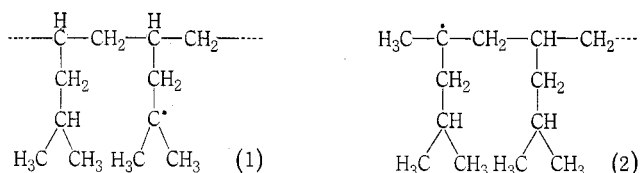


RADICAL SCAVENGING IN γ -IRRADIATED POLY-4-METHYLPENT-1-ENE

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A recent electron spin resonance investigation by Whelan and Pinkerton¹ of the radical species produced in γ -irradiated poly-4-methylpent-1-ene (p4mpl) resulted in the identification of two radicals. When p4mpl was irradiated in a vacuum at 77°K, radical (1) was identified. This radical was unstable and upon thermal treatment decayed rapidly to yield radical (2). The conversion process was not reversed by re-cooling to 77°K.



Evidence for radical (1) was based upon spectroscopic considerations, with the unpaired electron on the tertiary carbon atom interacting equally with the methyl protons and, due to restricted rotation about the C-C bond, with only one of the methylene β -protons. In this communication we wish to report chemical evidence indicative of the production of radical (1).

Irradiation of p4mpl in a vacuum, at room temperature, yielded hydrogen, methane, propane, n-butane, and isobutane.² These products also occurred when the polymer was irradiated in oxygen at room temperature but, in addition, acetone was a major product. There was no evidence for acetone production when the irradiation was conducted in a vacuum. Figure 1 shows the yield of acetone as a function of dose adsorbed in p4mpl. The dose was deliberately kept to low values, compared to many radiation chemical studies of polymers, in an endeavour to avoid secondary reactions. The linearity of the dose-yield curve indicates that secondary reactions were not important up to a radiation dose of 6.2×10^{20} eV g⁻¹. From Figure 1, we obtain $G(\text{acetone}) = 1.2$.

The identification of acetone in the radiolysis products appears to be strong evidence for the production of radical (1). We suggest that oxygen then reacts with

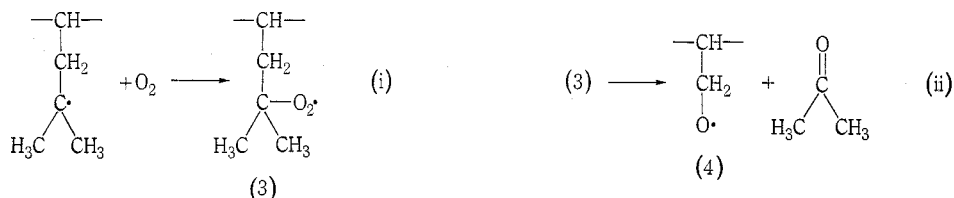
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¹ Whelan, D. J., and Pinkerton, D. M., *Aust. J. Chem.*, 1970, **23**, 391.

² Pinkerton, D. M., and Sach, B. T., unpublished data.

radical (1), by reaction (i), to form the unstable peroxy radical, which then decomposes according to reaction (ii) in a reaction analogous to the production of acetone from isopropylbenzene (cumene).



In the light of this scheme, the production of acetone by reaction of radical (2) with oxygen does not appear likely. In addition, acetone production is quite efficient [$G(\text{acetone}) = 1.2$], hence while the conversion (1) \rightarrow (2) will be favourable at the temperature of irradiation (c. 305°K), it appears that the conversion process is either reduced or inhibited by more efficient, competitive oxygen scavenging.

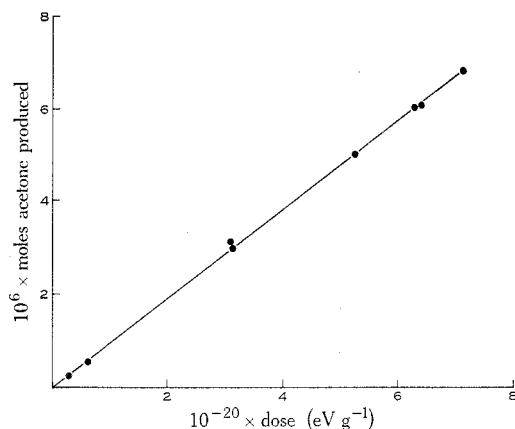


Fig. 1.—Acetone production in γ -irradiated p4mpl and oxygen mixtures as a function of radiation dose.

