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A COMPARATIVE STUDY OF SOME OXYGEN AND SULPHUR SUBSTITUTED ALKYL RADICALS

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Abstract—Several sulphur containing alkyl radicals have been generated and their ESR spectra and hyperfine coupling constants compared with those of the oxygen analogues. Deviations from planarity are smaller when a tervalent carbon atom is bonded to sulphur than when bonded to oxygen. Moreover greater delocalization of the unpaired electron is apparent in the sulphur radicals and this leads to higher barriers to internal rotation in radicals of the form $\dot{C}H_2SR$ compared with $\dot{C}H_2OR$.

INTRODUCTION

The ESR spectra of oxygen substituted alkyl radicals have been extensively investigated in both aqueous and non-aqueous solvents and in a recent paper Norman *et al.*[1] have summarized much of the information available on these species. There have been rather fewer studies of the corresponding sulphur containing radicals. Adams[2] has observed a few radicals derived from sulphides and disulphides during photolysis of solutions containing di-t-butyl peroxide and recently there have been three reports of radicals substituted in the β-position with sulphur.[3-5] The conformational properties of these β-mercaptoalkyl radicals have been discussed by Krusic and Kochi.[3]

In a previous paper from this laboratory[6] the radicals derived by abstraction of a hydrogen atom from anisole and phenetole were compared with those from thioanisole and thiophenetole. We have now extended this investigation to include a wider range of thioethers and the results will be compared with those from earlier work on cyclic and acyclic ethers.[7] The radicals have been prepared either by abstraction of hydrogen by t-butoxy radicals,[8] or by abstraction of chlorine or bromine by triethylsilyl radicals.[9]

DISCUSSION

The hyperfine coupling constants of fifteen alkyl radicals substituted in the α-position with either oxygen or sulphur are given in Figs 1–3. Of these I and II were prepared by abstraction of chlorine from chloroalkyl compounds and the remainder by abstraction of a hydrogen atom. The radicals I–IV all exhibit temperature dependent line-width variations attributable to restricted rotation of the methylene group. Typical spectra for the radical obtained from methyl t-butyl sulphide are shown in Fig. 4: spectra for the methoxymethyl[7] and t-butoxymethyl[10] radicals are already in the literature. We shall discuss these alternating line-width effects[11, 12] further in a later section.

On comparing the coupling constants of related pairs of radicals such as V and VI or XIV and XV, it is apparent that the α- and β-proton hyperfine interactions

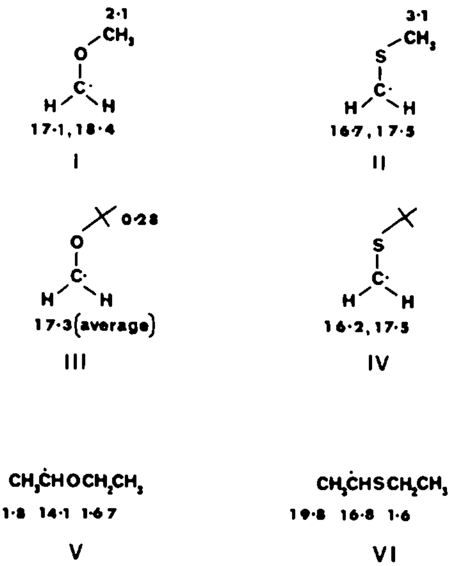

FIG 1. Hyperfine coupling constants of some radicals from acyclic ethers and thioethers. The values for III are from ref. 10 and those for VI from ref. 2

exhibit opposite trends. The α-splitting increases when oxygen is replaced by sulphur whereas the β-splitting decreases. This feature was noted for V and VI by Adams[2] who deduced from the α-splittings that there is greater spin density on the radical carbon in the sulphur compound and suggested that the β-splitting was anomalous. We prefer an alternative explanation already proposed[6] for the radicals IX and X.

