

Origins of Oil, a Correction and Further Comment on the Brunnock¹ Even C-Number Predominance in Certain Higher Alkanes of African Crudes, and on the Biogenesis of Nonacosane

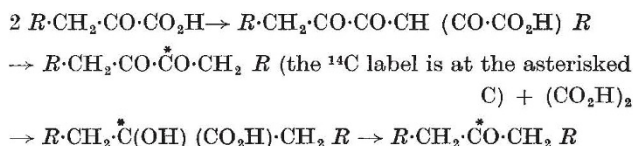
It has been pointed out to me (J. V. Brunnock, personal communication) that the simple arithmetical explanation of even C-number predominance recently advanced² fails if, in addition to the categories of chances of recombination previously considered, namely even-even, odd-odd, even-odd, that of odd-even is added. The probability of getting even and odd C-numbered products is then the same, and I concur. In fact, if it is assumed that four chains break up to give four even and four odd radicals, there are thirty-two chances each for the formation of even and odd chains by random coupling. Yet there can be little doubt that the predominant even C-numbered *n*-alkanes are derived by break-up of fatty acids and recombination of the fragments.

The only reasonable explanation appears to be a process analogous to Kolbe's synthesis and it may even be exactly that, namely, the result of electrolysis, or more generally, of an equivalent process. Thus $R\cdot\text{CO}_2\text{H}$ and $R'\cdot\text{CO}_2\text{H}$ would yield $R\cdot R'$ and, since R, R' are odd C-numbered, $R\cdot R'$ would be even C-numbered. Obviously, this would also apply to $R\cdot R$ and $R'\cdot R'$.

Recent studies by Purdy and Truter³ and Kolattukudy⁴ have greatly advanced our knowledge of the biosynthesis of nonacosane. These authors do not suggest detailed full mechanisms but Purdy and Truter gave reasons for believing that there are 10- and 15-oxygenated precursors of nonacosane. Kolattukudy, as the result of radioactive isotopic tracer work, concluded that palmitic acid is incorporated as a unit and extended to form nonacosane.

Two hypotheses are now advanced. First, head to tail condensation of 6 C_6 -units derived from succinate (or aspartate) and acetate (or glycine) with loss of 7 CO_2 molecules at some stage and reduction of carbonyls to $-\text{CH}_3$. The precursor could be that which gives rise to porphyrinogen. This allows of keto-groups to be located at 10- and 15-. But in view of Kolattukudy's findings, succinate would need to be derived by degradation of palmitic acid (C_{16}) and in this process one tritium in the ditritiated acid would be lost. So far as I understand them, the results do not allow of this.

Second, the most obvious mechanism starts with α -oxidation of palmitic acid to lanopalminonic acid which occurs in wool-wax. This undergoes self-condensation, doubtless with the help of co-enzyme-A as usual. Omitting the co-enzyme, we have ($R = \text{C}_{13}\text{H}_{27}$):



\rightarrow nonacosane. This scheme does not provide CO in position -10, but the use of a second reduced chain is not obligatory. Kolattukudy⁴ could not confirm the final stage experimentally, but it occurs in the plant, if at all, while the molecules are "in the works" and it is probably very difficult to get a sparingly soluble wax on to the "production line" by external application to the leaf.

ROBERT ROBINSON

Shell Centre,
London, S.E.1.

Received February 16, 1967.

¹ Brunnock, J. V., *Nature*, **212**, 385 (1966).

² Robinson, R., *Nature*, **212**, 1291 (1966).

³ Purdy, S. J., and Truter, E. V., *Proc. Roy. Soc.*, B, **158**, 536, 544 (1963).

⁴ Kolattukudy, P. F., *Biochemistry*, **5**, 2265 (1966).

