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AN ELECTRON SPIN RESONANCE STUDY OF SOME ALIPHATIC AND ALICYCLIC ETHER RADICALS

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Abstract—The reactions of photochemically generated t-butoxyl radicals with a wide range of aliphatic and alicyclic ethers have been investigated by ESR. The spectra of several new radicals are described and the identity of the radicals is compared with the species formed by other oxidizing systems. Restricted rotation giving rise to line-width alternation has been observed in the spectrum of $\dot{C}H_2OCH_3$ formed from dimethylether.

RADICALS formed from saturated ethers have been the subject of several ESR investigations. The oxidizing systems Ti(III) + H_2O_2, and Fenton's reagent (Fe(II) + H_2O_2) have been used to prepare free radicals in rapid continuous flow systems[1–5] and Zeldes and Livingston[6] have reported the reactions of OH radicals from photolysed H_2O_2 with diethylether and dioxan. Oriented radicals of the type $R\dot{C}HOR'$ have been studied in x-irradiated inclusion compounds of urea and aliphatic ethers.[7] In some cases different radicals have been formed depending on the method of preparation. Thus the reactive species in the Ti(III) + H_2O_2 system gives[1,3] the radical MeCHOEt with diethylether whereas Fenton's reagent gives $\cdot CH_2CH_2OEt$.

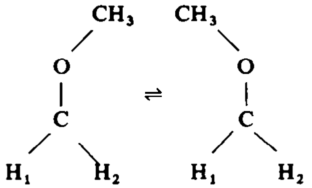
Recently it has been shown that free radicals in sufficient concentrations for ESR studies can be conveniently generated by the steady state photolysis of static solutions containing di-t-butyl peroxide.[8–12] This technique facilitates the investigation of temperature dependent effects in the ESR spectra and is more economical in chemicals than the continuous flow methods. A flow method has been used to investigate the reactions of t-butoxyl radicals with alcohols[13] but we have found it unnecessary to flow our solutions in order to obtain a steady concentration of radicals.

In this paper we report the results of an investigation by ESR of the reactions of t-butoxyl radicals with an extensive selection of saturated ethers. Several new radicals have been obtained and improved resolution has led to the assignment of additional small coupling constants in a number of radicals previously observed by other workers.

DISCUSSION

All of the dialkylethers studied gave a single ESR spectrum in the reaction with t-butoxyl radicals. The spectra could be unequivocally assigned to the products expected on abstraction of a H atom from a position adjacent to oxygen and thus resemble those found utilizing the Ti(III) + H_2O_2 system.[1–5]

The spectrum of $CH_3O\dot{C}H_2$ obtained from dimethylether is markedly temperature dependent as shown in Fig. 1. At −40° the M = O components of the triplet from the methylene protons are considerably broader than the M = ± 1 components. This line-width alternation is attributable to a restricted rotation about the $\dot{C}$—O bond and is similar to effects found in the hydroxymethyl radical.[14] It implies that the two methylene protons H_1 and H_2 in each of the two rotamers have different hyperfine coupling constants, and the observed splitting of 17·3 G is a time averaged value.



This type of inequivalence has previously been found in radicals such as allyl,[15,16] $\dot{C}H_2COMe$ and $\dot{C}H_2CHO$,[17] 2- and 3-thenyl[10] and the 2,3-dimethylbutadiene radical anion,[18] and seems to occur quite generally whenever the methylene protons are not related by a plane of symmetry.

In the present instance the inequivalence of the two α-protons is resolved at −100° (Fig. 1 (C)) into two doublet splittings of 16·8 G and 18·3 G respectively. There is also a slight increase in the quartet splitting to 2·1 G. From the linewidth variations we estimate an activation energy of ca. 3 kcal. mole^{-1} for the restricted rotation.

