

### 1144. Radicals from Aliphatic Ethers.

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The reduction, in dilute aqueous acid, of hydrogen peroxide with titanous ion leads to the production of hydroxyl radicals. These have been used in an electron spin resonance investigation of the oxidation of some aliphatic ethers, using a flow technique. Well-defined spectra, which can be assigned to specific radicals, were obtained. Some general conclusions regarding the reactivity of ethers are drawn.

EXTENSIVE electron spin resonance (e.s.r.) studies on radicals produced by hydrogen-atom abstraction from alcohols have been reported.<sup>1-3</sup> Earlier work involved ultraviolet irradiation of frozen mixtures of alcohols and hydrogen peroxide, in which the initial hydroxyl radicals diffuse throughout the solid glass and react with the alcohol.<sup>1,2</sup> In this technique, however, the e.s.r. spectra may suffer from loss of resolution, owing to broadening of the individual lines by anisotropic interactions.

Irradiation of liquids is generally not practicable, for the radicals are then so short-lived and generated so slowly that their steady-state concentration is too low to be observed. Recently, Fessenden and Schuler<sup>4</sup> have reported observations of a number of alkyl radicals formed by electron bombardment of the corresponding liquid hydrocarbon. Also, Dixon and Norman<sup>3</sup> have observed radicals produced by the reaction of alcohols with the titanous sulphate-hydrogen peroxide system in a flow apparatus.

We have used a similar procedure to investigate qualitatively the oxidation of ethers, and their susceptibility to radical attack. When acidified solutions of titanous sulphate and hydrogen peroxide are mixed in a flow system immediately before entering the microwave cavity, an intense single e.s.r. peak is observed.<sup>5</sup> This singlet, having a line-width of 0.8 gauss, occurs some 35 gauss to low field of the free-spin position, and is ascribed to the hydroxyl radical. However, if the two solutions contain an ether ( $M/20$ ), this intense singlet disappears and is replaced by signals attributable to organic free radicals. Accordingly, a series of ethers has been studied in this way at 20°, using ether-saturated solutions where the solubility is less than  $M/20$ . Unfortunately, acetone cannot be used to improve the solubility as it reacts with the hydroxyl radical to give  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ . As found previously,<sup>3</sup>

<sup>1</sup> Fujimoto and Ingram, *Trans. Faraday Soc.*, 1958, **54**, 1304.

<sup>2</sup> M. C. R. Symons and M. G. Townsend, *J.*, 1959, **263**; J. F. Gibson, M. C. R. Symons, and M. G. Townsend, *ibid.*, p. 269; M. C. R. Symons *ibid.*, p. 277.

<sup>3</sup> W. T. Dixon and R. O. C. Norman, *J.*, 1963, **3119**.

<sup>4</sup> R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

<sup>5</sup> W. T. Dixon and R. O. C. Norman, *Nature*, 1962, 891. **196**,

when titanous ion is replaced by ferrous ion, no radicals from the ethers are found, which suggests that titanous ion is a stronger reducing agent for hydrogen peroxide than is ferrous ion.

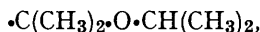
The coupling constants for the radicals obtained are listed in the Table.

Coupling constants of radicals.

Ether	Type of spectrum	Coupling constants (gauss)		
		$\alpha$ -H	$\beta$ -H	$\gamma$ -H
$\text{CH}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_3$	Four (1:3:3:1) doublets (1:1) of triplets (1:2:1)	13.8	21.5	1.4
$(\text{CH}_3\cdot\text{O})_2\text{CH}\cdot\text{CH}_3$	Triplet (1:2:1) of doublets (1:1)	17.1		1.1
1,4-Dioxan	Doublet (1:1) of doublets (1:1)	16.6	45.3	
$\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$	Triplet (1:2:1) of triplets (1:2:1)	16.6		2.1
$\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_3$	Triplet (1:2:1) of triplets (1:2:1)	16.6		2.0
$\text{CH}_3\cdot\text{O}\cdot[\text{CH}_2\cdot\text{CH}_2\cdot\text{O}]_2\cdot\text{CH}_3$	Triplet (1:2:1) of triplets (1:2:1)	16.6		2.1
$\text{CH}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$	Four (1:3:3:1) doublets (1:1) of triplets (1:2:1)	13.8	22.0	1.5
$\text{CH}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}\cdot\text{CH}_2$	Quartet (1:3:3:1) of doublets (1:1)	14.4	21.6	
[Acetone]	Triplet (1:2:1) of quartets (1:3:3:1)	17.3		1.1

