Photolysis of the 3-Methylpentyl Radical at 77 K

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Summary Photolysis ($240 \leqslant \lambda \leqslant 270$ nm) at 77 K of 3-methylpentyl radicals gives ethyl radicals.

It is known that alkyl radicals can isomerize or be converted into allyl-type radicals[2] under irradiation with light of wavelength $\lambda \leqslant 300$ nm at 77 K. A study of the sensitized photolysis of polypropylene at 77 K has shown that photodissociation of alkyl radicals is possible.[3] It has also been noted that 3-methylpentyl radicals can be photolysed to form methyl radicals.[4]

We have observed an absorption band with a maximum at 240 nm from γ-irradiated 3-methylpentane at 77 K. This band remained after photo bleaching of the stabilized electron and disappeared during thermal treatment of the sample (Figure 1); it can be assigned to the 3-methylpentyl radical observed in the e.s.r. spectrum of γ-irradiated 3-

methylpentane (Figure 2a). The radical extinction coefficient (ϵ_{240}) was 1800 ± 600 $\mathrm{l\ mol^{-1}\ cm^{-1}}$.

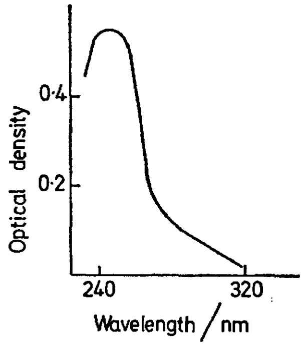

FIGURE 1. Absorption spectrum of the 3-methylpentyl radical.

Exposure to light of wavelength $240 \leqslant \lambda \leqslant 270$ nm of γ-irradiated ($\leqslant$ 1 Mrad) samples of 3-methylpentane 99·9% pure) causes substantial changes in the e.s.r. spectrum (Figure 2).

These changes may be due to the overlapping of the initial 3-methylpentyl radical spectrum (Figure 2a) with the spectrum of methyl or ethyl radicals formed. However, during light irradiation, a change in the components of the extreme parts of the 3-methylpentyl radical spectrum takes place, thus showing that the e.s.r. spectrum of the radical formed is rather extended, much more so than the spectrum of the methyl radical. The e.s.r. spectrum observed on photolysis can be formed by graphic addition of spectra of the ethyl and 3-methylpentyl radicals. An analogous spectrum was obtained from γ-irradiated solutions of EtI in 3-methylpentane.[5]

The radical formed during photolysis is quite stable in the 3-methylpentane matrix. Kinetic studies show that the decay of the radicals in the dark is a first-order process, with $t_{\frac{1}{2}}$ = 180 min, which is much greater than $t_{\frac{1}{2}}$ for methyl radical decay in this matrix (16 min).[6] Loss of two radicals with different half-lives in comparable amounts should give linear sections on the kinetic curve. Since these were not observed we associate the change in the e.s.r. spectrum on exposure of γ-irradiated 3-methylpentane to light with the formation of ethyl radicals only. Mass spectrometric and g.l.c. analyses of the gaseous products in the γ-irradiated samples exposed to light showed the presence of ethane and the absence of methane.

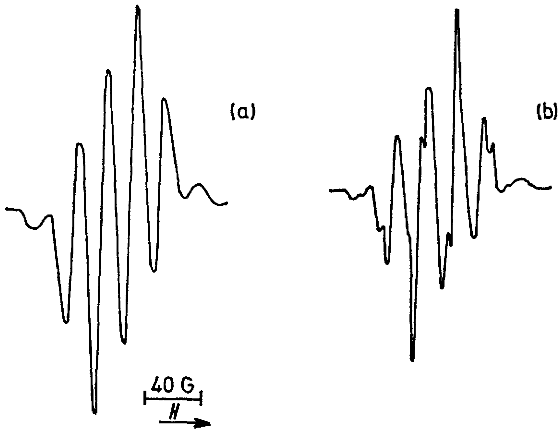

FIGURE 2. E.s.r. spectrum recorded in γ-irradiated 3-methylpentane at 77 K: (a) after photo bleaching of stabilized electrons; (b) after irradiation ($240 \leqslant \lambda \leqslant 270$ nm) for 180 min.

Formation of the ethyl radical seems to show that the six-component e.s.r. spectrum in γ-irradiated 3-methylpentane should be assigned to a radical formed from rupture of a secondary C-H bond, $\cdot\mathrm{CHMeCHMeCH_2Me}$,[7] rather than a tertiary bond, $\mathrm{MeCH_2\dot{C}MeCH_2Me}$,[8] since formation of the ethyl radical from the latter would be inexplicable.

The overall reaction appears to be as in equation (1)

$$\cdot\mathrm{CHMeCHMeCH_2Me} \rightarrow \mathrm{MeCH_2}\cdot + \mathrm{CH_2{=}CHCH_2Me} \text{ or } \mathrm{MeCH{=}CHMe} \quad (1)$$

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