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A Linear Energy Transfer Effect in the Radiolysis of *Cyclohexane*

PREVIOUS experiments[1,2] with aliphatic hydrocarbons have shown little dependence of product yields on the type or incident radiation over the range of linear energy transfer (LET) used, although substantial variations have been reported for aromatic[3,4] and unsaturated[5] substances. We have irradiated carefully dried and degassed *cyclo*hexane (Phillips Research Grade) with 1·5-MeV α-particles from a Van de Graaff generator at currents of 0·01–0·1 μamp to doses of 2–6 $\times$ 10^{19} eV g^{-1}, using a method already described[3,5]. Although $G(H_2)$ varied only slightly from the value accepted for lightly ionizing radiation, $G(cyclo$hexene$)$ and $G(bicyclo$hexyl$)$ were considerably lower, as the following figures show:

	$G(H_2)$	$G(C_6H_{10})$	$G(C_{12}H_{22})$
γ-Rays and fast electrons	5·66 ± 0·23	3·01 ± 0·16	1·83 ± 0·13
α-Particles	5·33 ± 0·15	1·92 ± 0·05	0·94 ± 0·07

Irradiations to the same total dose with γ-radiation (dose rate 2–7 $\times$ 10^{17} eV g^{-1} min^{-1}) and with fast electrons from the Wantage Research Laboratory linear accelerator (dose-rate $\sim$ 10^{21} eV g^{-1} min^{-1}, comparable with those in the irradiated zone in the α-particle irradiations) gave essentially the same G values for these products.

In an independent study of this system Falconer and Burton have recently adduced evidence[6] for an LET effect, using cobalt γ-radiation, 1·8-MeV electrons and polonium α-radiation. Since, however, the energy input was not measured in the last case, it was not possible to determine absolute yields of the products, and the conclusion was therefore drawn from a study of the variation in the ratio $G(cyclo$hexene$)/G(bicyclo$hexyl$)$.

It has been pointed out[7,8] that the expected competition between inter-radical reactions and the abstraction reactions of the hydrogen atom would be expected to give rise to a decrease in $G(H_2)$ with increasing LET for the values of LET used in previous work unless the migration of energy or of excited molecules was occurring over distances larger than a normal spur size. At the high values of LET used here (mean LET with respect to energy,

$$z = \frac{1}{E_0} \int_0^{E_0} \left(-\frac{dE}{dx} \right) dE = 22 \text{ eV/Å at } 20° \text{ C})$$

an appreciable fall in $G(H_2)$ for a spur size as large as 50 Å would be expected, and the substantial reductions in both $G(C_6H_{10})$ and $G(C_{12}H_{22})$ may result, wholly or in part, from a decrease in net $G(C_6H_{11})$ occasioned by the afore-mentioned competition. The lack of dependence of $G(H_2)$ on LET would seem to indicate the growing importance at higher LET of processes leading to other hydrogen-deficient products. This work, including a search for these products, is continuing and will be reported fully later.

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CHEMISTRY

X-Ray Diffraction of Actinomycin C_3

IN a recent article Bachmann and Müller[1] discuss the crystal symmetry of actinomycin C_3, and suggest that this molecule has trigonal or pseudotrigonal symmetry. This leads them to the conclusion that the peptide part of the molecule consists of two pentapeptides rather than of one decapeptide. However, there are certain difficulties in their argument, which arise partly from a misunderstanding of space group theory. They give $R\bar{3}m$, $R32$, and $R3m$ as the possible space groups for the rhombohedral form, and $P2_1$ or $P2_1/m$ for the monoclinic form. The presence of one of the two enantiomorphs of an optically active compound, such as occurs in the peptide part of actinomycin, excludes space groups with reflexion planes or inversion centres, since they require each L-amino-acid to be matched by a corresponding D-amino-acid. Therefore the only permissible space groups of those listed are $R32$ and $P2_1$.

The authors' X-ray data and density indicate that the rhombohedral unit cell (hexagonal setting) contains six molecules; if this were true, the molecules would have to lie on triad axes and possess threefold symmetry. The authors point out that this may be only a pseudosymmetry, especially in view of the limited range of reflexions observed.

A molecule which consists of three approximately equal scattering masses might give rise to threefold pseudo-symmetry at low resolution, even if the chemical structure of the three parts differed in detail. However, in actinomycin C_3 the scattering mass of the phenoxazin ring, including all its immediate substituents, is 150 electrons, and the scattering mass of each of the two pentapeptides is 268 electrons. Such disparity among the three scattering masses excludes pseudo-threefold symmetry, even at low resolution. In fact, the X-ray pattern is reported to extend to spacings of about 3 Å, so that the argument about low resolution scarcely applies.

Actinomycin C_3 does appear to possess a pseudo-twofold axis of symmetry in the plane of the phenoxazin ring. This is true of both the two alternative chemical structures, that is, the penta- and the deca-peptide, and would require either a pseudo-space group with symmetry lower than $R32$ or more than 6 molecules in the unit cell. Conceivably the crystals are disordered and their true symmetry is lower than the X-ray pattern suggests.

Whatever the answer turns out to be, it should be made clear that actinomycin C_3 is basically an asymmetric molecule. This means that a choice between the two alternative chemical structures cannot be made from considerations of space group symmetry alone, but requires a detailed X-ray analysis.

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