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β-Radiolysis of Crystalline ^{14}C-Labeled Amino Acids

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In an investigation of the possible validity of the Vester-Ulbricht β-decay parity violation mechanism[1-3] for the abiotic origin of molecular chirality, one of us has recently shown[4,5] that 10-20% net longitudinally polarized 120-keV electrons produced in a linear accelerator caused the asymmetric degradation of DL-leucine. "Natural" antiparallel spin polarized electrons preferentially degraded the D-leucine component of the racemate, and parallel spin electrons selectively destroyed the L-enantiomer. This was the first positive demonstration of asymmetric degradation by β-particles since Garay's 1968 report[6] that 0.36 mCi of $^{90}SrCl_2$ in aqueous solution caused more rapid decomposition of dissolved D-tyrosine than of L-tyrosine. Earlier studies[1-3,7] and our subsequent attempts[8,9] to duplicate and extend Garay's experiments to other amino acids, both solid and dissolved, using a 61,700-Ci ^{90}Sr-^{90}Y source at Oak Ridge National Laboratory led to no observable asymmetric radiolyses. More recently Darge and coworkers[10] made the remarkable report that DL-tryptophan in frozen aqueous solution suffered 33% total degradation and (based on its optical rotation of $0.0007 \pm 0.0004°$) a 19% optical enrichment of the D-enantiomer during its 12-week exposure to 0.63 mCi of dissolved ^{32}P phosphate. In view of the several positive reports of asymmetric β-radiolysis reviewed above we have been encouraged to examine for β-induced optical activity a number of ^{14}C-labeled DL-amino acids of high specific radioactivity (ca.300-600 mCi/mole) prepared 17 to 25 years ago at the Lawrence Berkeley Laboratory, University of California.

The racemic amino acids studied and the radiochemical and analytical data pertaining to them are recorded in Table 1. Three of the amino acids listed in Table 1 (DL-Ala, DL-Asp, and DL-Norval) have been examined previously[11] for optical activity (using ORD measurements) and percent

decomposition (using the amino acid analyzer), with the observation of no selective radiolysis. In the present study we have used quantitative gas chromatography (g.c.) as our analytical criterion for both the enantiomeric composition of the undecomposed amino acid residues as well as for percent degradation (using the "enantiomeric marker" technique[12]). G.c. not only provides the important advantage (over optical rotation) of looking at only the residual enantiomers of interest (uncontaminated by accompanying degradation products which may or may not be optically active), but is capable, particularly with micro-quantities, of a superior accuracy and precision (ca. 0.2%)[13] in the quantitative analysis of enantiomers. The DL-amino acids in Table 1 were converted to their N-trifluoroacetyl isopropyl esters as previously described[13] and analyzed in replicate with the aid of a digital electronic integrator,[13] using 150' x 0.02" stainless steel capillary g.c. columns[13] coated with the optically active g.c. phases, N-lauroyl-[14] or N-docosanoyl-L-valyl-tert-butylamide.[15] All g.c. analyses were interspersed "back-to-back" with an equal number of replicate g.c. analyses of the corresponding non-radioactive, authentic DL-amino acid as a control. For comparison purposes Table 1 also summarizes radiochemical, percent decomposition, and enantiomeric composition data, similarly obtained, for a number of labeled D- and L-amino acids which had been prepared by optical resolution of several of the racemic amino acids in Table 1.

The enantiomeric compositions in Table 1 indicate that the radioactive DL-amino acids examined are 50:50/D:L within experimental error and that they suffered no asymmetric degradation, despite self-radiolyses as high as 67%. The enantiomeric compositions of the resolved amino acids show further that racemization does not necessarily accompany self-radiolysis in the dry state, although comparison of the enantiomeric compositions noted

Table 1.

Radioactive Amino Acid	Radio-activity mCi/mole	Age,[a] years	Total Dose, Rads$\times 10^{-7}$	Percent Decomposed	Molecules Decomposed per electron $\times 10^{-4}$	G[b]	Enantiomeric Composition %D	%L	(±)[d]
DL-Alanine-2-^{14}C	285	16.9	5.05	26.5	2.84	56.8	50.06[c]	49.94	0.85
DL-Valine-4,4'-^{14}C	316	25.8	6.51	30.0	1.90	38.0	50.19[c]	49.81	0.20
DL-Norvaline-3-^{14}C	574	24.9	11.41	17.4	0.63	12.6	49.94[c]	50.06	0.18
DL-Leucine-3-^{14}C	446	24.0	7.63	67.8	3.26	65.2	50.15[c]	49.85	0.22
DL-Norleucine-3-^{14}C	551	24.9	9.78	24.1	0.90	18.0	50.10[c]	49.90	0.17
DL-Aspartic-4-^{14}C acid	319	24.1	5.40	~50	3.35	67.0	50.23[c]	49.77	1.02
D-Valine-4,4'-^{14}C	316	21.3	5.37	31.2	2.39	47.8	100.00	0.00	-
L-Valine-4,4'-^{14}C	316	21.3	5.37	47.1	3.62	72.4	0.00	100.00	-
D-Norvaline-3-^{14}C	574	20.5	9.39	21.1	0.92	18.4	93.95	6.05	0.21
L-Norvaline-3-^{14}C	574	20.5	9.39	20.3	0.89	17.8	0.87	99.13	-
D-Leucine-3-^{14}C	446	20.6	6.55	39.5	2.22	44.4	92.55	7.45	0.11
D-Norleucine-3-^{14}C	551	20.6	8.09	25.9	1.17	23.4	99.80	0.20	-
L-Norleucine-3-^{14}C	551	20.6	8.09	18.6	0.84	16.8	0.80	99.20	-

