matters arising

Asymmetric degradation of DL-leucine with longitudinally polarised electrons

BONNER et al. reported that when DL-leucine was irradiated with natural, antiparallel, polarised electrons of 120 keV energy, D-leucine was decomposed to a greater extent than L-leucine: with unnatural, parallel, polarised electron irradiation, however, L-leucine was degraded to a greater extent[1].

The mechanism of this phenomenon is not known. The authors were unable to decide whether the asymmetric degradations was caused by the longitudinally polarised electrons themselves, or by their bremsstrahlung. I wish to point out that the degradations measured could not have been caused by the bremsstrahlung of the bombarding electrons.

Analysing the data given in Table 1, of ref. 1, I calculated the average energy spent by the electrons to decompose a single leucine molecule (ΔE) and the relative defference of the decomposition rates for L-, and D-leucine ($2Z = (\varepsilon_L - \varepsilon_D)/\varepsilon_0$). For this purpose the following simple equation was used (which assumes an exponential decomposition of the molecules under constant irradiation[2])

$$\frac{N_L - N_D}{N_L + N_D} = PZ \ln \frac{1}{1-D} \qquad (1)$$

where the left side is the relative difference in the number of remaining L and D molecules, that is, the enantiomeric selectivity ($\%L - \%D$) defined in ref. 1; P is the polarisation of the incoming electron beam (percentage excess in Table 1 of ref. 1); and D is the sample decomposition (percentage divided by 100). The thickness of the irradiated DL-leucine samples (~ 20 mg cm^{-2}) was nearly equal to the range of the bombarding electrons.

The data are presented in Table 1.

The fact that $\Delta E = 29$ eV for three cases is remarkable and shows that the law of exponential decomposition is applicable in the analysis. The value of ΔE coincides with the same values in the case of bremsstrahlung irradiation[3]. The ΔE value is very reasonable, showing that there is no need to assume any chain-type reaction mechanism.

The values of relative difference in the decomposition rates ($2Z$) show a broader spread. This, and the large value of ΔE in experiment (2), can be understood by taking into account the remarks of Bonner et al., that it was difficult to control many of the experimental parameters of the polarised electron source. Even so, I feel that the value $2Z \simeq 10\%$ can be accepted. (The upper limit for the same quantity in the case of DL-alanine was $2Z \simeq 0.1\%$ (ref. 4).)

The energy of the incoming electrons is lost in the sample by ionisation and radiation; the latter is the bremsstrahlung.

The fraction of the incident energy which is converted into bremsstrahlung in a thick target is approximately[5]

$$I/E = 7ZE \times 10^{-4} \qquad (2)$$

where Z is the atomic number of the bombarded material (~ 7) and E is the energy of electrons in MeV.

Even if the whole energy of the bremsstrahlung had been absorbed in the sample, less than 0.1% of the degradated molecules would have been decomposed by bremsstrahlung. If the low degree of polarisation of the low energy bremsstrahlung ($P \simeq 10^{-3}$) and the very low upper limit for $Z (< 3 \times 10^{-3}$ according to the measurements in ref. 2) were also taken into account, the upper limit of the enantiomeric selectivity would be $\sim 10^{-6}\%$. It is not possible therefore to understand the great difference found by Bonner et al. if the asymmetric degradation is caused by bremsstrahlung. There is no known mechanism to explain the effect of

$2Z \simeq 10\%$. A mechanism based on the direct interaction of polarised electrons with the asymmetric molecules, which was first outlined in ref. 6 and needs to be worked out in detail, may provide an approach to the understanding of asymmetric degradation.

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BONNER ET AL. REPLY—Keszthelyi calculates that the average energy spent by the electrons to decompose a single leucine molecule is about 29 eV, that less than 0.1% of the degradations were due to bremsstrahlung, and that therefore ionisation must have engendered > 99.9% of the degradation as well as (in some unspecified manner) the observed asymmetric effect. We wish to comment on Keszthelyi's interpretation[1] of our results.

Using the sample weight, percentage degradation and total coulombs used in our experiments[2], one readily calculates that more than 3,000 molecules of DL-leucine were decomposed for each impinging primary electron. If each leucine decomposition requires an average 29 eV (ref. 1), each primary 120-keV electron thus loses an average total of about 87 keV in decomposing the leucine substrate. The remaining 32 keV presumably is lost in decomposing the collodian binder and in the rather inefficient geometry of the leucine target. There are thus some 3,000 primary processes initiated by each incident chiral electron. If primary ionisation is the predominant chiral process, the chiral efficiency of each such event must on average approach 5% to explain the asymmetric effect observed. If, as is possible, the incident electron loses its chirality after fewer collisions, the chiral efficiency must be still greater. What mechanisms might permit this?

Keszthelyi is correct that < 0.1% of the chiral primary electron energy is available as bremsstrahlung, which would

Table 1 Analysis of the asymmetric degradation of DL-leucine

Experiment	Irradiation nA h	Sample decomposition	Energy/decomposed molecule (eV)	$\dfrac{\varepsilon_D - \varepsilon_L}{\varepsilon_0}$	Weighted average
(1)	331	52.9	29.3	0.189 ± 0.039	0.151 ± 0.024
(2)	498	50.9	55	0.129 ± 0.030	
(3)	795	73.9	29	0.085 ± 0.015	0.081 ± 0.012
(4)	860	75.6	29	0.074 ± 0.020	