Electron Paramagnetic Resonance Spectra of Aliphatic Thioketyl Radical Anions in Fluid Solution

Alwyn G. Davies* and Anthony G. Neville
Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK

The first EPR spectra of the radical anions of simple aliphatic thioaldehydes and thioketones have been observed by photolysis of solutions of the corresponding potassium thiolates in *tert*-butyl alcohol.

Radical anions $M^{\cdot -}$ may be regarded as the conjugate bases of the neutral radicals $MH^{\cdot}$, and can be prepared by the abstraction of a proton and a hydrogen atom from a precursor MH_2 [eqn. (1)]. This approach to the preparation of radical anions

$$MH_2 \xrightarrow{-H^+} MH^- \xrightarrow{-H^{\cdot}} M^{\cdot -} \qquad (1)$$

may be valuable when the parent molecules M are not available or give some unwanted reaction under the conditions needed for one-electron transfer, and we have recently made use of this principle to generate a number of new radical anions of aliphatic aldehydes and of ketones from the corresponding primary or secondary alcohols.[1] We now report the extension of this principle to the preparation of the radical anions of some thioaldehydes and thioketones from the corresponding primary or secondary thiols.

Simple thioaldehydes and thioketones are not stable as monomers, and are rapidly converted at room temperature into oligomers. Thus the thioketyl radical anions which are known are derived mainly from more complex thiones which do not oligomerise, such as aryl thiones,[2–5] α-thioxoacetamides[6] or thioketenes.[7] The only EPR spectra of aliphatic thioketone radical anions which appear to have been observed in liquid solution are those of di-*tert*-butyl thioketone[8] and of bis(trifluoromethyl) thioketone[9] both of which are stable as monomers. No spectrum of an aliphatic aldehyde radical anion appears to have been described, but while this work was in progress, Casarini *et al.* reported the generation of the thiobenzaldehyde and 2,4,6-tri-*tert*-butylbenzaldehyde radical anions by the photolysis of a solution of the benzylthiol and of potassium ethoxide in ethanol.[10]

The methods which we developed for generating ketyl radical anions from alcohols for EPR studies involved photolysis of solutions of the potassium alkoxides in the corresponding alcohols or in *tert*-butyl or *tert*-pentyl alcohol, or photolysis of static or slowly flowing solutions of di-*tert*-butyl peroxide and the potassium alkoxides in the same tertiary alcohols. Whereas alcohols undergo abstraction of hydrogen from the α-CH group to give α-hydroxyalkyl radicals which then lose a proton under basic conditions [eqn. (2)], free thiols undergo hydrogen abstraction preferentially from the SH group to give thiyl radicals which will not deprotonate [eqn. (3)].

$$R_2CHOH \xrightarrow[-H^{\cdot}]{X^{\cdot}} R_2\dot{C}OH \xrightarrow{-H^+} R_2C{=}O^{\cdot -} \qquad (2)$$

$$R_2CHSH \xrightarrow[-H^{\cdot}]{X^{\cdot}} R_2CHS^{\cdot} \qquad (3)$$

We have therefore avoided the extension of our first technique which would involve using the free thiol as solvent, and have investigated methods based on photolysing solutions of potassium thiolates in *tert*-alcohols or photolysing solutions of mixtures of di-*tert*-butyl peroxide and potassium thiolates in tertiary alcohols. If small amounts of thiols were present and gave thiyl radicals by reaction (3), they would not interfere with the spectra of the thioketyl radical anions because their own spectra are too broad to be detected because of their orbital degeneracy.

Results

The best spectra of the thioketyl radical anions were obtained by photolysing solutions of the potassium thiolates in *tert*-butyl alcohol [eqn. (4)]. If *tert*-butyl peroxide was present, extraneous

$$R_2CHS^- \xrightarrow[Bu^tOH]{h\nu} R_2C{=}S^{\cdot -} \qquad (4)$$

signals rapidly developed, reducing the useful lifetime of the sample to *ca.* 4 min.