a. Between date of preparation and date of analysis.

b. Molecules decomposed per 100 eV, assuming average energy per $\beta = 5.0 \times 10^4$ eV.

c. Corrected to a 50:50/D:L Composition of authentic DL-standard.

d. Denotes standard deviation.

for D-norvaline-3-^{14}C and D-leucine-3-^{14}C with those estimated from the original optical rotations of the samples suggests that some racemization may be possible. From the specific radioactivity of the samples and their ages one can calculate the number of β-particles emitted during the lifetimes of the samples. From these numbers (not shown) and the percent decompositions one can calculate the numbers of molecules decomposed per β-particle, which proves to vary between about 6000 and 36,000 among our samples. These numbers are higher than ca. 3000 molecules decomposed per electron observed during our previously reported[4] asymmetric degradations of DL-leucine with longitudinally polarized linear accelerator electrons. The variability in the percent decomposition and hence the number of molecules decomposed per electron as well as the G-values observed for comparable samples (e.g. D-, L-, and DL-valine-4,4'-^{14}C, D- versus DL-leucine-3-^{14}C, etc.) is noteworthy and may be due, we suspect, to the variability of trace impurities, including moisture, in the 17 to 25 year old samples. Finally, the racemic nature of the radiolyzed DL-amino acids in Table 1 further indicates that microbial degradation could not have been operative during the lifetimes of the samples, since if it had an excess of D-enantiomer should be observed in the residual materials.

Even though ^{14}C-betas are relatively low energy (endpoint energy 155 keV[16] ; mean energy ca. 50 keV), their polarization is substantial. Both theoretically and experimentally[17], $\beta^{\pm}$ particles emitted with velocity v during weak nuclear decays have a helicity (longitudinal polarization along their direction of motion of $\mp$ v/c. This is a direct consequence of the two component neutrino theory, which predicted the non-conservation of parity.[18] Since the kinetic energy of the electron is related to its rest energy mc^2 by (1)[19], it follows that v/c is given by (2). Since the rest energy mc^2 of the electron is 511 keV[20],

$$T = mc^2 [(1 - v^2/c^2)^{1/2} - 1] \qquad (1)$$

$$v/c = (2T/mc^2)^{1/2} \cdot (1 + T/2mc^2)^{1/2} / (1 + T/mc^2) \qquad (2)$$

this implies a polarization for ^{14}C-betas of 64.1% at the end point energy and 41.3% at the middle (50keV) of the energy spectrum. Subsequent ionization processes which slow down the primary electron decrease its energy on the average only by ca. 30 eV per ion pair produced[21], and furthermore it is known[22] that such ionizations leave the longitudinal polarization of the primary electron virtually unchanged until it has been slowed down to a few keV[23]. We thus conclude that the polarization of the primary electrons available for initiating chiral destruction of the substrate in the ^{14}C-experiments is somewhat greater than the polarization (10 - 20%) of the electrons employed in the accelerator experiments[4,5].

Thus the failure to observe asymmetric β-radiolysis in the solid DL-amino acid samples listed in Table 1, as compared to the small but successful asymmetric degradations previously induced[4,5] in DL-leucine by the 10 - 20% net longitudinally polarized linear accelerator electrons is at first appearance puzzling. We believe, however, that the discrepency may be rationalized as follows. As is apparent (Table 1) from the large number of molecules decomposed for each ^{14}C-beta emitted, the majority of the degradations must be engendered by secondary electrons produced by numerous subsequent ionizations caused by the primary ^{14}C-betas. The degree of polarization, if any, of such secondary electrons is not known[3], but presumably it is at best considerably less than that of the primary β-particles, and furthermore the energies of the secondary electrons (ca.

