaline	1.7	59.6	4.2	95.8	8.4
5. L-Norleucine	1.7	52.8	5.3	94.7	10.6
6. L-Valine	1.7	55.3	5.5	94.5	11.0
7. L-Leucine	1.7	54.4	2.6	97.4	5.2

racemization takes place. Table IV indicates that increasing radiation dosage causes increasing radiolysis of leucine salts in aqueous solution as well as increasing radioracemization of the sodium salt. Again the hydrochloride salt samples underwent little or no racemization. A plot (see Figure 1) of the data in Table IV shows that radiolysis of the sodium salt of leucine occurs slightly faster than radiolysis of its hydrochloride salt, and that for both salts the extent of radiolysis is roughly proportional to total dosage up to *ca.* 60% degradation. Tolbert *et al.* (1962) have found a similar initial linear relation between radiolysis and dose for crystalline amino acids, and we have previously noted a linear decomposition-dose relationship during the first 80% of the γ-radiolysis of solid leucine (Bonner, 1973). Figure 1 also indicates an approximately linear relationship between extent of radioracemization and dosage for the sodium salt of leucine within the dose range studied. A rough indication of the overall reproducibility of the radiolysis and racemization data in the above Tables is seen in Nos. 2 and 3 of Table II, duplicate experiments in which identically sized samples of the dissolved sodium salt of 2-aminobutyric acid were irradiated simultaneously.

For reasons discussed below, it became desirable to investigate the γ-radiolysis and possible radioracemization of isovaline (α-amino-α-methyl-butyric acid, III), and to com-

TABLE III

γ-Radiolysis and radioracemization of amino acid hydrochloride salts (0.10 M aqueous solution)

No. Amino acid	Radiation dose (Rads x 10^{-7})	Decomposition, %	Residual amino acid		
			%D	%L	Racemization, %
1. L-Alanine	2.2	53.4	0.2	99.8	0.4
2. D-2-Aminobutyric acid	2.2	52.1	100.0	0.0	0.0
3. L-Norvaline	2.2	57.9	0.0	100.0	0.0
4. L-Norleucine	2.2	63.5	0.0	100.0	0.0
5. L-Valine	2.2	54.8	0.0	100.0	0.0
6. L-Leucine	2.2	55.3	0.0	100.0	0.0

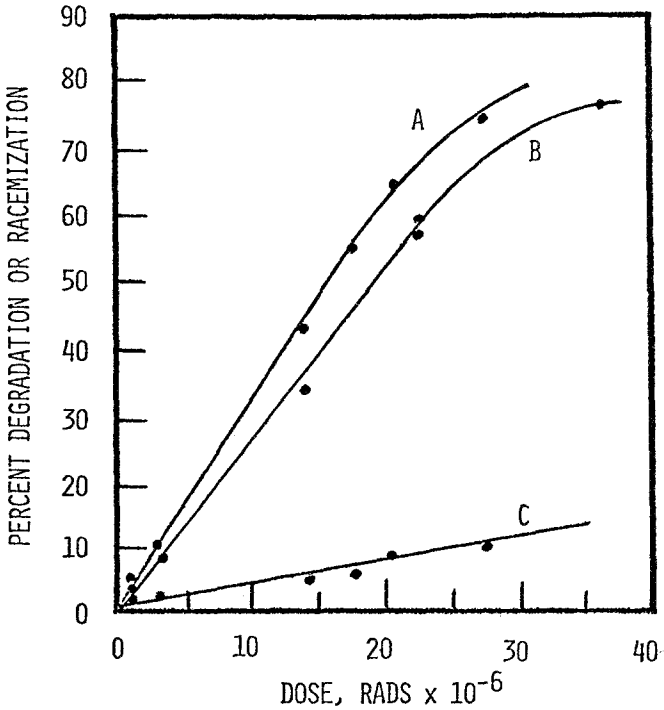


Fig. 1. Radiolysis and radioracemization of leucine salts (0.1M aqueous solution) by γ-radiation. (A) Degradation, Na Salt. (B) Degradation, HCl Salt. (C) Racemization, Na Salt.