The spectra of the thioketyl radical anions which were obtained were generally weaker than those which we observed for the ketyl radical anions.[1] This may be due in part to the broader lines which result from the larger *g* anisotropy in the sulfur compounds, and in part to the low solubility of the potassium thiolates in tertiary alcohols, even in the presence of 18-crown-6. We were unable to obtain any satisfactory spectra from methanethiol or from hexadecane-1-thiol, and we believe that this was due to the very low solubility of the salts.

A typical spectrum (that for the thioacetone radical anion) is shown in Fig. 1. This should be compared with the spectrum of the acetone radical anion which is illustrated in Fig. 1 of ref. 1, and in which the ^{13}C satellites could be detected in natural abundance. EPR parameters for all the radicals which were observed, and for some other related radicals, are collected in Table 1.

Discussion

In the generation of ketyl radical anions by the photolysis of alkoxyl anions in alcohols, we assumed that the reaction involved electron transfer to the solvent to leave the alkoxyl radical which then abstracted a hydrogen atom from the α-position of the alkoxyl anion (or from the alcohol with subsequent loss of a proton). A similar mechanism is probably involved in the generation of thioketyl radical anions: photolysis induces the formation of the alkoxyl or alkylthiyl radical [eqn. (5); X = O or S] which then abstracts hydrogen from the α-position in the thiolate anion [eqn. (6)]. An alkylthiyl radical

$$\begin{array}{c} R_2CHS^- \\ \text{or} \\ R'O^- \end{array} \longrightarrow \begin{array}{c} R_2CHS^{\cdot} \\ \text{or} \\ R'O^{\cdot} \end{array} + e^-_{solv} \qquad (5)$$

Table 1 EPR spectra of thioketyl radical anions and related radicals

Radical	$a[n(\alpha\text{-H})]/\mathrm{G}$[a]	$a[n(\beta\text{-H})]/\mathrm{G}$[a]	g	Ref.
$\mathrm{MeHC{=}S^{\cdot -}}$	16.8 (1)	18.8 (3)	2.0055	*b*
$\mathrm{EtHC{=}S^{\cdot -}}$	16.3 (1)	18.7 (2)	2.0052	*b*
$\mathrm{C_7H_{15}HC{=}S^{\cdot -}}$	16.4 (1)	18.5 (2)	2.0052	*b*
$\mathrm{Me_2C{=}S^{\cdot -}}$	—	18.6 (6)	2.0049	*b*
cyclo-$\mathrm{C_5H_{10}C{=}S^{\cdot -}}$	—	17.9 (4)	2.0050	*b*
$\mathrm{CH_2{=}CH{-}CH{=}S^{\cdot -}}$	a(1 Hβ) 2.21 a(1 H) 15.5 a(2 H) 14.0		2.0044	*b*
$\mathrm{PhHC{=}S^{\cdot -}}$	a(α-H) 13.3 a(*p*-H) 5.3 a(*o*-H) 4.2 and 3.8 a(*m*-H) 1.4 and 1.2		2.0057	*b*
$\mathrm{MeH\dot{C}{-}SEt}$	16.8 (1)	19.8 (3)	2.0044	*c*
$\mathrm{Me_2\dot{C}{-}SCHMe_2}$	—	20.4 (6 H)	2.0038	*d*
$\mathrm{MeHC{=}O^{\cdot -}}$	12.05 (1)	19.85 (3)	2.0036	*e*
$\mathrm{EtHC{=}O^{\cdot -}}$	11.72 (1)	20.99 (2)	2.0036	*e*
$\mathrm{Me_2C{=}O^{\cdot -}}$	—	16.9 (6)	2.0036	*e*
$\mathrm{(CH_2)_5C{=}O^{\cdot -}}$	—	20.65 (4)	2.0032	*e*
$\mathrm{CH_2{=}CH{-}CH{=}O^{\cdot -}}$	a(β-H) 2.21 a(1 H) 13.17, 12.26 and 10.32		2.0034	*e*
$\mathrm{PhHC{=}O^{\cdot -}}$	a(α-H) 12.60 a(*p*-H) 6.17 a(*o*-H) 5.01 and 4.18 a(*m*-H) 1.56 and 1.27			*f*

