

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. Gurdipe, 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

O₂

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.

it has become possible to apply a double tracer technique to the study of atoms produced by nuclear recoil.⁸ We report here preliminary results of such studies on carbon atom reaction mechanisms.

Technique.—C¹¹ atoms are produced by C¹²(γ ,n)C¹¹ reaction induced by 40 Mev. Bremsstrahlung irradiation of the appropriate isotopically mixed system. (Either a mixture of protonated and deuterated molecules or a single partially deuterated compound is used.) Nuclear techniques for production of the recoil atoms under conditions of low radiation damage are described elsewhere.¹⁻⁴ Analysis of products involves gas chromatography followed by flow counting.¹⁻⁴ Isotopic separation is effected by a 100-ft. ethylene glycol-silver nitrate column (25° and 0°). This column was calibrated for isotopic ethylenes using C₂D₄, C₂H₄, C₂H₃D, CH₂CD₂, and a mixture prepared by reducing C₂H₂ with D₂ on a platinum catalyst. The five equally spaced compounds found are assumed to correspond to C₂H_nD_{4-n} ($n = 0-4$). No information on possible separation of the three C₂H₂D₂ isomers was obtained. Allene calibrations were based on C₃H₄ and C₃D₄. Retention volumes of partially deuterated isomers were interpolated. These were checked by irradiation with C¹¹ of a C₂H₆-C₂D₆-C₂H₂ mixture. The predicted unsymmetrical distribution of allenes, corresponding to the expected production⁹ of C₃H₄, C₃H₃D, and C₃H₂D₂, was found. The effectiveness of the column for separating isotopic propylenes was checked using a propylene mixture prepared by catalytic reduction of CH₃C≡CH with D₂.

Allene from C Atom Reactions with Ethylene.—Allene is a principal product of the reaction of C with ethylene.¹ When produced from an equimolar mixture of C₂H₄ and C₂D₄ the following isotopic yield ratios were found: C₂C¹¹H₄:C₂C¹¹H₃D:C₂C¹¹H₂D₂:C₂C¹¹HD₃:C₂C¹¹D₄ = 7:1 ± 0.3:0.2:1 ± 0.3:7 ± 1. Thus allene is produced predominantly by interaction of a carbon atom with a single ethylene molecule. This result is consistent with the two previously postulated mechanisms of insertion into the double bond,¹ and into the C-H bond,^{1,2} of ethylene. It seems plausible that the isotopic mixing that does occur is associated with radical production following insertion into the C-H bond.

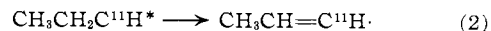
Propylene from C Atom Reaction with Ethane.—The formation of propylene from ethane has a formal similarity to the formation of allene from ethylene. However, it has a much lower yield.^{1,2} This was attributed to the different nature of the intermediates formed by the C=C and C-H insertions.¹ This difference in predominant mechanisms is reflected in the results on propylene formation from an equimolar mixture of C₂H₆ and C₂D₆. Four propylene peaks are found, probably C₃H₆, C₃H₅D, C₃HD₅, and C₃D₆. The peak ratios are C₃H₆:C₃H₅D = C₃D₆:C₃HD₅ ≅ 1.3:1. Regardless of peak identities it is obvious that there is very extensive, though probably incomplete, isotopic mixing involving one hydrogen atom. Thus, unlike allene from ethylene, most propylene from ethane seems to have a radical precursor. This result is consistent with the previously postulated² carbon insertion into a C-H bond



The intermediate can de-excite by several modes and is thus a precursor for a number of products.¹⁻⁴ One such mode is H atom elimination

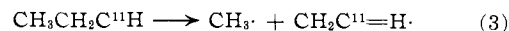
(8) The use of stable isotopes as tracers for recoil atom reactions should not be confused with their use to measure isotope effects.

(9) The allene produced in this system appears to result from addition of acetylene of methylene arising from reaction of C atoms with ethane.

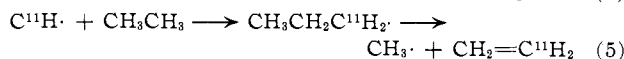


The resulting radical then abstracts a hydrogen atom from C₂H₆ (or C₂D₆).¹⁻⁴

Ethylene from C Atom Reaction with Ethane.—One of the more important products from the C atom reaction in saturated hydrocarbons is ethylene.²⁻⁴ When produced in an equimolar C₂H₆-C₂D₆ mixture we find approximately equal amounts of CC¹¹H₄, CC¹¹H₃D, CC¹¹HD₃, and CC¹¹D₄. The ratio of CC¹¹-H₂D₂ to CC¹¹HD₃ is less than 1:5. This finding excludes a number of possible mechanisms, but is consistent with C atom insertion into a C-H bond. The intermediate formed by reaction 1 de-excites by C-C rupture (a favorable mode)



The vinyl radical then abstracts hydrogen from C₂H₆ or C₂D₆. The data are equally consistent with a postulated alternative mechanism involving insertion into the C-H bond by a C¹¹H intermediate.^{10,11}



Acknowledgments.—We are indebted to the operating staff of the Yale linear electron accelerator. This work was supported by the U. S. Atomic Energy Commission.

(10) Insertion by CH has been recognized as a possible alternative to insertion by C.² It was suggested as a specific precursor of ethylene by A. P. Wolf (Hot-Atom Conference, Amsterdam, May, 1963).

(11) It may be relevant to point out that the conclusions drawn from this work regarding the existence of radical precursors could not be derived from work with scavengers. Thus the yields of neither allene from ethylene nor ethylene from ethane are markedly oxygen-sensitive. Yet the double tracer experiments show that the former does not generally involve a radical precursor, while the latter does. This limitation of the scavenger technique in atomic carbon systems is probably due to the very high thermal reactivities of the radicals involved. (Scavengers are only effective when radicals have a relatively long lifetime in the given system.)

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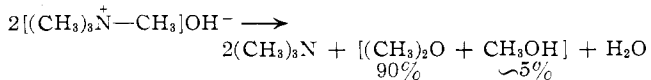
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A Reinvestigation of the Pyrolysis of Tetramethylammonium Hydroxide

Sir:

The thermal decomposition of tetramethylammonium hydroxide has been found to yield *trimethylamine and dimethyl ether* as the major decomposition products rather than the reported products, trimethylamine and methanol.¹ The ether is formed in >90% yield based on the recovered trimethylamine. Minor prod-



ucts are methanol (*ca.* 5%), and apparently small quantities of higher alcohols and polyethylene.

The pyrolysis was carried out in a vacuum line using a stock solution of 10% tetramethylammonium hydroxide in water. Most of the water was removed by heating the solution at 65° to give a white amorphous solid. The solid decomposed at 135-140° and the products were collected continuously during the course of the reaction in a series of cold traps; water and methanol were removed at -78° (CO₂-isopropyl alcohol bath), and the amine and ether at -196° (liquid N₂ bath).

(1) A. W. Hofmann, *Ber.*, **14**, 494 (1881).