TABLE IV
γ-Radiolysis and radioracemization of leucine salts (0.10 M aqueous solution) as a function of γ-ray dosage

Enantiomer	Salt	Radiation dose (Rads x 10^{-6})	Decomposition, %	Residual leucine		
				%D	%L	Racemization, %
D	Na	1.0	1.8	99.2	0.8	1.6
D	Na	3.0	9.4	99.2	0.8	1.6
D	Na	14.0	41.7	97.9	2.1	4.2
L	Na	17.3	54.4	2.6	97.4	5.2
D	Na	20.5	63.1	96.2	3.8	7.6
D	Na	27.0	73.6	95.4	4.6	9.2
D	HCl	1.0	3.3	99.8	0.2	0.4
D	HCl	3.0	7.6	99.7	0.3	0.6
D	HCl	14.0	32.5	99.2	0.8	1.6
L	HCl	22.0	55.3	0.0	100.0	0.0
D	HCl	22.1	57.6	–[a]	–	–
D	HCl	36.1	75.7	–[a]	–	–

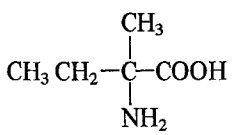
[a] G.C. traces obscured by peaks for degradation products.

TABLE V
γ-Radiolysis and radioracemization of isovaline

No.	Substrate	Radiation dose (Rads x 10^{-8})	Degradation, %	Racemization, %
1.	D-Ival[a]	9.0	79.6	4.9
2.	L-Ival[a]	9.0	78.0	4.7
3.	D-Ival[a]	12.0	86.5	6.1
4.	L-Ival[a]	12.0	86.8	6.4
5.	D-Ival · H_2O[b]	9.0	80.0	2.5
6.	L-Ival · H_2O[b]	9.0	79.0	3.2
7.	D-Ival Na salt[a]	9.0	87.7	3.8
8.	L-Ival HCl salt[a]	9.0	91.8	3.3
9.	D-Ival Na salt (aq)[c]	0.25	68.1	0.0
10.	L-Ival Na salt (aq)[c]	0.25	68.8	0.0

[a] Solid, anhydrous
[b] Monohydrate crystals
[c] 0.1 M aqueous solution

pare these with the results for the ordinary amino acids in Tables I-III. The principal



III

results of these experiments are summarized in Table V, where we observe that isovaline samples in the solid state, either hydrated or anhydrous, or as the solid sodium (No. 7) or hydrochloride salt (No. 8), undergo significant radioracemization accompanying their γ-radiolysis. Again (Nos. 3,4 *versus* 1,2) as with solid (Table I) or dissolved (Table IV) leucine, increasing radiation doses cause an increase in both radiolysis and racemization. Isovaline in the hydrated crystal form (Nos. 5,6) appears slightly less susceptible to radioracemization than does the anhydrous form (Nos. 1,2) for the same radiation dose, though the two forms are approximately equally prone to radiolysis. While the radiolyses and radioracemizations of isovaline in the solid state are roughly comparable to those of the other amino acids in Table I, the complete absence of radioracemization for the aqueous sodium salt of isovaline (Nos. 9,10) is noteworthy in its contrast to the facile racemizations summarized in Table II. This difference is discussed below. Again, the approximate reproducibility of our radiolysis and radioacemization data are indicated by the effects noted at equivalent dosages for the various enantiomeric pairs in Table V (Nos. 1,2; 3,4; 5,6; 9,10).

4. Mechanistic Speculations

At the present time we have not experimentally established any mechanisms whereby the above radioracemization of solid amino acids or their aqueous sodium salts might occur, nor have we characterized the radiolysis products responsible for the several extraneous peaks in the various G.C. traces of our enantiomeric composition analyses. One can presently only speculate on mechanisms for radioracemization as they might be superimposed upon currently accepted mechanisms for the radiolysis of solid amino acids or their aqueous solutions. Garrison (1968, 1972) has recently discussed such mechanisms in detail.

