

This demonstration of the conversion of CS to DS, a major secretory product of the adrenal,⁷ lends further support to the concept that sulfated intermediates, such as CS, PS, etc., are involved in the biosynthesis of the steroid hormones. Although the possibility of other pathways has not been excluded, the evidence available to date suggests that the conversion proceeds via C₂₁ intermediates as shown in Scheme I.

(7) R. L. VandeWiele, P. C. MacDonald, E. Gurside, and S. Lieberman, *Recent Progr. Hormone Res.*, **19**, 275 (1963).

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Identification of Peroxy Radicals by Electron Paramagnetic Resonance

Sir:

In e.p.r. studies free radicals are identified by their characteristic hyperfine splittings, their *g* values (line positions), and their relaxation times in a particular milieu. The last parameter is the least specific and the first parameter gives the most information. Peroxy radicals, RO₂·, have no hyperfine structure detectable by present methods except that due to O¹⁷. Because of the difficulty of O¹⁷ labeling only one experiment on the O¹⁷ hyperfine splittings of free radicals has been reported,¹ so that method is not yet broadly applicable.

We wish to report evidence that the *g* values of peroxy radicals easily distinguish them from RO· and R·. We have measured the *g* value of the cumyl peroxy radical which is 2.0155 ± 0.0005. Lontz² found that the radical CF₃CFCONH₂ reacts in the solid state with molecular oxygen to form a free radical without noticeable hyperfine splitting and with *g* values measured along the three principal axes of 2.0102, 2.0193, and 2.0267. He assumed this is the corresponding peroxy radical CF₃CFCONH₂. Fessenden and

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Schuler³ found that alkanes irradiated with fast electrons in the absence of oxygen formed hydrogen atoms plus readily identifiable alkyl radicals. In the presence of oxygen under the same conditions radicals without noticeable hyperfine splitting were produced. The *g* values of these latter radicals ranged from 2.0155 when pentane was used to 2.0148 for paraffin oil, the *g* value decreasing with increasing molecular weight of the parent alkane. These were also presumed to be peroxy radicals.

Our cumyl peroxy radicals were produced in benzene solution as a result of the reaction of cumene with oxygen in the presence of azobisisobutyronitrile. No other radicals were detected in this system by e.p.r. Evidence that the principal radical formed in this system is in fact the cumyl peroxy radical, and the experimental arrangement, are discussed by Thomas.⁴

Ordinary free radicals of the type R· or RO·⁵ (or even R₂NO·¹) all have *g* values of less than 2.0100. Consequently, the location of the solution *g* values of peroxy radicals in the range 2.0140 to 2.0190 clearly

distinguishes them from these other radicals. One of McConnell and Robertson's generalizations⁶ originally applied to aromatic radicals, *i.e.*, the *g* value of a radical increases with the spin orbit coupling parameter, ζ , of the atoms that have significant spin density, applies also to this case.

To remove some spin density from the terminal oxygen atom and distribute it to any extent on the R group requires the polarization of the O-O bond so as to make the terminal oxygen more negatively charged. For this reason radicals with electron-withdrawing groups in R, such as the radical of Lontz, should have the greatest spin density on the terminal oxygen atom and therefore the highest *g* value. In solution this radical would have the averaged *g* value of 2.0187.

Our microwave frequency was measured by a Hewlett-Packard 524C counter with a Hewlett-Packard 540B transfer oscillator. The magnetic field was determined by proton magnetic resonance using a marginal oscillator whose frequency was measured on the same 524C counter. The line broadening effect of the presence of molecular oxygen was a principal source of error in the *g* value measurement.

(6) H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957).

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Studies of Reactions of Atomic Carbon by a Double Tracer Technique

Sir:

Reaction mechanisms of atomic carbon have recently been studied using C¹¹ (20.5 min.) as produced by nuclear transformation.¹⁻⁴ The C¹¹, being radioactive, serves as its own tracer. However, it would also be greatly desirable to trace the origin of the atoms with which the C¹¹ combines. Because the nuclear recoil technique provides only a small number of carbon atoms (~10⁸) and hence of product molecules, this has not been practical thus far. Labeling the molecules with which the carbon reacts with another radioisotope is not feasible because the amount of such a secondary label which could be incorporated in the product is too small to detect.⁵

The use of stable isotopes, such as deuterium, as secondary tracers has faltered on the formidable problem of product analysis. Mass spectrometric separation of isotopic deuterated molecules followed by counting of their C¹¹ content is possible in principle, but very difficult in practice.⁶ The alternative, gas chromatographic separation of isotopic molecules followed by C¹¹ radioassay, has been restricted by the unavailability of columns of sufficient resolving power.

With the recent publication by Cvetanovic, *et al.*,⁷ of a technique for separation of deuterated light olefins

(1) C. MacKay, *et al.*, *J. Am. Chem. Soc.*, **84**, 308 (1962).

(2) C. MacKay and R. Wolfgang, *ibid.*, **83**, 2399 (1961).

(3) G. Stöcklin and A. P. Wolf, *ibid.*, **85**, 229 (1963).

(4) C. MacKay and R. Wolfgang, *Radiochim. Acta*, **1**, 42 (1962).

(5) In a typical experiment 10⁸ carbon atoms might react with a hydrocarbon labeled with tritium. Even if the hydrocarbon were completely labeled this would result in only an order of 10 to 100 tritium disintegrations per min. in the 10⁸ product molecules. Furthermore with a totally labeled molecule tritium self-radiolysis would be a serious problem.

(6) Mass spectrometric separation of trace isotopic product molecules would require high throughput efficiencies. Furthermore special counting techniques for the separated C¹¹ labeled molecules would have to be developed.

(7) R. J. Cvetanovic, F. J. Duncan, and W. E. Falconer, *Can. J. Chem.*, **41**, 2095 (1963).

(1) J. C. Baird, *J. Chem. Phys.*, **37**, 1879 (1962).

(2) R. Lontz, *Bull. Am. Phys. Soc.*, **8**, 328 (1963).

(3) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(4) J. R. Thomas, *J. Am. Chem. Soc.*, **85**, 591 (1963).

(5) M. S. Blois, H. W. Brown, and J. E. Maling in "Free Radicals in Biological Systems," Academic Press, New York, N. Y., 1961.