[a] The value of n is given in parentheses. [b] This work. [c] D. Griller, D. C. Nonhebel and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1817. [d] B. C. Gilbert, D. K. C. Hodgeman and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1748. [e] Ref. 1. [f] P. Neta, M. Z. Hoffmann and M. Simec, *J. Phys. Chem.*, 1972, **76**, 847.

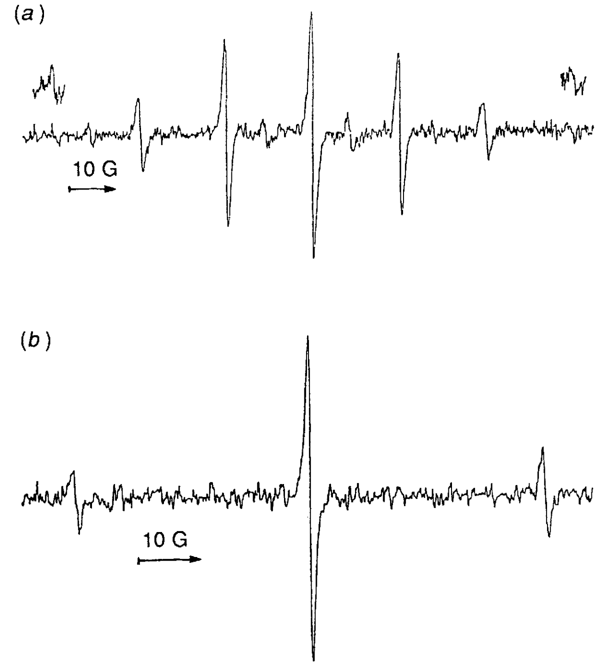
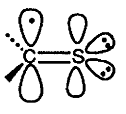
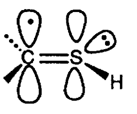


Fig. 1 (*a*) EPR spectrum of the thioacetone radical anion in *tert*-butyl alcohol at 290 K. (*b*) EPR spectrum of the cyclohexanethione radical anion in *tert*-butyl alcohol at 290 K.

$$\begin{array}{c}\mathrm{R_2CHS^{\cdot}}\\ \text{or}\\ \mathrm{R_2CHO^{\cdot}}\end{array} + \mathrm{R_2CHS^-} \longrightarrow \begin{array}{c}\mathrm{R_2CHSH}\\ \text{or}\\ \mathrm{R_2CHOH}\end{array} + \mathrm{R_2C{=}S^{\cdot -}} \qquad (6)$$

would not normally be expected to be capable of abstracting hydrogen from a C–H bond, but in a thiolate ion the C–H bond is probably weaker, and the canonical form $[\mathrm{RS^-H^{\cdot}\ R_2C{=}S}]$ may contribute to lowering the energy of the transition state.


1



2

The electronic configuration of the thiocarbonyl radical anions and of the mercaptoalkyl or alkylthiylalkyl radicals are illustrated in **1** and **2**. The unpaired electron should occupy a π* orbital with the largest coefficient at the carbon atom, and the principal difference between the two species should be that **1** has two pairs of non-bonding electrons in the nodal plane of the π system, but in **2**, one of these pairs is shared with hydrogen or an alkyl group. The π electron distribution and hence the hyperfine coupling constants (hfcc) in **1** and **2** would therefore be expected to be broadly similar. The same argument applies to the ketyl radical anions and the α-hydroxyalkyl radicals.[1]