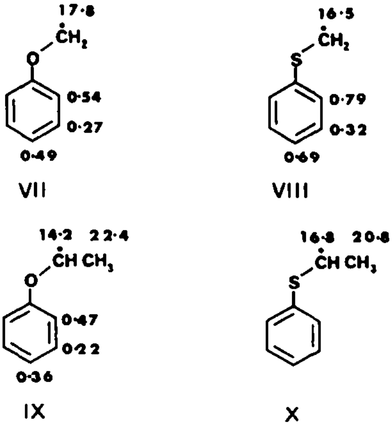

FIG 2. Hyperfine coupling constants for radicals from aromatic ethers and thioethers from ref. 7

It is suggested that the oxygen radicals are less planar than the sulphur analogues and thus have smaller α-proton splittings in spite of a larger spin density on the radical centre. It is well established[1] that α-proton interactions are quite sensitive to bending at the radical carbon whereas β-proton splittings are far less sensitive. The greater planarity of the sulphur radicals is supported by electronegativity considerations.

The increased delocalization of the unpaired electron in the thio radicals is evidenced by the larger methyl proton splitting in II compared with I, by the larger ring proton splittings in VIII compared with VII, and by the larger γ-methylene proton splittings in XII, XIII and XV compared with XI and XIV. A quantitative estimate of the spin withdrawing influence of an α-substituent X_i is provided by the parameter ΔX_i introduced by Fischer.[13] We calculate $\Delta(\text{SPh}) = 0{\cdot}229$ and $\Delta(\text{SEt}) = 0{\cdot}265$ whereas $\Delta(\text{OPh}) = 0{\cdot}169$ and $\Delta(\text{OEt}) = 0{\cdot}172$.

In most of the systems we have studied there is no ambiguity in the identity of the radical. However, in the case of 1,4-thioxane there is a possibility of hydrogen abstraction from carbon atoms adjacent to oxygen or sulphur. Only a single species was observed in the reaction with t-butoxy radicals and we assign it to the α-thio radical XII. The coupling constants then follow the expected pattern of an increase in a_H^α and a decrease in a_H^β when compared with those of XI. This assignment is supported by a consideration of the g-factors of XI–XIII (Fig. 3). The higher values found for XII and XIII are consistent with the presence of an α-thio radical. Similar differences in g-factors between oxygen and sulphur containing species have been found in studies of radical cations from aromatic sulphides and ethers.[14] The specific formation of XII from thioxane is an indication of the increased stabilisation due to electron delocalisation in the α-thio radical.

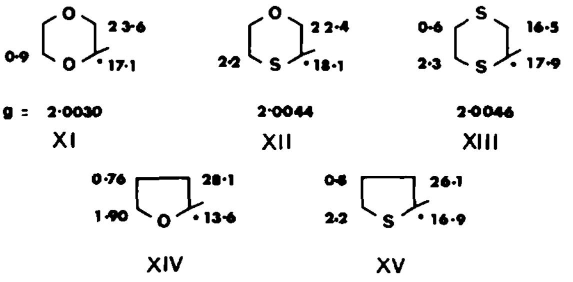

FIG 3. Hyperfine coupling constants for some cyclic radicals

The six membered ring radicals XI–XIII all exhibit line broadening due to ring inversion. At room temperature the central (M = 0) lines of the β-proton triplets are very broad and they are no longer detectable at lower temperatures. At − 40° line-width alteration is also apparent in the small triplet splitting from the γ-protons.

The ESR signals obtained from *p*-dithiane were much weaker than those from dioxane and thioxane and it was not possible to detect the broadened lines of the β-proton triplet. However, the g-factor and coupling constants would seem to establish the identity of the radical as XIII. The α- and γ-splittings are very similar to those of

XII but there is a marked reduction in the β-proton splitting and a 0·6 G splitting from the remaining pair of protons which is not resolved in XI or XII. The unique feature of this radical is that it has α- and β-thio substituents.