The initial step in the γ-radiolysis of a solid amino acid zwitterion (IV) is thought to be carbon-hydrogen scission at the α-carbon atom producing an α-radical (V), a proton, and a secondary electron, e^-_s (Eq. (1)). The secondary electron as well as the α-radical V then attack both IV and other intermediate species trapped in the crystal lattice,

$$\underset{\text{IV}}{R{-}\overset{{}^+NH_3}{\overset{|}{C}}H{-}COO^-} \xrightarrow{\gamma\text{-photon}} \underset{\text{V}}{R{-}\overset{{}^+NH_3}{\overset{|}{\overset{\cdot}{C}}}{-}COO^-} + H^+ + e^-_s \qquad (1)$$

ultimately affording the observed radiolysis products. In such a reaction sequence, to the extent that the α-radical V abstracts hydrogen atoms from other constituents of the crystal lattice to re-form IV, the regenerated IV should be totally or partially racemic, since V is presumably unable fully to maintain its original stereochemical configuration. Clearly, some similar sequence of degradative reactions, one or more of which regenerates the original but racemized amino acid, must apply also to the radioracemization of solid isovaline. Since isovaline has no α-hydrogen, however, the initial radiation-induced α-carbon scission must involve a C-C rather than a C-H band.

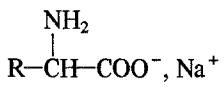
The radiolysis of amino acids in aqueous solution is believed (Garrison, 1968, 1972) to be initiated by hydrated electrons, e_{aq}, or hydroxyl radicals, HO·, produced by prior radiolysis of the water solvent (Eq. (2)). These species in turn attack the amino acid and

$$H_2O \xrightarrow{\gamma\text{-photon}} e^-_{aq} + HO\cdot + H^+ + H_2 + H_2O_2 \qquad (2)$$

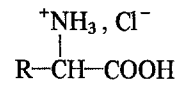
initiate a series of degradation reactions similar to those postulated for solid state radiolysis, ultimately affording the observed fatty acid and α-keto acid degradation products. In particular, α-hydrogen abstraction by HO· can produce a key radiolysis intermediate, α-radical V (Eq. (3)). Reversal of reaction (3) would clearly provide a facile mechanism for the radioracemization of zwitterion IV in aqueous solution.

$$\underset{\text{IV}}{HO\cdot + R{-}\overset{{}^+NH_3}{\overset{|}{C}}H{-}COO^-} \longrightarrow \underset{\text{V}}{H_2O + R{-}\overset{{}^+NH_3}{\overset{|}{\overset{\cdot}{C}}}{-}COO^-} \qquad (3)$$

Our solution radiolysis, however, were conducted using sodium (VI) or hydrochloride salts (VII) of the amino acids in question. Here the mechanism for radioracemization

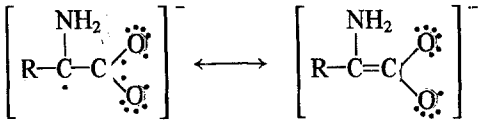


VI

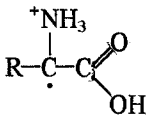


VII

would again presumably be HO· attack to form a stereochemically labile α-radical analogous to V, followed by solvent attack to regenerate racemized IV or VII, akin to the reversal of Eq. (3). However, our findings were that the sodium salts VI were particularly susceptible to radioracemization, while the hydrochloride salts VII under similar conditions were essentially unracemized. The facile radioracemization of the aqueous sodium salts of amino acids has been rationalized (Bonner and Lemmon, 1978b) as resulting from the ready formation of the α-radical from the anion of salt VI, due to its stabilization as the highly symmetrical resonance hybrid VIII. Such a resonance-stabilized intermediate cannot arise from the corresponding α-radical (IX) from the cation of VII, thus



VIII



IX

explaining its apparent slow formation and the lack of accompanying radioracemization. Other speculations regarding the radioracemization of VI and the optical stability of VII have been advanced by Bonner and Lemmon (1978b).

The complete absence of radioracemization for the sodium salt of aqueous isovaline (Table V) is noteworthy in its contrast to the extensive racemization of the sodium salts of common amino acids (Table II). This observation is understandable in terms of Eq. (3). If the radioracemization of the sodium salts of amino acids is intitiated by analogous α-hydrogen abstraction by HO· to form the resonance stabilized α-radical VIII, such a mechanism is not available to isovaline as it lacks the requisite α-hydrogen atom. The sodium salt of isovaline is thus immune to radioracemization in aqueous solution (but not in the solid state), although gross radiolysis (by other reaction paths) is extensive (Table V).