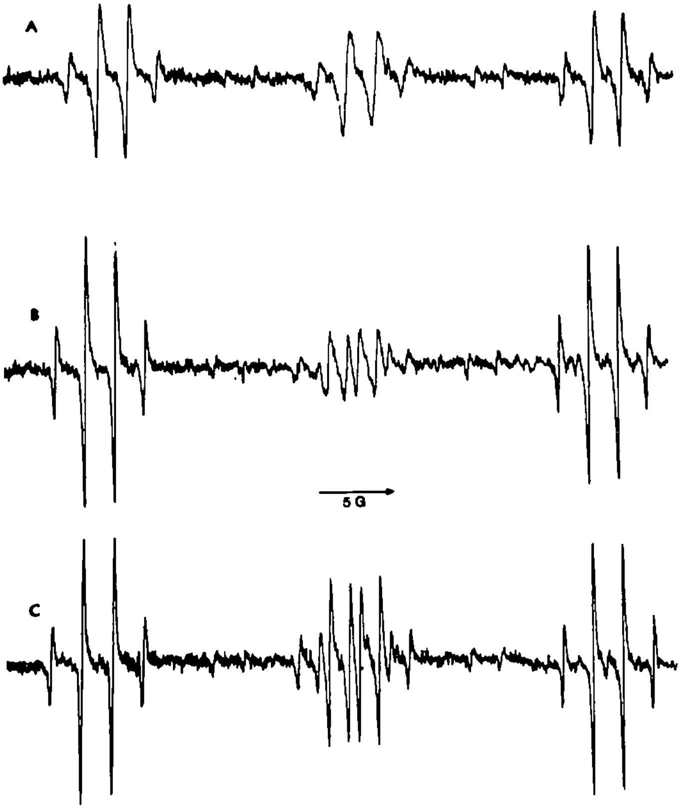


FIG. 1 The ESR spectrum of the radical $CH_3O\dot{C}H_2$ at (A) −36°, (B) −81° and (C) −100°.

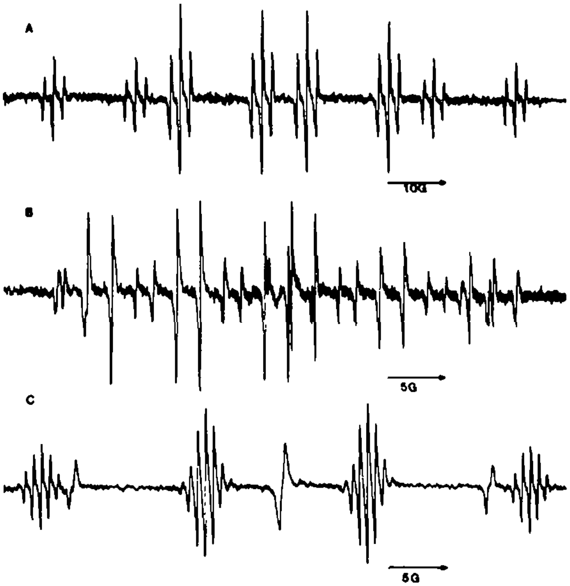


FIG. 2 The ESR spectra of free radicals derived from (A) diethylether, (B) 1:2 dimethoxyethane, (C) 1:1 dimethoxyethane, at −60°.

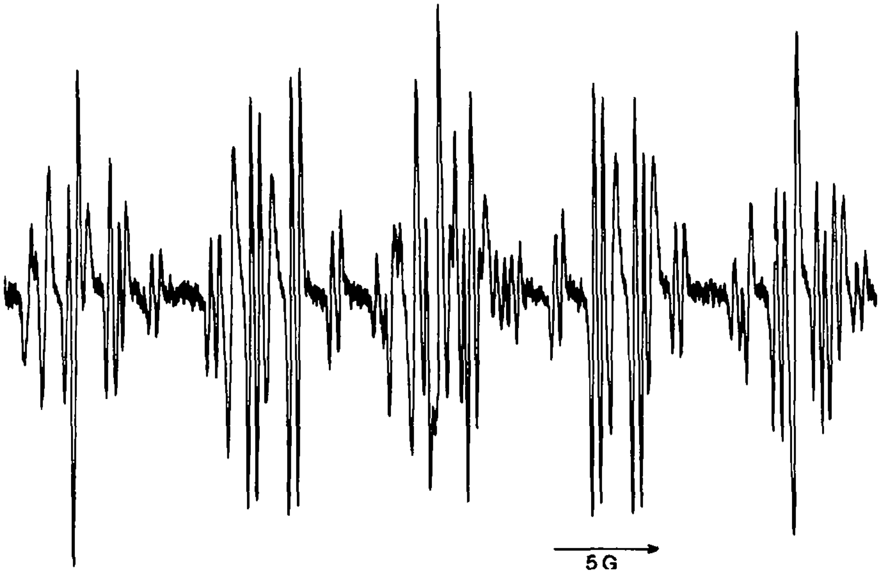


FIG. 3 The ESR spectra of the free radicals derived from 2-methoxyethanol.

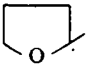
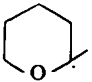
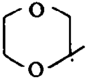
The spectra of the other dialkylether radicals exhibit well resolved splittings from γ and γ' protons and we find that invariably a $(\gamma') >$ a (γ). This implies that delocalization of the unpaired electron is more effective through a β-oxygen than through a β-methylene group. The assignment of the two small triplets in the case of di-n-butylether has been made by analogy with the other radicals studied.