As mentioned in the introduction there have recently been several reports of β-mercaptoalkyl radicals.[3–5] The methylmercaptoethyl radical[3] has $a_{\mathrm{H}}^{\alpha} = 21{\cdot}6$ and $a_{\mathrm{H}}^{\beta} = 14{\cdot}89$ G at − 70° and $a_{\mathrm{H}}^{\beta} = 13{\cdot}5$ G at − 124°. The low value of a_{H}^{β} in this species has been interpreted in terms of a preferred conformational orientation in which the sulphur atom eclipses the p-orbital at the radical centre. Similar effects are found in radicals substituted in the β-position with Si, Ge, or Sn[3, 10] and in the 2-chloroethyl radical.[15] In contrast the 2-methoxyethyl radical has a preferred conformation in which the oxygen atom occupies the nodal plane of the π-orbital containing the unpaired electron. We have generated this radical by abstracting chlorine from 2-chloroethylmethyl ether and have investigated the temperature dependence of its β-proton splitting. The results together with those for a variety of other β-substituted ethyl radicals will be discussed elsewhere.

Returning to the discussion of radical XIII we see that the influence of a β-sulphur is similar in cyclic and acyclic radicals. We can rationalise our ESR results if the β-sulphur in XIII prefers to eclipse the p-π orbital on the radical centre. This distortion also moves the methylene protons into a more favourable position for a long range interaction. Krusic and Kochi[3] did not resolve splittings from the methyl group in $\dot{C}H_2CH_2SCH_3$ but found a substantial fluorine coupling (4·4 G) in $\dot{C}H_2CH_2SCF_3$.

Line-width variations

The determination of activation energies and rate constants for a variety of dynamic processes from the analysis of alternating line-width effects is well established.[11, 12] As mentioned earlier spectral changes due to restricted internal rotation have been observed in the ESR spectra of I–IV. By recording spectra over a wide temperature range we have obtained barriers for the radicals $\dot{C}H_2OCH_3$ and $\dot{C}H_2SBu^t$ and also for $\dot{C}H_2OEt$ ($a_{\mathrm{H}}^{\alpha} = 16{\cdot}7, 18{\cdot}2$; $a_{\mathrm{H}}^{\gamma} = 2{\cdot}35$ G). The latter was prepared by extracting a chlorine atom from chloromethylethyl ether. At high temperatures the spectra exhibit a triplet from the methylene protons whereas at low temperatures these protons become inequivalent on the ESR time scale and two doublet splittings are observed. The form of the line-width variations is illustrated in Fig. 4 for CH_2SBu^t. Similar effects are found in the hydroxymethyl radical.[16, 17]

A possible difficulty in recording the spectra of photolytically generated radicals arises from the slow decay of the ESR signal with time. This is not normally serious but must be considered in making line-width measurements. We have attempted to overcome this difficulty by time averaging several spectra accumulated using short sweep times. This was achieved with a Micro 16 computer interfaced to the spectrometer.

To obtain estimates of the barriers to internal rotation the spectra have been matched to calculations using the modified Bloch equations for a two site model.[11, 12] The theoretical spectra were computed on-line and plotted directly on the pen recorder of the ESR spectrometer. We have found that the use of an on-line computer greatly speeds up the process of matching theoretical and experimental spectra. Typical results are shown in Fig. 4. The activation energies and pre-exponential factors obtained by a least mean squares fit to an Arrhenius equation are: $\dot{C}H_2OCH_3$,