5. Geochemical and Cosmochemical Implications

The racemization of natural amino acids under diagenetic environmental conditions is a phenomenon of considerable current interest to geochemists, paleontologists and archeologists, since it has been widely assumed that the D/L ratios for residual amino acids isolated from ancient specimens may provide a measure of the age of the specimen. Assuming that the amino acids isolated from a prehistoric sample are of protein origin

and were therefore originally of the L-configuration and that the simple first order kinetics applicable to the racemization of amino acids in solution are similarly valid for the natural diagenetic racemization of these amino acids, it is possible – after establishing the D/L ratios of several amino acids in a sample of known age – to calculate the specific rate constants for the diagenetic racemization of those amino acids. Assuming also a uniform external environment at the given sample site within the geological epoch in question, one can then use the calculated rate constants to estimate the ages of other prehistoric samples from the same general area, again by determining the D/L ratios of the same amino acids isolated from the latter samples. In this general way D/L enantiomer ratios have been utilized during the past decade or so for the age dating of ancient specimens of geological sediments (Bada *et al.*, 1970; Wehmiller and Hare, 1971), shells (Hare and Mitterer, 1968), bones (Bada, 1972; Bada and Protsch, 1973; Dungworth *et al.*, 1974), teeth (Helfman and Bada, 1975, 1976), and corals (Wehmiller *et al.*, 1976). In addition, having once independently established the age of a particular prehistoric bone sample (e.g., by ^{14}C dating), and having then also determined in the laboratory the temperature effects on the rates at which certain amino acids in modern bones racemize or epimerize, several investigators have thereupon used subsequently determined enantiomer or epimer ratios of these amino acids in the sample to estimate the temperatures prevailing over the past geological lifetime of the sample i.e., as paleotemperature indicators (Bada *et al.*, 1973; Schroeder and Bada, 1973; Mitterer, 1975).

The validity of applying amino acid racemization criteria to geochronology and geothermometry has recently been critically questioned (Dungworth, 1976; Williams and Smith, 1977), and a host of previously ignored environmental and other factors have been enumerated which could cause serious errors in estimates of the rate constants for the diagenetic racemization of amino acids. Such errors in turn could seriously invalidate geochronological or geothermometric conclusions based on the simple measurement of D/L enantiomer ratios for the amino acids in question. To these formidable pitfalls challenging the validity of D/L ratios alone as criteria for estimating geological ages or temperatures must now be added the possibility of radioracemization during the epoch in question. While uniform radioactivity in the earth's crust might conceivably contribute relatively uniformly to the diagenetic racemization of amino acids in ancient samples, the proximity of additional radioactive material – either in an indigenous mineral matrix or dissolved in ground waters – would clearly induce additional indeterminate amounts of radioracemization in the samples in question, and thus suggest their spurious antiquity. Furthermore – a question which we are now investigating experimentally – it seems possible that clay minerals (in conjunction with radioactive sources) might enhance the effectiveness of radioracemization, as they apparently do for thermal racemization (Kroepelin, 1968; Flores and Bonner, 1974), thus shortening further the time required for the diagenetic racemization of ancient amino acid samples. In summary we would argue that unless specific knowledge of the radiation exposure history of a given ancient amino acid sample is available, the phenomenon of radioracemization might unwittingly cause considerable error in geochronological or geothermometric conclusions based solely

on the measurement of the simple D/L enantiomer (or epimer) ratio of the amino acid in question.