PHYSICS

Paraffin Mirrors for Ultrasoft X-rays

OUR search for a suitable dispersion technique to identify ultrasoft X-radiation (wavelength $\lambda > 20 \text{ \AA}$) led us to consider the wavelength dependence of the critical angle of total reflexion. A critical angle of total reflexion exists only if the reflector is transparent to radiation. Thus, one reason for the unsatisfactory results reported by Franks and Braybrook¹ could be the high absorption of the ultrasoft X-rays in the beryllium reflector used by these authors. At first glance beryllium is the best choice for a low-absorption reflector, but commercial beryllium is contaminated by heavy metals. Even a small proportion of, say, iron or nickel, combined with the beryllium oxide that always forms on the surface where total reflexion occurs, can destroy the critical angle.

In contrast, paraffin, that is, high molecular weight alkanes of the general formula $\text{C}_n\text{H}_{2n+2}$, can be obtained free from contamination, because the general inertness of these compounds makes them easy to purify effectively. Their high content of hydrogen (roughly 66 mole per cent) and their low density ($\rho \approx 0.8 \text{ g/c.c.}$) mean that they absorb only slightly at X-ray wavelengths which do not excite fluorescent carbon radiation.

To evaluate paraffin as an ultrasoft X-ray reflector and to compare its reflecting qualities with those of quartz, for which reliable data exist², reflexion curves for both materials were calculated for the characteristic *K*-radiations of fluorine, oxygen, nitrogen, carbon, boron and beryllium. Wavelengths were taken from ref. 3. The calculations were based on Fresnel's formulae in the form presented in ref. 4. The unit decrement of the refractive index $\delta = 1 - \mu$ was obtained from $\delta/\lambda^2 \approx 1.36 \times 10^{10} \rho$ (λ in cm; ρ = density of reflector; ref. 5), while β , the index of absorption, was extracted from ref. 4 and ref. 6. Table 1 summarizes values of δ and β .

Table 1. VALUES OF δ AND β FOR CHARACTERISTIC WAVELENGTHS OF LIGHT ELEMENTS FOR COMPUTATION OF REFLEXION CURVES ON PARAFFIN AND THEIR DERIVATIVES (FIGS. 1 AND 5)

Element	Wavelength (ref. 3) (\AA)	δ	β
Fluorine	18.32	3.5×10^{-4}	$5.2 \times 10^{-2*}$
Oxygen	23.62	5.7×10^{-4}	$1.3 \times 10^{-4*}$
Nitrogen	31.60	1.0×10^{-3}	$3.7 \times 10^{-4*}$
Carbon	44.7	2.1×10^{-3}	$5.0 \times 10^{-2\dagger}$
Boron	67.7	4.7×10^{-3}	$2.4 \times 10^{-1\dagger}$
Beryllium	114.0	1.3×10^{-2}	$1.8 \times 10^{-3\dagger}$

* Computed from ref. 6.

† Ref. 4.

‡ Computed from ref. 4.

The results of these calculations are shown in Fig. 1, where the fraction of totally reflected intensity (I/I_0) is plotted against incident angle (θ). Paraffin shows a sharp drop in intensity at the critical angle for the characteristic radiations of carbon and boron.

Lukirskii *et al.* reported measured reflexion coefficients of ultrasoft X-radiation on polystyrene⁷, without mentioning possible application in a dispersing device. Although chemically similar, polystyrene is inferior to

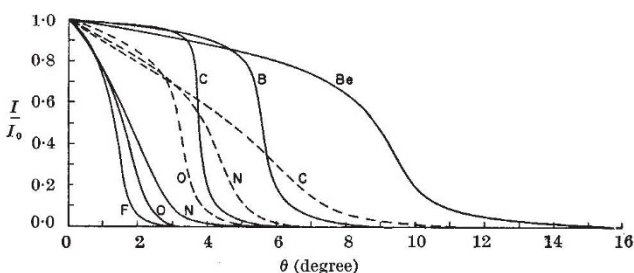


Fig. 1. Reflexion curves of characteristic radiations from oxygen, nitrogen and carbon on quartz (---) and from fluorine, oxygen, nitrogen, carbon, boron and beryllium on paraffin (—).