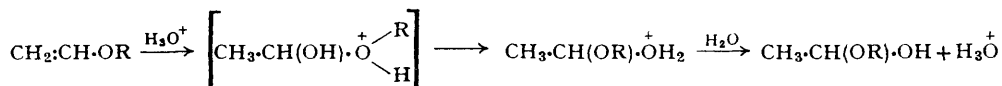
*Simple Ethers.*—Diethyl ether gave a large quartet of doublets, each line being further split into small triplets. This corresponds to the radical  $\cdot\text{CH}(\text{CH}_3)\cdot\text{O}\cdot\text{C}_2\text{H}_5$  being formed by  $\alpha$ -hydrogen-atom abstraction.

Similarly, di-isopropyl ether gave a septet corresponding to the radical



but in this case no splitting from the  $\alpha$ -hydrogen on the second isopropyl group was observed. This is likely to be very small ( $< 1$  gauss), and may have been submerged by the line-broadening caused by the high modulation-amplitude necessary for the dilute solution of this ether.

*Ethyl Vinyl Ether.*—Unlike the radical formed on oxidation of allyl alcohol, in which there is hydroxyl-radical addition<sup>3</sup> to the olefinic bond, the radical from vinyl ether shows a large quartet of slightly smaller doublets, which at first sight can be assigned to  $\cdot\text{CH}(\text{CH}_3)\cdot\text{O}\cdot\text{CH}:\text{CH}_2$ . However, Prilezhaeva *et al.*<sup>6</sup> have shown that alkyl vinyl ethers are rapidly hydrolysed in dilute aqueous acid according to the sequence:



which is first order in both ether and acid. The hemiacetal is rapidly hydrolysed to acetaldehyde, and the radical observed is that formed by addition of the hydroxyl radical to the aldehyde double bond.

*Diethers.* In all these methyl ethers, having the general formula  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OR}$ , the radical formed gave a simple triplet of triplets, and must be of the form  $\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OR}$ . That this radical is always produced is indicative of the electrophilic nature of the hydroxyl radical,<sup>7</sup> for it here attacks the methyl group, which is influenced only by one protonated ether oxygen, and not the methylene groups, each of which is  $\alpha$  to one protonated ether-oxygen and  $\beta$  to the other. This again is somewhat different from  $\alpha\beta$ -glycols, which undergo C-C bond cleavage with Fenton's reagent.

The radical from 1,1-dimethoxyethane gave a triplet, which showed further very small doublet splitting. This is evidently due to the radical  $\cdot\text{CH}_2\text{O}\cdot\text{CH}(\text{OCH}_3)\cdot\text{CH}_3$ , where the small doublet splitting arises from the interaction of the tertiary hydrogen atom, showing that the radical is formed before hydrolysis of the acetal in the dilute acid. A triplet of

<sup>6</sup> Prilezhaeva, Shapiro, and Shostakovskii, *Zhur. obshchei Khim.*, 1948, **18**, 1663.

<sup>7</sup> J. H. Merz and W. A. Waters, *J.*, 1949, S15.

doublets would arise from the radical  $(\text{CH}_3\cdot\text{O})_2\text{CH}\cdot\text{CH}_2\cdot$ , but in this case the magnitudes of the two splittings would be closer than those found.