Our subsequent interest (Bonner *et al.*, 1979a, 1979b) in the possible radioracemization of isovaline (III) was occasioned by the cosmological importance of this non-protein amino acid. In September 1969, a type II carbonaceous chondrite fell to earth near Murchison, Victoria, Australia, and shortly thereafter extensive investigations were undertaken into the organic constituents of this fragment, using G.C. and other analytical techniques (Kvenvolden *et al.*, 1970, 1971; Oró *et al.*, 1971a, 1971b; Cronin and Moore, 1971; Lawless, 1973; Lawless and Peterson, 1975). As early as 1971 Kvenvolden *et al.* reported 18 amino acids to be present in the Murchison chondrite, 12 of which including isovaline, were non-protein and 6 of which were common to terrestrial proteins, and by 1973 Lawless had extended the number of amino acids present to 45. During their G.C. analyses, the optically active amino acids from the Murchison meteorite were found to consist of approximately equal amounts of D- and L-enantiomers (Kvenvolden *et al.*, 1971, 1972; Oró *et al.*, 1971b), a fact interpreted as indicating their probable abiotic origin. The presence of non protein amino acids in the Murchison and Murray meteorites has led to the same interpretation (Kvenvolden *et al.*, 1971; Lawless *et al.*, 1971).

Of the non-protein amino acids from the Murchison chondrite isovaline has been of particular interest cosmologically since, in contrast to other amino acids thus far isolated, it lacks a hydrogen atom on its α-carbon atom. Accordingly, isovaline cannot undergo racemization by the known mechanisms responsible for the racemization of common amino acids, namely, reactions involving reversible scission of the α-C-H bond (Pollock *et al.*, 1975). For this reason, it has been argued (Lawless, 1973) that the enantiomeric composition of the Murchison isovaline should be that which prevailed at the time of its original synthesis in the meteorite, thus giving a clue as to the primordial enantiomeric composition of other amino acids in the meteorite. In 1975 Pollock *et al.* achieved a partial G.C. resolution of authentic D,L-isovaline as well as of the isovaline from the Murchison meteorite, obtaining comparable analytical results from each (D-III, *ca.* 52%; L-III, *ca.* 48%). This led to the conclusion that the Murchison isovaline was in fact racemic and that therefore it and the other amino acids in this meteorite had originated as racemic mixtures by abiotic, extraterrestrial syntheses. Since these conclusions were based on the demonstrated (Pollock *et al.*, 1975) non-racemization of isovaline under the ordinary laboratory conditions and did not take into account the then unknown possibility of radioracemization, the possible radioracemization susceptibility of isovaline clearly became a cosmologically pertinent question.

Our finding that solid isovaline (Table V) is approximately as susceptible to radioracemization as are the solid common amino acids having α-hydrogen atoms (Table I) indicates that this structural difference is not pertinent as regards the racemization of solid amino acids by ionizing radiation. The probable mechanistic reason, in terms of its lack of an α-hydrogen atom, for the immunity to radioracemization of isovaline as its dissolved sodium salt, however, has been discussed above. While the enantiomeric com-

position of the isovaline in the Murchison meteorite was found (Pollock *et al.*, 1975) to be *approximately* D:L/50:50, our observed radioracemization of solid isovaline suggests the need to reevaluate the earlier conclusion (Pollock *et al.*, 1975; Lawless, 1973) that the primordial enantiomeric composition of the isovaline and other amino acids in the Murchison meteorite must therefore have been racemic. Although the time since the Murchison chondrite fragmented from its parent body is only *ca.* 1.2×10^6 years (Cressy and Bogard, 1976), resulting in a cosmic ray radiation dose of *ca.* 3×10^7 rads during this period (based on 10^8 rads during 3.5×10^6 years for the Orgueil meteorite (Studier *et al.*, 1965)), the natural radioactivity of a meteorite parent body would have provided an integrated dose of *ca.* 5×10^8 rads during the 4.5×10^9 years of its existence (Anders, 1961; Studier *et al.*, 1965). Thus, the isovaline in the Murchison chondrite has received a total radiation dose of *ca.* 5.3×10^8 rads, some 60% of the dose which caused 4.8% racemization of anhydrous isovaline (Table V). Although it is not presently known how the mineral matrix of the meteorite might alter the efficacy of radioracemization, it would seem probable that significant radioracemization of any non-racemic amino acids indigenous to meteorite parent bodies could have occurred during the 4.5×10^9 years since their origin. These speculations, of course, carry no implication whatsoever that the racemic amino acids found in present day meteorites were originally optically active or of biological origin. Nevertheless we believe that the phenomenon of radioracemization, in principle, makes the question of the primordial enantiomeric composition of amino acids in meteorites a fundamentally indeterminate one.

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