When p4mpl is irradiated at 77°K in the presence of oxygen (500 torr) and warmed for a short time above the boiling point of oxygen (90°K), a peroxy radical is formed. It has e.s.r. characteristics: $g_{\parallel} = 2.034_5(\pm 0.0013)$ and $g_{\perp} = 2.001_6(\pm 0.0007)$, which gives $g_{\text{iso}} = 2.012_6(\pm 0.0013)$, a value of the same order (2.013–2.016) as observed elsewhere for several peroxy radicals.^{3–5} We therefore believe it to be (3). Alkoxy radicals^{4,6} have g_{iso} values near 2.002, hence the signal does not originate from (4). The same peroxy radical is formed from p4mpl, irradiated in a vacuum at 77°K and then exposed to air, the polymer being momentarily warmed to keep the oxygen gaseous.

However, when these samples were allowed to warm to room temperature, the e.s.r. signals disappeared and no stable free radical products could be detected. Similarly, we found that no signals could be obtained when p4mpl was irradiated at

³ Ingold, K. U., and Morton, J. R., *J. Am. chem. Soc.*, 1964, **86**, 3400.

⁴ Bersohn, M., and Thomas, J. R., *J. Am. chem. Soc.*, 1964, **86**, 959.

⁵ Fessenden, R. W., and Schuler, R. H., *J. chem. Phys.*, 1963, **39**, 2147.

⁶ Svejda, P., and Volman, D. H., *J. phys. Chem.*, 1969, **73**, 4417.

room temperature in the presence of oxygen or irradiated at room temperature in a vacuum and then exposed to oxygen.

Dole and Böhm⁷ have expressed the view that, in polyethylene, oxygen diffuses only slowly (if at all) into the crystalline regions of the polymer, and that any radicals situated in such regions appear to migrate to the amorphous regions of the polymer. Our results with p4mp1 are consistent with this idea, especially as radical (1) is rapidly scavenged by gaseous oxygen.

The fate of the radicals produced by reaction (ii) is uncertain, but this does not alter the conclusions of this communication. One would expect that the radicals (4) will disappear either by hydrogen atom abstraction, disproportionation, or cross-linking. In other polyolefins,^{2,8} work has shown that polyolefins do cross-link by a free radical mechanism, but we have found here that the presence of oxygen inhibits the cross-linking found in vacuum-irradiated p4mp1; this suggests that the free radical (1) is a precursor for the formation of a cross-link² whereas radical (3) is not.

Experimental

Powdered isotactic p4mp1, in the unstabilized form, was degassed at pressures less than 10^{-5} torr (1.33×10^{-3} N m⁻²) for c. 50 hr. In some cases oxygen (500 torr pressure) was added to c. 0.5 g samples contained in borosilicate vessels of c. 100 ml volume. Cobalt-60 irradiations, at a dose rate of c. 4.2×10^{17} eV g⁻¹ min⁻¹, to a maximum total dose of 6.2×10^{20} eV g⁻¹, were performed at ambient temperature (c. 305°K). The dose absorbed in the polymer was calculated using ferrous sulphate dosimetry.

Product analysis was performed with gas chromatography using thermal conductivity detection and a Porapak Q column operated isothermally with He carrier gas. The irradiation cells were designed so that all the products condensable at 77°K could be injected directly into the gas chromatograph. Confirmation of the identity of the suspected acetone peak was obtained by mass spectral analysis of the collected peak.

Acknowledgments

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⁷ Dole, M., and Böhm, G. G. A., "Radiation Research." Proc. 3rd Int. Congr. Radn Res. p. 284. (North Holland: Amsterdam 1967.)

⁸ Geymer, D. O., *Makromolek. Chem.*, 1967, **100**, 186.