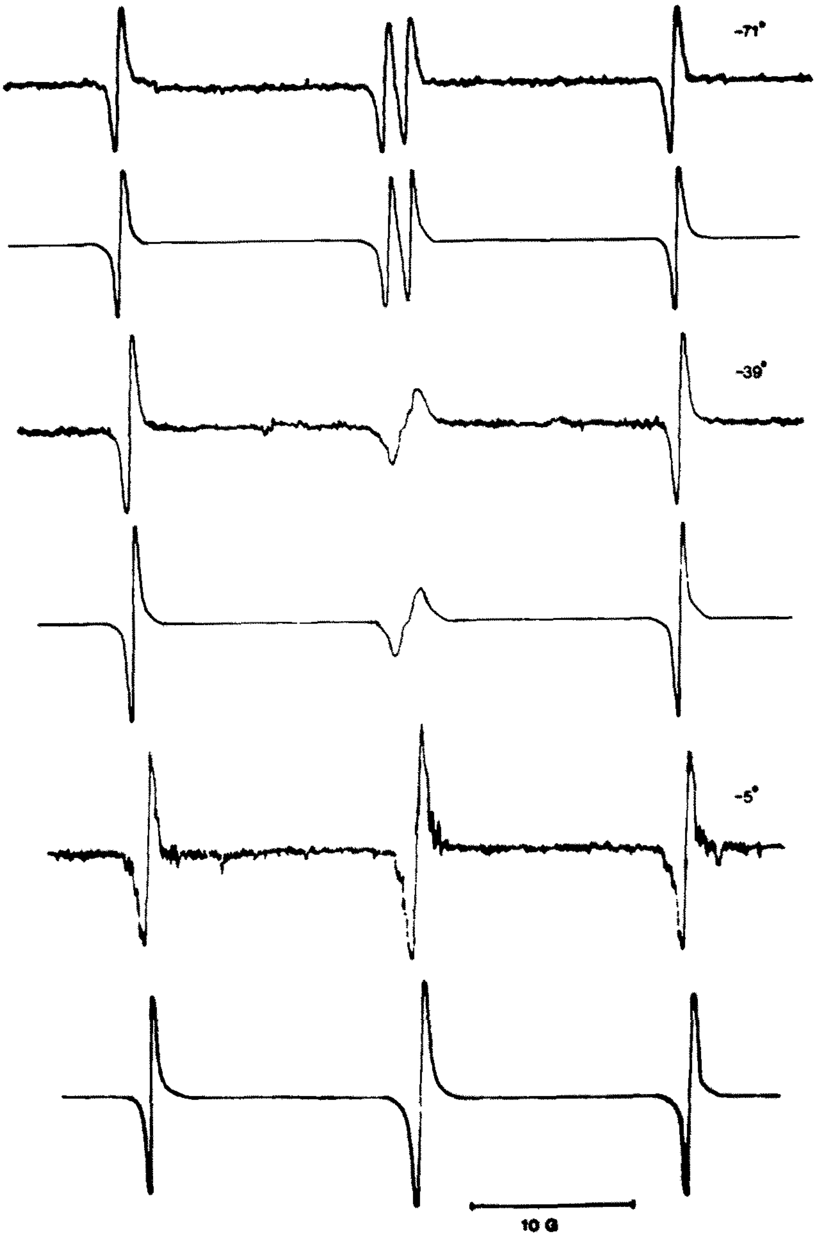

FIG 4. Experimental and theoretical spectra for the radical $\dot{C}H_2SBu^t$ as a function of temperature

22·2 kJ mol^{-1} and $10^{12 \cdot 6}$: $\dot{C}H_2OEt$, 23·9 kJ mol^{-1} and $10^{12 \cdot 6}$: $\dot{C}H_2SBu^t$, 25·4 kJ mol^{-1} and $10^{12 \cdot 5}$ sec^{-1}. These barriers are probably accurate to ± 2 kJ mol^{-1}.

As might be expected if there is greater delocalisation in the thio radicals, the barrier in $\dot{C}H_2SBu^t$ is slightly higher than those found for methoxymethyl and ethoxyethyl. A more direct comparison would be possible if barriers were available for two radicals with the same alkyl group. In a published spectrum[10] of the t-butoxymethyl radical recorded at − 107° the central line of the α-proton triplet is very broad but the spectrum is still in the fast exchange region. If the frequency difference between the α-proton coupling constants is similar in the two radicals, it would appear that the barrier is significantly smaller than in $\dot{C}H_2SBu^t$. The barriers in both these radicals may be lowered by increased steric interactions in the planar configuration due to the bulky nature of the t-butyl group.