When the substrate contains chemically distinguishable α-protons, two or more species are seen in the ESR spectrum. Thus 1,1- and 1,2-dimethoxyethane both give two radicals (Fig. 2, (B) and (C)).

In the case of 1,1-dimethoxyethane the relative abundance of the two radicals formed varied considerably with temperature. At $-60°$ as shown in Fig. 2(C), the radicals (a) $(\mathrm{Me\ O})_2\dot{\mathrm{C}}\mathrm{Me}$ and (b) $\mathrm{Me\ CH(OMe)O\dot{C}H_2}$ are apparent with the former predominant. Spectra were also recorded at room temperature by irradiating the solution in the Varian flat aqueous solution cell. The strongest spectrum was that of (b) with $a(\alpha) = 17{\cdot}43$ G and $a(\gamma') = 0{\cdot}53$ G, and the other radical was barely detectable.

We rationalize these observations as follows. Thermodynamically radical (a) is expected to be more stable than (b) since it is a tertiary radical with two O atoms adjacent to the C atom bearing the unpaired electron. At low temperatures the smaller activation energy for the formation of (a) determines the relative proportions of products. At room temperature the difference in activation energies is less significant.

TABLE 1. HYPERFINE COUPLING CONSTANTS IN GAUSS OF RADICALS FROM SATURATED ETHERS AT $-40°$

Substrate	Radical	a(α)	a(β)	a(γ)	a(γ′)	a(other)
Dimethylether	$\mathrm{MeO\dot{C}H_2}$	17·24	—	—	2·04	
Diethylether	$\mathrm{MeCH_2O\dot{C}HMe}$	14·09	21·82	—	1·67	
Di-n-propylether	$\mathrm{EtCH_2O\dot{C}HCH_2Me}$	13·91	20·83	0·43	1·61	
Di-isopropylether	$\mathrm{Me_2CHO\dot{C}Me_2}$	—	19·28	—	1·06	0·2[a]
Di-n-butylether	$^{n}\mathrm{PrCH_2O\dot{C}HCH_2Et'}$	14·21	18·85	0·74	1·73	
1:1-Dimethoxyethane	$\mathrm{(MeO)_2\dot{C}Me}$	—	13·95	—	0·69	
	$\mathrm{MeCH(OMe)O\dot{C}H_2}$	17·80	—	—	0·21	
1:2-Dimethoxyethane	$\mathrm{MeOCH_2CH_2O\dot{C}H_2}$	17·40	—	—	2·41	
	$\mathrm{MeOCH_2\dot{C}HOMe}$	17·55	7·51	—	2·04	
2-Methoxyethanol	$\mathrm{MeO\dot{C}HCH_2OH}$	16·38	8·59	—	1·95	0·42[b]
	$\mathrm{\dot{C}H_2OCH_2CH_2OH}$	17·24	—	—	2·22	
	$\mathrm{MeOCH_2\dot{C}HOH}$	18·23	8·84	—	—	1·79[b]
Triethylorthoformate	$\mathrm{(EtO)_3\dot{C}}$	—	—	—	0·37	
	$\mathrm{(EtO)_2CHO\dot{C}HMe}$	15·64	22·75	—	0·67	
Tetrahydrofuran		13·60	28·06	0·76	1·90	
Tetrahydropyran		16·07	24·41	0·69	0·76	
Dioxan		17·06	23·61	—	0·90	
Trioxan	?	0·25[b]				

[a] septet from six equivalent protons

[b] doublet from a single proton.

If (a) and (b) are formed with equal ease such that the abstraction of α-hydrogens is random, then since there are six OMe protons to each tertiary one, (b) should form six times as fast as (a). The relative proportions observed also depend on the rates of termination but if these are diffusion controlled they should not vary much for the different radicals.

Similar effects are found with triethylorthoformate: at −60° the tertiary radical $(EtO)_3\dot{C}$ is predominant whereas at room temperature $(EtO)_2CHO\dot{C}HMe$ is the most abundant species.