30 eV average[21]) are in a range more suitable for initiating chemical changes[24]. For these reasons it seems possible that the differing sample geometries in the two types of experiments might be crucial. In the accelerator expriments the amino acid target was a thin layer in a plane perpendicular to the impinging 120 keV electron beam, while the ^{14}C-amino acids were thick bulk samples isotropically irradiated by internally produced betas. The latter geometry clearly allows for the preferential production and intervention of less polarized (or unpolarized) secondary electrons, which in turn cause greater degradation of a less asymmetric (or totally symmetric) nature. This possibility is emphasized by the fact that up to 36,000 molecules were decomposed per primary beta in the ^{14}C-labeled samples (Table 1), whereas only ca. 3000 molecules per (higher energy) electron were destroyed in the accelerator experiments[4,5]. Another difference of possible significance is the differing time scale involved in the two types of experiment. The accelerator samples were irradiated for a matter of hours only and were analyzed immediately thereafter, whereas the ^{14}C-labeled samples suffered self-radiolysis during several decades prior to their g.c. analyses. Clearly the possibility of migration within the crystal lattice of the initial degradation fragments and possible secondary decompositions subsequently engendered by them is much greater in the ^{14}C-samples. Such presumably symmetrical processes could certainly reduce the net asymmetric effect to undetectable levels. It should be mentioned finally that circularly polarized Bremsstrahlen produced by the initial longitudinally polarized β-particles, which had been originally postulated[1-3] as the source of asymmetric photochemical effects which might produce optical activity, have recently been shown[25,26] on energetic grounds to be ineffective in engendering even significant gross degradation of the target sample. Other problems regarding the

β-decay mechanism for the origin of optical activity involving ^{14}C and ^{40}K β-particles have recently been discussed by us[27].

References

1. Vester, F., Ulbricht, T. L. V., and Krauch, H., Naturwissenschaft, 46, 68 (1959).

2. Ulbricht, T. L. V., Q. Rev. Chem. Soc., 13, 48 (1959).

3. Ulbricht, T. L. V., and Vester, F., Tetrahedron, 18, 629 (1962).

4. Bonner, W. A., Van Dort, M. A., and Yearian, M. R., Nature, 258, 419 (1975); 264, 198 (1976).

5. Bonner, W. A., Van Dort, M. A., Yearian, M. R., Zeman, H. D., and Li, G. C., Israel J. Chem. (in press).

6. Garay, A. S., Nature, 219, 338 (1968).

7. Goldanskii, V. I., and Khrapov, V. V., Sov. Phys. JETP, 16 (3), 582 (1963).

8. Bonner, W. A., J. Molec. Evol., 4, 23 (1974).

9. Bonner, W. A., and Flores, J. J., Origins of Life, 6, 187 (1975).

10. Darge, W., Laczko, I., and Thiemann, W., Nature, 261, 522 (1976).

11. Bernstein, W. J., Lemmon, R. M., and Calvin, M., in: "Molecular Evolution, Prebiological and Biological", Rolfing, D. L., and Oparin, A., eds.; Plenum, New York, 1972; pp. 151-155.

12. Bonner, W. A., J. Chromatogr. Sci., 11, 101 (1973).

13. Bonner, W. A., Van Dort, M. A., and Flores, J. J., Analyt. Chem., 46, 2104 (1974).

14. Feibush, B., Chem. Commun., 544 (1971).

15. Charles, R., Beitler, U., Feibush, B., and Gil-Av, E., J. Chromatogr., 112, 121 (1975).

16. Gray, D.E., ed., American Institute of Physics Handbook, McGraw-Hill, New York, 1957; pp. 8-98.

17. Frauenfelder, H. and Steffen, R., in: "α, β, and γ-Ray Spectroscopy", Siegbahn, K., ed.; North-Holland, Amsterdam, 1965; Vol. 2, pp.1431 - 1452.

18. Lee, T.D., and Yang, C.N., Phys. Rev., 104, 254, (1956).

19. Bergmann, P.G., "Introduction to the Theory of Relativity", Prentice-Hall, New York, 1942; p. 92, eq. 6.20.

20. Barash-Schmidt, N., et al., Rev. Mod. Phys., 48, No. 2., Part II (1976).

21. Spinks, J.W.T., and Woods, R.J., "An Introduction to Radiation Chemistry", John Wiley & Sons, New York, 1964; p. 70 ff.

22. Heintze, J. Zeitsch. für Physik., 150, 134 (1958).

23. Jackson, J.D., private communication to H.P.N.

24. Klots, C.E., in: "Fundamental Processes in Radiation Chemistry", Ausloos, P.J., ed.; Interscience Publishers, New York, 1968; p. 36.

25. Keszthelyi, L., Nature, 264, 197 (1976).

26. Walker, D.C., Origins of Life, 7, 383 (1976).

27. Noyes, H.P., Bonner, W.A., and Tomlin, J.A., Origins of Life. (In press).