Only two EPR spectra of α-mercaptoalkyl radicals appear to have been reported. The mercaptomethyl radical, $\mathrm{H_2\dot{C}{-}SH}$, was obtained by UV irradiation of the thiol in a frozen aqueous glass,[11] and shows $a[2(\alpha\text{-H})] = 19$ G with no observable coupling to the thiol hydrogen, and photolysis of phenyltriphenylsilylthione gave the corresponding mercaptoalkyl radical with $a[\mathrm{H\ (SH)}] = 0.98\text{–}1.21$ G depending on the solvent.[12] The undetectable or small coupling by the thiol hydrogen supports the contention that the S–H bond lies in the nodal plane of the π system. Again, the general similarity between the spectra of $\mathrm{MeHC{=}S^{\cdot -}}$ and $\mathrm{MeH\dot{C}{-}SEt}$, and of $\mathrm{EtHC{=}S^{\cdot -}}$ and $\mathrm{EtH\dot{C}{-}SCHMe_2}$ (see Table 1), supports the above description of the nuclear and electronic structure of **1** and **2**.

There has been a great deal of discussion in the literature regarding a possible pyramidal structure for ketyl radical anions, and we found evidence for this in the values of $a(^{13}\mathrm{C}\text{-}\alpha)$ in $\mathrm{Me_2CH^{\cdot}}$ (41.3 G) and $\mathrm{Me_2C{=}O^{\cdot -}}$ (52.2 G). A similar question arises in the case of the thioketyl radical anions.

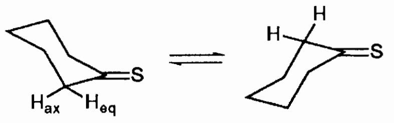
The best evidence in the literature comes from Voss' study of the radical anion of di-*tert*-butylthione, $\mathrm{Bu^t{}_2C{=}S^{\cdot -}}$, in both liquid[8] and solid[13] solution which showed $a(^{13}\mathrm{C}\text{-}\alpha)$ 41.9 G and $a(^{33}\mathrm{S})$ 1.6 G, compared with $a(^{13}\mathrm{C}\text{-}\alpha)$ 52.7 G in $\mathrm{Bu^t{}_2C{=}O^{\cdot -}}$. They concluded that there was no need to postulate a pyramidal structure for thioketyl radical anions. Similarly they found that the observed temperature dependence of the spectra of thioketyl radicals was in agreement with a planar structure.[13] However, Griller, Nonhebel and Walton[14] have shown that an RS group accepts spin better than an RO group, and from the above description of the structures of $R_2\dot{C}$–XR and $R_2C{=}X^{\bullet -}$ (X = O or S), spin delocalisation onto sulfur in the thione radical anions might be expected to be appreciable. Voss *et al.* have calculated (on the apparent assumption of C_{2v} symmetry) that the ratio of π spin density on carbon and on sulfur is 3:1.[13] The value of $a(^{13}\text{C-}\alpha)$ in the radical $Bu^t_2CH^{\bullet}$ is 42.98 G, very similar to that in the thioketyl radical anion, and if there is appreciable transfer there of spin density to sulfur some other effect must operate to restore $a(^{13}\text{C-}\alpha)$. We believe that the question of a non-planar radical ion cannot be ruled out: that there is significant spin delocalisation from carbon onto sulfur, but the effect of this on $a(\text{C-}\alpha)$ is offset by some pyramidalisation at the carbon centre.

A few aldehyde and ketone radical anions are included in Table 1 for comparison with their thione analogues. It will be seen that, as expected from the above description, the hfcc values are generally similar in both families of compounds, but the number of examples is too small to warrant more detailed comparisons being drawn.

Only one radical was observed for the propenthial radical anion, and we assume that this is the s-*trans* isomer; a similar situation held with propenal itself.[1] The spin density distribution which we observe is similar to that reported by Schmüser and Voss for some cyclic α,β-unsaturated thioketone radical ions.[6] The spectrum of the thiobenzaldehyde radical anion was similar to that reported by Placucci.[10] The observation of five distinct coupling constants to aromatic protons is consistent with a planar molecule in which rotation about the Ph–CHS bond is slow on the spectroscopic time scale. The hfcc values are assigned by analogy with those for benzaldehyde itself which shows similar behaviour.[15,16]

The spectrum of the cyclohexanethione radical anion could be obtained over only a small temperature range at *ca.* 290 K, and its appearance is illustrated in Fig. 1. At lower temperatures the signal became too weak, perhaps because the solution was more viscous and anisotropic effects broaden the lines; at higher temperatures, unwanted signals developed too rapidly.