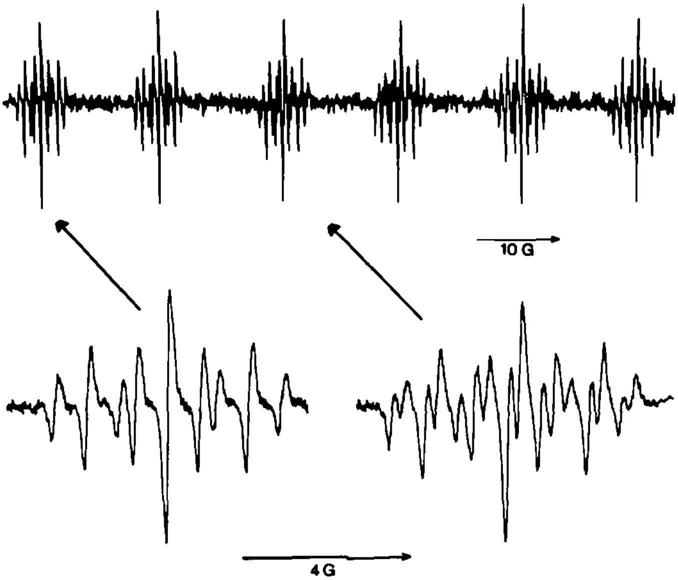


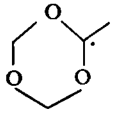
FIG. 4 The ESR spectrum of the free radical obtained by abstraction of an α-hydrogen atom from tetrahydrofuran together with an expanded spectrum showing the second order splitting of the central lines.

2-methoxyethanol gives a complicated pattern (Fig. 3) which can be analysed as a superposition of three spectra. The analysis was simplified by the fact that the β-proton and OH proton coupling constants were slightly temperature dependent and overlapping peaks could be resolved by changing the temperature. Shiga *et al.* found the radicals $MeOCH_2\dot{C}HOH$ and $\dot{C}H_2OCH_2CH_2OH$ in the Ti(III) + H_2O_2 system[4] whereas Fenton's reagent gave a mixture of $\dot{C}H_2OCH_2CH_2OH$ and $MeO\dot{C}HCH_2OH$. Our spectra show additional splittings from the OH proton which undergoes rapid exchange under the conditions of the flow experiment.

Three of the radicals in the Table have β-proton coupling constants of the order of 8 G. Similar low values have been observed before and can be explained in terms of anisotropic rotational averaging about the C(α) – C(β) bond. The temperature dependence of the splittings noted earlier supports this interpretation.[19] The results for the radical $MeOCH_2\dot{C}HOH$ are of some interest since at −40° we find a(β) to be 8·8 G indicating restricted rotation whereas in aqueous solutions at room temperature a value of 22·6 G has been reported.[4] No dramatic change in coupling constant was observed on raising the temperature of our solution to 20° and it would seem that the change in medium is important in determining the barrier to rotation in this case.

The cyclic ethers studied all gave well resolved spectra. Second order splitting[20] was observed in the spectrum from tetrahydrofuran and is illustrated in Fig. 4. The observed value of 0·23 ± 0·01 G is in good agreement with the calculated splitting of 0·24 G. The radical from dioxan has been reported several times.[2, 5, 6] At room temperature the central lines of the β-proton triplets are very broad because of ring inversion. At lower temperatures they disappear completely and line-width alternation is also observed in the triplet from the γ′ protons. Similar effects are found in the radical from tetrahydropyran. Attempts were made to freeze out the ring inversion process but the solutions solidified before this could be achieved.

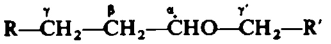
Finally we consider the radical formed from trioxan: Shiga *et al.* found that instead of the doublet of quintets expected for the radical



only one small doublet was observed in the ESR spectrum. Both Ti(III) + H_2O_2 and Fenton's reagent gave the same spectrum and we have obtained an identical result in the reaction with t-butoxyl radicals. At −30° the doublet splitting of 0·25 G is well resolved; the g-factor is 2·0031 ± 0·0001· No further splitting was observed although the modulation amplitude was reduced to 50 mG and the microwave power to 1 mW. The identity of the radical is therefore open to speculation. If the doublet splitting is due to an α-proton it is indicative of a non planar geometry around the radical carbon; a determination of the ^{13}C splitting would be informative in this respect. The g-factor is very close to the values obtained for other radicals from saturated ethers.

EXPERIMENTAL

The ESR spectra were recorded with a Varian E3 spectrometer in the manner previously described.[11] The field sweep of the spectrometer was calibrated with aqueous solns of Fremy's salt (a_N = 13·091 ± 0·004 gauss) and the splittings are believed to be accurate to ±1%. The compounds were obtained commercially and used without further purification. The coupling constants of all the radicals are listed in the Table and typical spectra are shown in Figs 1–4. The convention for labelling protons is



$$R—\overset{\gamma}{C}H_2—\overset{\beta}{C}H_2—\overset{\alpha}{\dot{C}}HO—\overset{\gamma'}{C}H_2—R'$$

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