The Electron Spin Resonance Spectra of Alkyl Radicals in Solution

By ALWYN G. DAVIES* and B. P. ROBERTS
(*William Ramsay and Ralph Forster Laboratories, University College, Gower Street, London, W.C.*1)

Summary The photolysis of di-t-butyl peroxide in the presence of an alkylborane provides a general method for preparing alkyl radicals in solution for e.s.r. spectroscopy.

THOUGH methods are available for generating some special alkyl radicals in solution for e.s.r. examination,[1] there appears to be no general method for specific alkyl radicals.

We have argued that the autoxidation of organometallic compounds involves rapid bimolecular homolytic attack of an alkylperoxy-radical at the metallic centre, displacing an alkyl radical (equation 1).[2]

$$ROO\cdot + MR \rightarrow ROOM + R\cdot[\xrightarrow{O_2} ROO\cdot] \qquad (1)$$

We have now found that t-butoxy-radicals from the photolysis of di-t-butyl peroxide will react similarly, (equations 2 and 3), and that the alkyl radical which is displaced can readily be observed by e.s.r. The spectra of a number of radicals have been recorded by this technique.

$$Bu^tO\text{–}OBu^t \xrightarrow{h\nu} 2Bu^tO\cdot \qquad (2)$$

$$Bu^tO\cdot + MR \rightarrow Bu^tOM + R\cdot \qquad (3)$$

For example, a 1M-solution of tri-n-butylborane in di-t-butyl peroxide [or each component (1M) in iso-octane] in the e.s.r. cavity at room temperature was irradiated with u.v. light from a 250 W high-pressure mercury arc lamp, giving the e.s.r. spectrum of the n-butyl radical shown below. A standing concentration of the radical of *ca.* 10^{-7}M could be maintained in a static system for about 1 hr.

Biacetyl and t-butyl hyponitrite have also been used as the primary source of radicals; similar reactions can also be brought about thermolytically rather than photolytically, and by using organometallic compounds other than boranes as the secondary source radicals. This provides for the first time a simple and general method for studying the e.s.r. spectra of a wide variety of alkyl radicals.

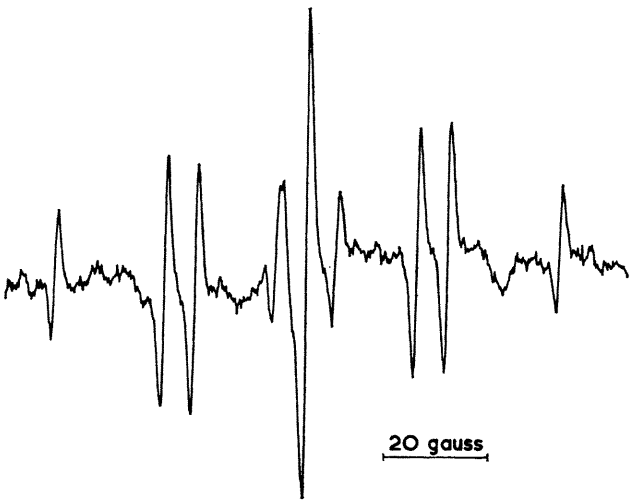

FIGURE. *The e.s.r. spectrum of the n-butyl radical obtained by the photolysis of di-t-butyl peroxide in the presence of tri-n-butylborane.* a_α^H 21·9 G, a_β^H 27·4 G.

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[2] A. G. Davies and B. P. Roberts, *J. Chem. Soc.* (*B*), 1967, 17; 1968, 1074; 1969, 311, 317.