**1,4-Dioxan.**—The radical from 1,4-dioxan gave a doublet of doublets, with coupling constants of 16.6 and 45.3 gauss. By analogy with the other ether radicals, the 16.6-gauss coupling can be assigned to the proton on the carbon atom from which the hydroxyl radical has abstracted a hydrogen atom. The remaining coupling constant is therefore assigned to one of the protons on the adjacent carbon atom. This is exactly analogous to the coupling constants observed for the cyclohexyl radical,<sup>4</sup> where the spectrum consists of a triplet (46.0 gauss), of triplets (0.67 gauss), with further doublet splitting (21.0 gauss); here, at each carbon atom adjacent to the site of hydrogen abstraction, there is one proton in the nodal plane of the *p* orbital containing the unpaired electron and one proton almost at right angles to it, giving rise to a large triplet of smaller triplets. In 1,4-dioxan, however, there is only one carbon atom adjacent to the site of hydrogen abstraction, so that one proton gives rise to a very large doublet, and the small doublet splitting, arising from the other proton, is submerged by modulation broadening.

**Coupling Constants.**—For the coupling constants listed in the Table, the probable error is 3%.  $\alpha$ -H denotes the coupling constant for the proton(s) at the carbon atom where hydrogen abstraction has taken place,  $\beta$ -H is that for protons on carbon atoms directly linked to the  $\alpha$ -carbon atom, and  $\gamma$ -H is that for protons on carbon atoms across an ether link from the  $\alpha$ -carbon atom.

**Conclusions.**—The following conclusions may be drawn from the e.s.r. spectra radicals derived from solutions of ethers in acid: (i) in aliphatic ethers, the hydroxyl radical abstracts a hydrogen atom more readily from  $\alpha$ -CH than from  $\beta$ -CH, and here there is a resemblance between the oxidation of ethers and of alcohols;<sup>3</sup> (ii) unpaired-electron density can be coupled through the ether link, as found for some aromatic ethers;<sup>8</sup> (iii) no coupling is observed from protons attached to oxygen in the acid medium, probably owing to rapid proton-exchange; (iv) with unsaturated ethers, the hydroxyl radical abstracts a hydrogen atom from the ethyl group, rather than adding to the double bond; (v) the angular-dependence of hyperfine coupling to  $\beta$ -protons is well demonstrated in the radical from 1,4-dioxan, which shows coupling only to one  $\beta$ -proton.

#### EXPERIMENTAL

A Varian V-4500 electron spin resonance spectrometer was used, employing a 12-in. electro-magnet and 100 kc./sec. modulation. The flow system has been described elsewhere;<sup>3</sup> the radicals were observed some 0.02 sec. after the mixing of the solutions, using a flow rate of 100 ml. of each solution per minute, and the spectra were recorded using a scan-rate of 7.6 gauss/min.

One reactant solution contained 15% titanous sulphate solution (B.D.H.; iron-free; 15 ml.), concentrated sulphuric acid (15 ml.), and water (1 l.), and the other solution contained 100-vol. hydrogen peroxide (5 ml.), concentrated sulphuric acid (15 ml.), and water (1 l.). To each solution, ether (M/20) was added, or the solutions were saturated at room temperature (20°).

The spectra were calibrated by reference to the quintet splitting of *p*-benzosemiquinone in alkaline ethanol.

[*Note added, December 7th, 1964.* Identical results have been reported earlier (W. T. Dixon, R. O. C. Norman, and A. Buley, *J.*, 1964, 3625) for radicals from diethyl ether and acetone. They find similar radicals as ours from 1,2-dimethoxyethane and di-isopropyl ether although their coupling constants appear to be slightly different. The radical we find from the hydrolysis product from ethyl vinyl ether appears to be the same as that found by abstraction from ethyl alcohol, *i.e.*,  $\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{OH}$ .

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<sup>8</sup> P. L. Kolker and W. A. Waters, *J.*, 1964, 1136.