In contrast the ESR spectrum of $\dot{C}H_2SCH_3$ corresponds to a locked conformation at − 60°. The signal intensity decreases rapidly at higher temperatures and we have not been able to make observations in the fast exchange region. However, by assuming an A factor of $10^{12 \cdot 6}$, we estimate a lower limit for the barrier of 30 kJ mol^{-1}. The barriers in the thio radicals are therefore higher than those in the oxygen analogues by 4–8 kJ mol^{-1}. Increased stabilisation of a radical centre by α-sulphur atoms is also found in chemical studies.[18]

In an earlier paper[16] the barrier for the hydroxymethyl radical was estimated to be 10 kJ mol^{-1} but it would appear[17] that the true barrier is nearer 20 kJ mol^{-1} and only slightly lower than those reported here. In the original work[16] the activation energy was determined from spectra in the fast exchange region by plotting $\log(2(A_1/A_0)^{\frac{1}{2}} - 1)$ against $1/T$ where A_1 and A_0 are the peak to peak amplitudes of the $M = 1$ and $M = 0$ components of the methylene triplet. This procedure which is particularly useful when spectra cannot be obtained in the slow exchange region, has been widely used in the literature and it is worthwhile inquiring into the reason for its failure to give a reliable barrier for $\dot{C}H_2OH$. We have used the same method for $\dot{C}H_2OCH_3$ and find that the barrier is again underestimated. A possible explanation lies in the neglect of second order splittings: for a methylene splitting of 18 G the two components of the $M = 0$ line should be separated by about 0·1 G. Although this splitting is not resolved it does have an effect on the peak to peak amplitude of the line which is most marked when the two components are least broadened. In principle the second order splitting should also be taken into account when using the modified Bloch equations but the implications are less serious if the spectra are fitted over a wide range of exchange rates since only the extreme fast exchange region is affected.

We conclude that when coupling constants are large enough for second order splittings to influence the line amplitudes, barriers obtained from observations on the fast exchange region should be treated with caution. However, for coupling constants of less than ten gauss the measurement of relative broadening from line amplitudes should be reliable. Procedures are available in the literature[19] for treating situations where the second order effects must be taken into account in simulating the spectrum.

CONCLUSIONS

Differences between the ESR spectra of radicals derived from ethers and thioethers can be understood if there is greater spin delocalisation and a higher spin density on the heteroatom in the sulphur compounds. This conclusion is in agreement with work on radical cations.[14] It is also concluded that deviations from planarity at the radical centre are smaller in the thio radicals. These deductions lead to a consistent interpretation of the hyperfine coupling constants from a variety of radicals and are supported by measurements of barriers to internal rotation about $\dot{C}H_2$—O and $\dot{C}H_2$—S bonds.

EXPERIMENTAL

The ESR spectra were recorded on a Varian E3 spectrometer with some modifications to previously described procedures.[8] The Osram ME/D lamp was replaced in some experiments by a Phillips CS 1000 light source and the spectrometer has recently been interfaced to a Micro 16 digital computer with a 16 bit word length 4K store. The addition of this computer facilitates spectrum accumulation and time averaging and it can also be used for on-line simulation of theoretical spectra for direct comparison with the experimental data. Spectra can also be integrated numerically, smoothed using least squares techniques,[20] etc. For more complicated numerical analysis the spectra can be dumped on paper tape and input to a larger computer.

In line-width studies the sample temperatures were recorded with a Comark 1605 electronic thermometer and a Cr/Al thermocouple. The latter was inserted into the sample, contained in a 4 mm od quartz tube, immediately before and after recording the spectrum. Microwave frequencies were determined by means of a Hewlett-Packard 5246L counter and 5255A frequency converter and g-factors were measured relative to DPPH ($g = 2{\cdot}0036 \pm 0{\cdot}0003$).

All the compounds used were obtained commercially. Di-t-butyl peroxide was washed with acidified KI solution and then with water before use. Samples were usually degassed on a vacuum line by the freeze thaw technique. In halogen abstraction reactions[9] the solutions typically contained two parts by volume of di-t-butyl peroxide, one part of triethylsilane and one part of the halide. However, in some cases, particularly with CH_3SCH_2Cl, better spectra were obtained with only a trace of the halide present.

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