The thione will have a chair structure as illustrated in eqn. (7). If ring inversion is slow on the time scale of the experiment, the EPR spectrum will consist of a triplet of triplets because of the different hyperfine coupling by the axial and equatorial protons. At higher temperatures when inversion is fast and there is rapid exchange of protons between axial and equatorial positions, the spectrum will consist of a quintet, with an observed hyperfine coupling equal to the average of the two which are observed at low temperature. At intermediate temperatures all the lines except the central and the wing lines will broaden as one spectrum is transformed into the other. This is the behaviour which we observed with the cyclohexanone radical anion. It is most likely that the spectrum which we observe reflects this intermediate rate of exchange, *i.e.* that it corresponds to spectrum (*a iii*) for the cyclohexanone radical ion in Fig. 5 of ref. 1, and the separation of the peaks is equal to the sum of the coupling constants of the axial and equatorial protons.



(7)

Experimental

Details of the EPR technique are given in ref. 1. The thiols (Aldrich) were used as supplied, except allyl mercaptan which was fractionally distilled.

Potassium in approximately equivalent amount to the thiol which was to be used was dissolved in purified *tert*-butyl alcohol under nitrogen. The thiol (*ca.* 10% by volume) was then added, and the solution was then treated with further potassium first at room temperature until any rapid reaction ceased, and then at elevated temperature until all the potassium dissolved. At this point the solutions, which often contained a precipitate of the salt of the thiol, were practically odourless, and could be degassed with a stream of nitrogen in the usual way.

Acknowledgements

This work was supported by the SERC.

References

1 A. G. Davies and A. G. Neville, *J. Chem. Soc., Perkin Trans. 2*, (preceding paper).
2 E. G. Janzen and C. M. DuBose, *J. Phys. Chem.*, 1966, **70**, 3372.
3 H. C. Heller, *J. Am. Chem. Soc.*, 1967, **89**, 4288.
4 L. Lunazzi, G. Maccagnani, G. Mazzanti and G. Placucci, *J. Chem. Soc. B*, 1971, 162.
5 L. J. Aarons and F. C. Adam, *Can. J. Chem.*, 1972, **50**, 1390.
6 W. Schmüser and J. Voss, *J. Chem. Res.*, 1978, (*S*) 149; (*M*) 1901.
7 C.-P. Klages, S. Köhler, E. Schaumann, W. Schmüser and J. Voss, *J. Phys. Chem.*, 1979, **83**, 738.
8 C.-P. Klages and J. Voss, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 726.
9 G. A. Russell and G. R. Underwood, *J. Phys. Chem.*, 1968, **72**, 1074.
10 D. Casarini, L. Lunazzi, G. Placucci, T. Ishida, A. Ishii and R. Okazaki, *J. Org. Chem.*, 1988, **53**, 1582.
11 D. H. Volman, J. Wolstenholme and S. G. Hadley, *J. Phys. Chem.*, 1967, **71**, 1798.
12 A. Alberti, M. Benaglia, B. F. Bonini and G. F. Pedulli, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 3347.
13 D. Helling, C.-P. Klages and J. Voss, *J. Phys. Chem.*, 1980, **84**, 3638.
14 D. Griller, D. C. Nonhebel and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1817.
15 R. Wilson, *Can. J. Chem.*, 1966, **44**, 551.
16 P. Neta, M. Z. Hoffman and M. Simic, *J. Phys. Chem.*, 1972, **76**, 847.

Paper 1/04342K
Received 20*th August* 1991
Accepted 10*th October* 1991